Extraction of nickel from spent catalyst using fresh and recovered EDTA

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ABSTRACT

This study investigates the possibility of recovering nickel from spent catalyst (NiO/Al_2O_3) used in the fertilizer industry. EDTA (ethylenediaminetetraaceticacid) di sodium salt was used as a chelating to extract the Ni after which sulfuric acid was added to obtain $NiSO_4$. The dechelation process takes 5–6 h to break the complex and EDTA which was recovered as H_4EDTA acid in the solid form and solution contains $NiSO_4$. The objective was to evaluate the nickel removal efficiency of EDTA and reusability of recovered EDTA. The parameters affecting nickel recovery were EDTA concentration, time of chelation, catalyst to liquid ratio (s:l), mixing speed, pH and catalyst particle size. The extraction was up to 95% under the following conditions: 0.8 M concentration of EDTA, solid to liquid ratio 1:50 (g/ml), particle size 100 μm, pH 10, 10 h of chelation time, 700 rpm and 100 °C. Up to 95% of the EDTA could be recovered without losing significant activity.

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1. Introduction

Primary reforming catalysts are used in many fertilizer production plants for reforming reactions. The catalyst deactivates after sometime due to deposition of coke on the metals. Most of the studies on fertilizer production catalysts focus on heavy metals and trace elements, due to their potential risks to human health. Other studies in a similar vien investigate their distribution in the solid phase, their mobility in the solution and their availability to the catalyst surface [1].

A variety of processing approaches for recovering metal values from spent catalyst have been proposed. In practice hydrometallurgy and pyrometallurgy are commonly used. Spent catalyst generated from fertilizer production can serve as a source of metals.

Nickel is recovered as nickel sulfate from spent catalyst (NiO/Al_2O_3) using sulfuric acid as a solvent. Previous studies have found up to 99% recovery under the following conditions: 50% acid concentration, s:l (1:12), particle size 500 μm, 5 h, 800 rpm and 100 °C, but in all cases solvent was not recovered and handling of mineral acid is hazardous [2,3].

In present study a well known chelating agent EDTA was used for extracting Ni metal. In order to make the process economical, it is necessary to reuse the EDTA. Because EDTA is non-biodegradable in nature, it can solubilize radioactive metals and increase their environmental mobility. Previous works have shown that there are

at least three possible techniques to recover and regenerate EDTA. The first method involves electrochemical reduction of metal–EDTA complexes in which the metal cations are reduced/deposited onto the cathode surface while EDTA is released into solution. A cation exchange membrane is used to isolate the EDTA from the anode [4,5]. The second method involves reacting the metal–EDTA complexes with zero-valent metals which can result in precipitation of the metallic contaminants while liberating EDTA [6]. These methods could be costly due to several operational problems such as membrane fouling and degradation. Therefore the method proposed of recovering EDTA in highly acidic condition was examined [7]. The ligand promoted dissolution process used in this study is composed of the following three steps: (1) fast ligand adsorption onto surface functional groups of solid particles, (2) slow metal detachment by acidification, and (3) fast protonation restoring the original surface functional groups. The different parameters measured include: recovered EDTA concentration, time of digestion, solid to liquid ratio, particle size and the effect of agitation (rpm). The optimum conditions for nickel extraction were defined as the condition at which extraction of various metals was of the highest efficiency possible aiming for small chemical dosages and short reaction times.

2. Materials and method

The chelating agent in terms of both kinetics and removal efficiency depends on a number of factors: metal type, concentration and speciation in the spent catalyst as well as chelating agent solution conditions. An optimal chelating agent should display high extraction efficiency, a high selectivity for the target contaminants, a high solubility and a high thermodynamic stability of the formed

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Table 1
Composition of the catalyst used in experiments.

Components	wt%
NiO	25–28
CaO	1–2
Al_2O_3	70–74

metal complexes as well as low tendency to absorb onto the solid in both the complexed and uncomplexed form [8].

2.1. Sample preparation

The spent catalyst used in this investigation was provided by DSCL Kota, Rajasthan, India. Composition of the spent catalyst used in process is given in Table 1. The shape of the catalysts was cylindrical with a particle size of 1 cm od, 0.5 cm id and 1 cm length. Calcination or coke removal was conducted by taking 100 g of air dried sample in dispersive manner of 2.3 mm depth in a porcelain disc and calcined in atmospheric oxygen flow in a temperature controlled muffle furnace for 5 h at 550 °C. After calcination the calcined materials were cooled down to room temperature. In order to measure the elemental composition, 5 g of sample was reduced to 100 μm and dissolved completely in 100 ml sulfuric acid. The reagents used in all experiments were Merck and of analytical quality. Water of high purity was obtained from a Millipore apparatus.

The metals were analyzed using a (Cary 5000, Varian) UV spectrophotometer. First the calibration was drawn for the nickel metal by dissolving pure $NiSO_4$ in 100 ml of water. The amount of Ni (0.5–2.5 g) was calculated from $NiSO_4$ and found the equation by plotting absorbance versus amount of Ni (g/ml):

$$Y = 0.4313X + 0.0056 \tag{1}$$

where Y is the absorbance of spectrophotometer and X is the amount of the Ni (g/ml). Peak of the Ni was found at 394 nm wavelength for pure Ni and in the solution of experiments. To calculate the amount of Ni in required solution the absorbance was found in spectrophotometer and by this equation the amount of Ni present in the solution was found out.

In the solutions from the experiments one peak was also found at 312 nm wavelength when the extraction was done for more than 7 h and for higher concentration of EDTA which was supposed to be of Al. The calibration was not done for Al because the aim was to know the concentration of Ni in solution. More emphasis was given on nickel extraction. The complex of Calcium and EDTA was also neglected and considered as an impurity for the experiments as it was also not desired.

2.2. Extractant solution

The extractant solution was prepared by dissolving crystals of EDTA di sodium salt (E-Na$_2$) in RO/DI water, so as to obtain the solution of 0.1–1 M solution of E-Na$_2$. A small amount of ammonia solution was used to raise the pH from 2 to 8 [9,10].

2.3. Experimental methodology

The experimental apparatus consisted of a stirring and temperature controlled rota mantle of 2 l capacity. Solution of EDTA and catalyst were placed in round bottom, one inlet/outlet flask. A magnetic stirrer was used to provide uniform distribution of liquid at the surface of the catalyst. Heating was maintained at 100 °C and a water circulating condenser was used to cool the vapors. The condenser was attached at the inlet/outlet port of the vessel.

2.4. Equilibrium experiments

To study the effect of EDTA concentration on the extraction of nickel from spent catalyst, extraction was performed using different EDTA levels ranging from 0.2 to 1 M.

For all extractions, 5 g of the catalyst sample was mixed with the extraction solution of EDTA with catalyst and stirred using an end-over-end stirrer. The catalyst–EDTA solution was filtered on a 0.45 μm glass filter with vacuum to permit the determination of the extracted metals.

2.5. EDTA recovery

EDTA recovery was performed by acidification of the filtrate, which precipitated the H_4EDTA acid from solution at pH 2. Sulfuric acid (98% by vol.) was added with stirring to initiate EDTA precipitation. The acid was added until the pH of the solution turns 2 and the color of the solution also changes from purple to green. The acidic solution was kept for 5–6 h for maximum precipitation of EDTA. Precipitated EDTA was filtered on a 0.45 μm glass filter and washed with water (Millipore) repeatedly. The EDTA and water solution was filtered. The washing solution was confirmed that it should not show any peak of nickel metal in the UV spectrophotometer by repeated washing with water. Filtered EDTA was dried in oven at 80 °C for 4–5 h and weighed to verify with the initial amount of EDTA added in the experiment [2]. Characterization was also done to check the presence of Ni in EDTA. This EDTA was used for the further experiments as recovered EDTA.

3. Results and discussion

3.1. Effect of catalyst particle size

The influence of particle size was studied using a particle range of 600–100 μm. Fig. 1 shows the effect of the particle size at 0.8 M concentration of EDTA, s:l 1:50, 700 rpm, 10 h of digestion time and pH 8. Fig. 1 represents the results of the extraction of nickel with fresh and recovered EDTA. Fig. 1 shows the higher % of Ni (for fresh and recovered) was extracted using the smallest particles of catalyst (89.6% Ni extracted with 100 μm particles). Thus 100 μm was taken as the optimum for both fresh and recovered EDTA.

3.2. Effect of stirring speed

A series of experiments were undertaken to study the speed of agitation on extraction of nickel. Different stirring rates ranging between 700 and 1100 rpm were applied (due to setup limitations).
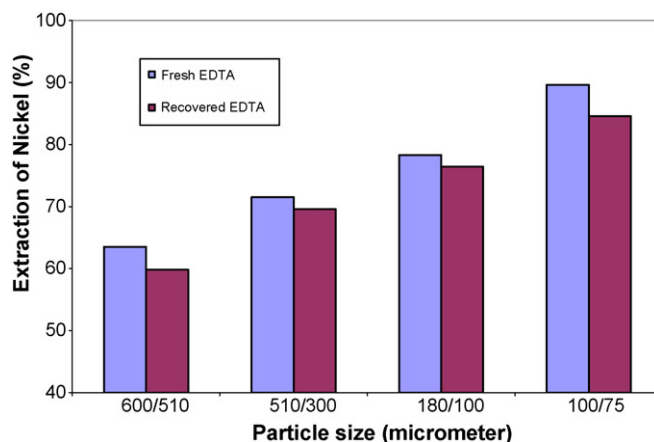

Fig. 1. Effect of particle size on the recovery of nickel in fresh and recycled EDTA.
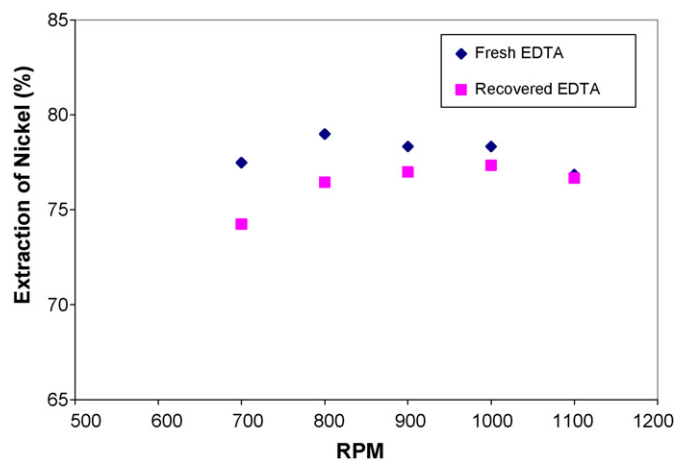
Fig. 2. Effect of stirring velocity on the recovery of nickel in fresh and recycled EDTA.

The experimental results shown in Fig. 2 indicate that there was no significant change in the extraction of nickel with stirring velocity in this range. The change in extraction was only 2–3%, therefore 700 rpm was taken as the optimum stirring speed in all other experiments.

3.3. Effect of concentration

It is generally observed that solubilization of metals increases with EDTA concentration [11]. The effect of concentration on cation extraction was determined using nine different concentrations of EDTA (from 0.2 to 1 M). Fig. 3 shows the variation of the metals extracted by EDTA solutions of increasing concentration at pH 8 and 700 rpm using 100 μm particles. For the nickel cation there is a maximum quantity extractable by EDTA which differs from its total concentration. The quantity of nickel extracted increases with increasing EDTA concentration. The higher the EDTA concentration, the greater the release of nickel metal, approaching a plateau at 0.8 M of EDTA. Above this level no significant change in extracted metal concentration is observed by increasing the reagent concentration further. The behavior of recovered EDTA is similar to that of fresh EDTA although 2–3% less extraction was achieved due to impurities in the recovered EDTA.

3.4. Effect of solid to liquid ratio

Experiments were carried out using different solid (catalyst particles) to liquid (EDTA solution) ratios fresh and recycled from 1:5 to
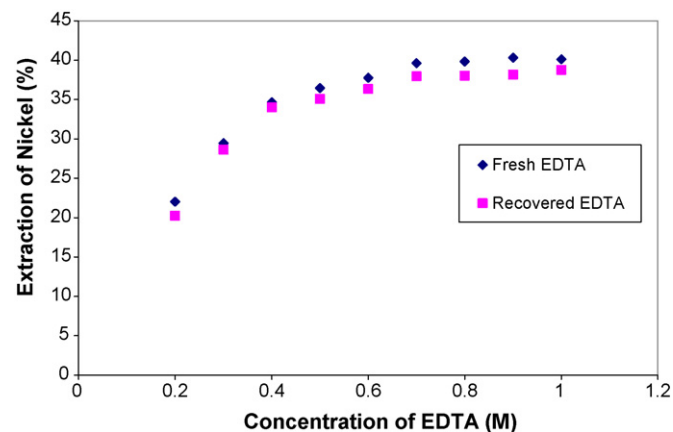

Fig. 3. Effect of concentration on recovery of nickel in fresh and recycled EDTA.
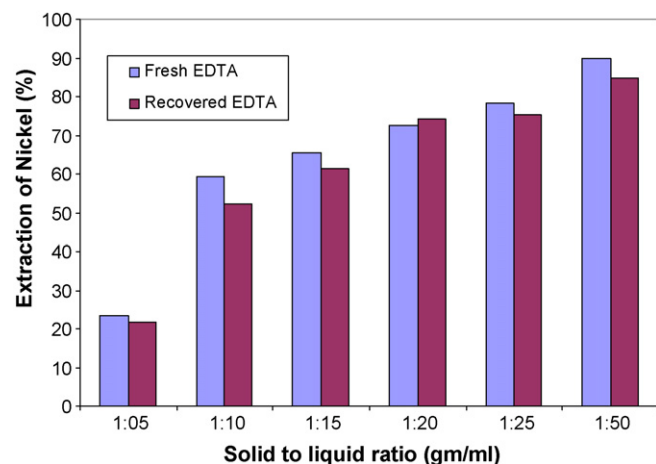

Fig. 4. Effect of solid to liquid ratio on the recovery of nickel in fresh and recycled EDTA.

1:50 g/ml. Using the 1:5 solid to liquid ratio a low extraction (23.3 and 24.6% from fresh and recovered EDTA, respectively) was found as shown in Fig. 4. It was observed that by increasing the amount of extractant solution and keeping the concentration of EDTA constant (0.8 M), an improvement in the extraction was obtained (reaching 89.6 and 84.6% at 1:50 g/ml and pH 8). 1:50 solid to liquid ratio was taken as the optimum ratio for use in all other experiments. It was assumed that further increase in extractant solution will not change significant number in Ni recovery and large amount of EDTA was used in 1:50 (s:l) and 0.8 M concentration of EDTA. So it was considered as optimum.

3.5. Effect of pH

To study the effect of pH on chelant-assisted washing, the extraction experiments were performed at pH values ranging from 8 to 13. Solution pH strongly affects the performance of the chelating agent when extracting the contaminants from sediments. The following are all influenced by pH: 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 the newly formed metal–chelant complexes [4,12]. As the H^+ ion concentration increases, the particle surface becomes increasingly protonated and acquires a positive charge, thus promoting sorption of negatively charged species like most metal–chelant complexes [13]. Conditions for fresh and recovered EDTA were kept at 0.8 M, 700 rpm, 100 μm particle size, and 10 h of digestion time. Fig. 5
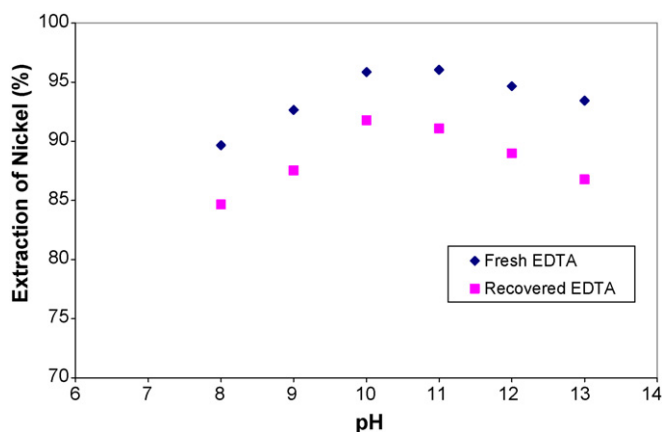

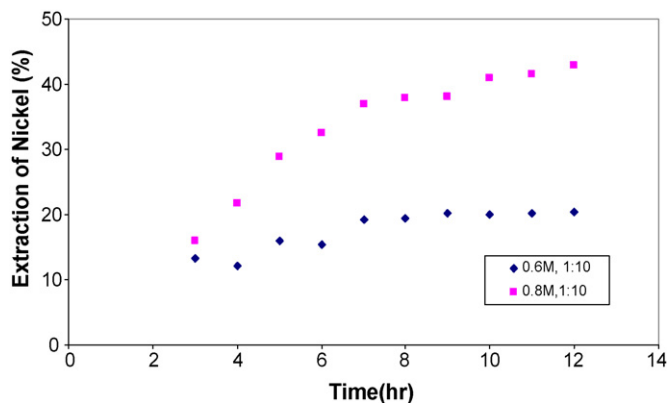**Fig. 5.** Effect of pH on the recovery of nickel in fresh and recycled EDTA.

Fig. 6. Effect of extraction time the recovery of nickel with fresh EDTA.

shows that extraction increased with an increase in concentration up to pH 10 and 11 after that it decreased. Therefore pH 10 was the optimum pH considered for both fresh and recovered EDTA.

3.6. Kinetic aspects of nickel extraction

It was assumed that thermodynamic equilibrium was obtained after 6 h of reaction time for low metal concentration with acid leaching [7,14]. The kinetic extraction experiments for fresh and recovered EDTA were carried out at two different concentrations 0.6 and 0.8 M. Also the following parameters were set: four different solid to liquid ratios 1:10, 1:20, 1:25 and 1:50, 100 μm particle size, 700 rpm and pH 8. Figs. 6 and 7 show the kinetic extraction of nickel with fresh EDTA. Using an excess of EDTA of 0.8 M concentration, the amount of extracted nickel reaches a plateau which corresponds to the maximum extractable quantity. This is due to the equilibrium attained by the EDTA. A similar kinetic is observed when keeping the concentration constant at 0.6 M and varying the solid to liquid ratio as shown in Fig. 7. Longer extraction times equate to higher releases of nickel, approaching 9–11 h, as also discussed in [15]. The same kinetic behavior is shown by the recovered EDTA in Fig. 8. Maximum extraction was achieved at 9–11 h at 0.8 M and 1:10 and 1:20 solid to liquid ratio. The time of achieving maximum extraction for both fresh and recycled EDTA was the same except reducing its efficiency. The combined fresh and recovered EDTA at 0.8 M concentration and 1:10 solid to liquid ratio in Fig. 9 depicts the extraction of nickel as 52 and 51.8% with fresh and recovered EDTA, respectively. It was maximum because of attaining the equilibrium.
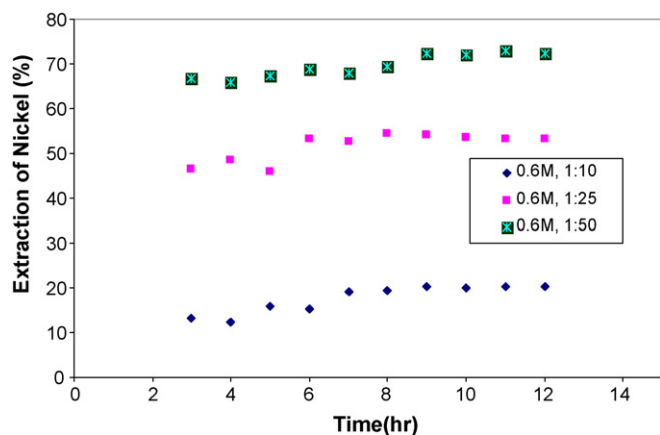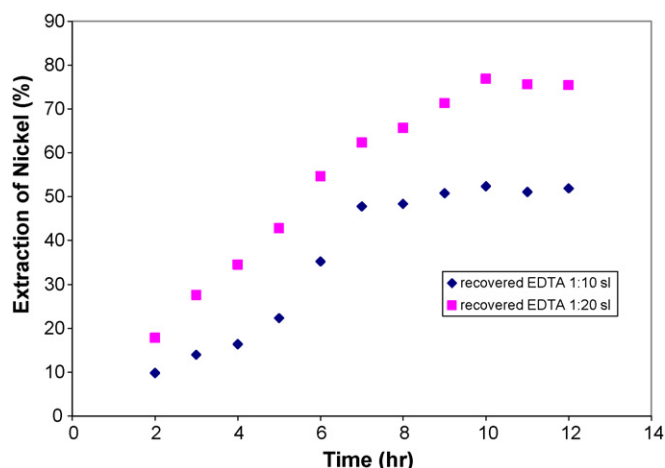

Fig. 8. Effect of extraction time on the recovery of nickel with recycled EDTA at different solid to liquid ratio.
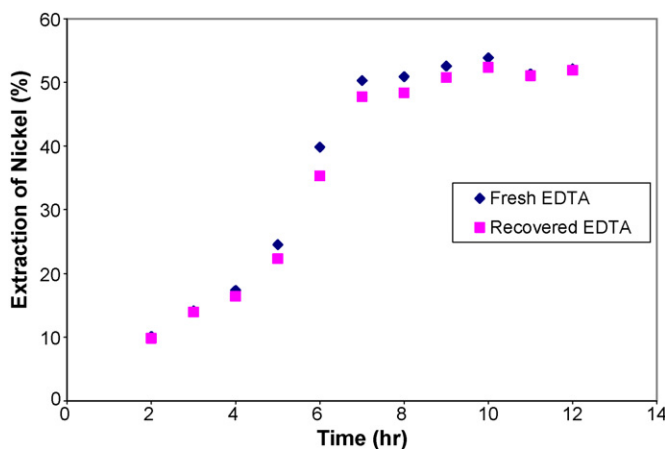

Fig. 9. Effect of time of digestion on the extraction of nickel using fresh and recycled EDTA.

3.7. Reusability of recycled EDTA

EDTA recovered from the experiments was filtered, washed and dried for use in experiments following the same procedure as for fresh EDTA. The solution extracting solution was made of same molarity as of fresh EDTA but the amount used in recovered EDTA is changed because of the change in molecular weight of the recovered EDTA. Recovered EDTA had the molecular structure H_4EDTA and the fresh EDTA had the structure $Na_2EDTA \cdot 2H_2O$. Fig. 10 shows

Fig. 7. Effect of extraction time on the recovery of nickel with fresh EDTA at different solid to liquid ratio.
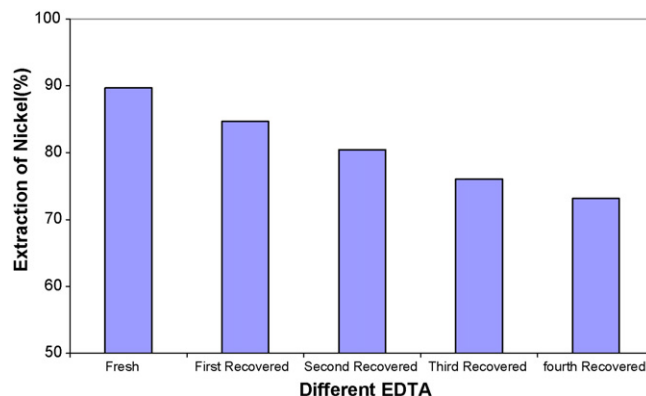

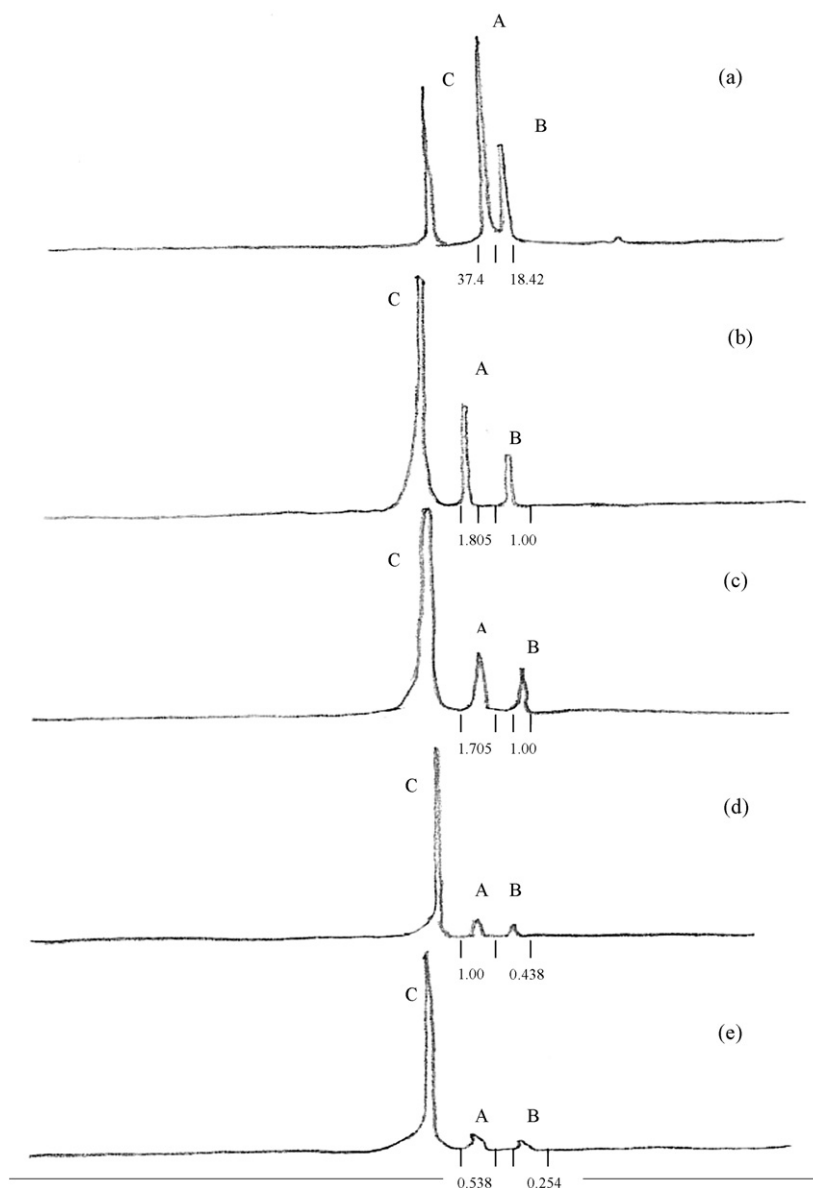**Fig. 10.** Effect of various EDTA on the extraction of nickel.

Fig. 11. Proton NMR spectrum of (a) fresh and recycled EDTA, (b) first time recycled EDTA, (c) second time recycled EDTA, (d) third time recycled EDTA, and (e) fourth time recycled EDTA.

that when using the recycled/regenerated 0.8 M EDTA, Ni extraction efficiency decreased slightly with each cycle. The percentages of nickel extracted remained above 73% over four cycles and after two and three cycles it was 80 and 76%, respectively. Obviously the recycled EDTA solution had a slightly decreased extraction power. This could be due to the interference of competing cations such as sulfur (which escaped precipitation or dechelation step) in the recycled extracted EDTA. Overall, the recycled EDTA was still effective in nickel extraction for up to four cycles in considerable amount.

3.8. Characterization of EDTA

3.8.1. Nuclear magnetic resonance (NMR)

Proton NMR of fresh and recycled EDTA revealed only two types of hydrogen as shown in Fig. 11. The solvent used for the proton NMR was D_2O. Hydrogen impurities were present in this sample as shown by a peak in Fig. 11(a–e) in the spectrum (peak C). There are three types of hydrogen in the EDTA structure. Due to the reaction with deuterium the acidic hydrogen was replaced by the deuterium

and the other two hydrogen atoms ethylene in acetic acid and ethylene with amine are labeled A and B, respectively. The structure of the EDTA is symmetric if divided down the middle. It should show a total of three peaks in the spectrum. The hydrogen atoms present at ethylene of acetic acid are twice of ethylene with amine. The area of peak B and A are in the ratio of 1:2 due to the number of hydrogen atoms in the EDTA structure. The fresh and recycled EDTA shows the same behavior and did not change during repetitive usage. The area

Table 2
Assignments of vibrational bands (cm^{-1}) obtained from FTIR.

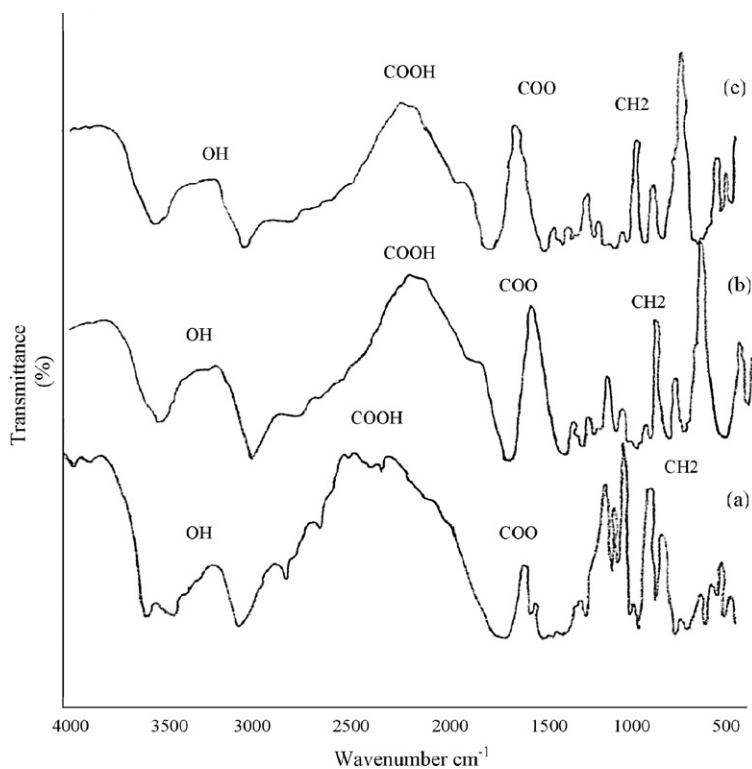| Assignments	Fresh EDTA	First time recovered EDTA	Second time recovered EDTA
ν_{as} CO_2^-	1625	1643	1648
ν_{sym} CO_2^-	1400	1425	1411
δNH^+	1360	1371	1368
$-COO^-$	1320	1314	1315
$-COOH$	1190	1256	1257
$S=O$	–	1044	1039

Fig. 12. FTIR spectrum of (a) fresh EDTA, (b) first time recycled EDTA, and (c) second time recycled EDTA.
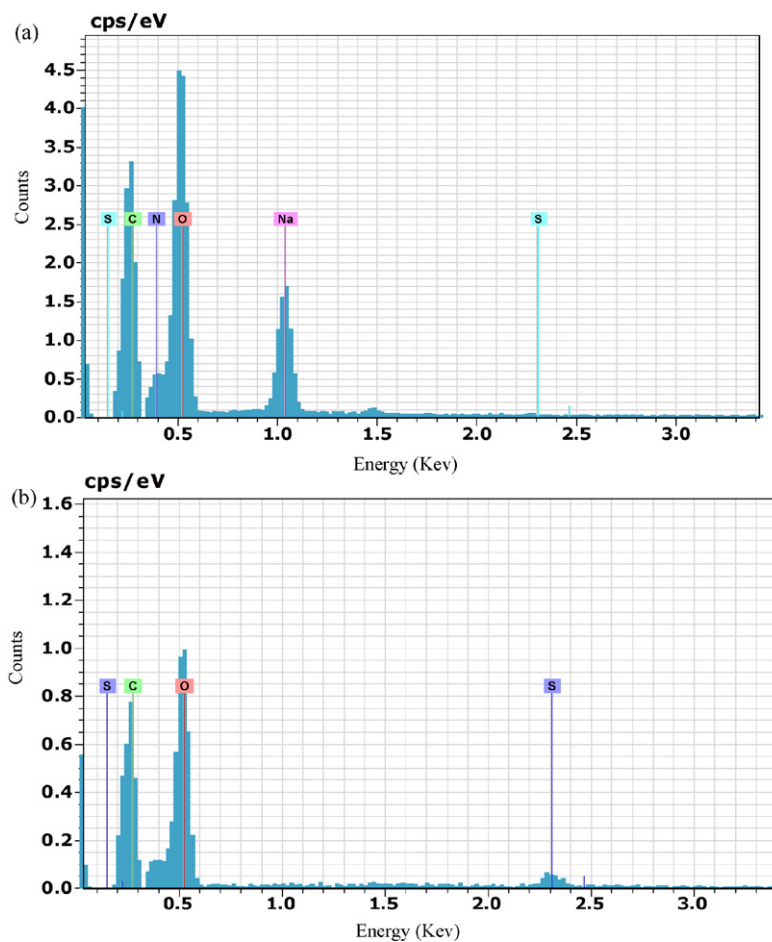

Fig. 13. EDX of (a) fresh EDTA, (b) first time recycled EDTA, (c) second time recycled EDTA, (d) third time recycled EDTA, and (e) fourth time recycled EDTA.
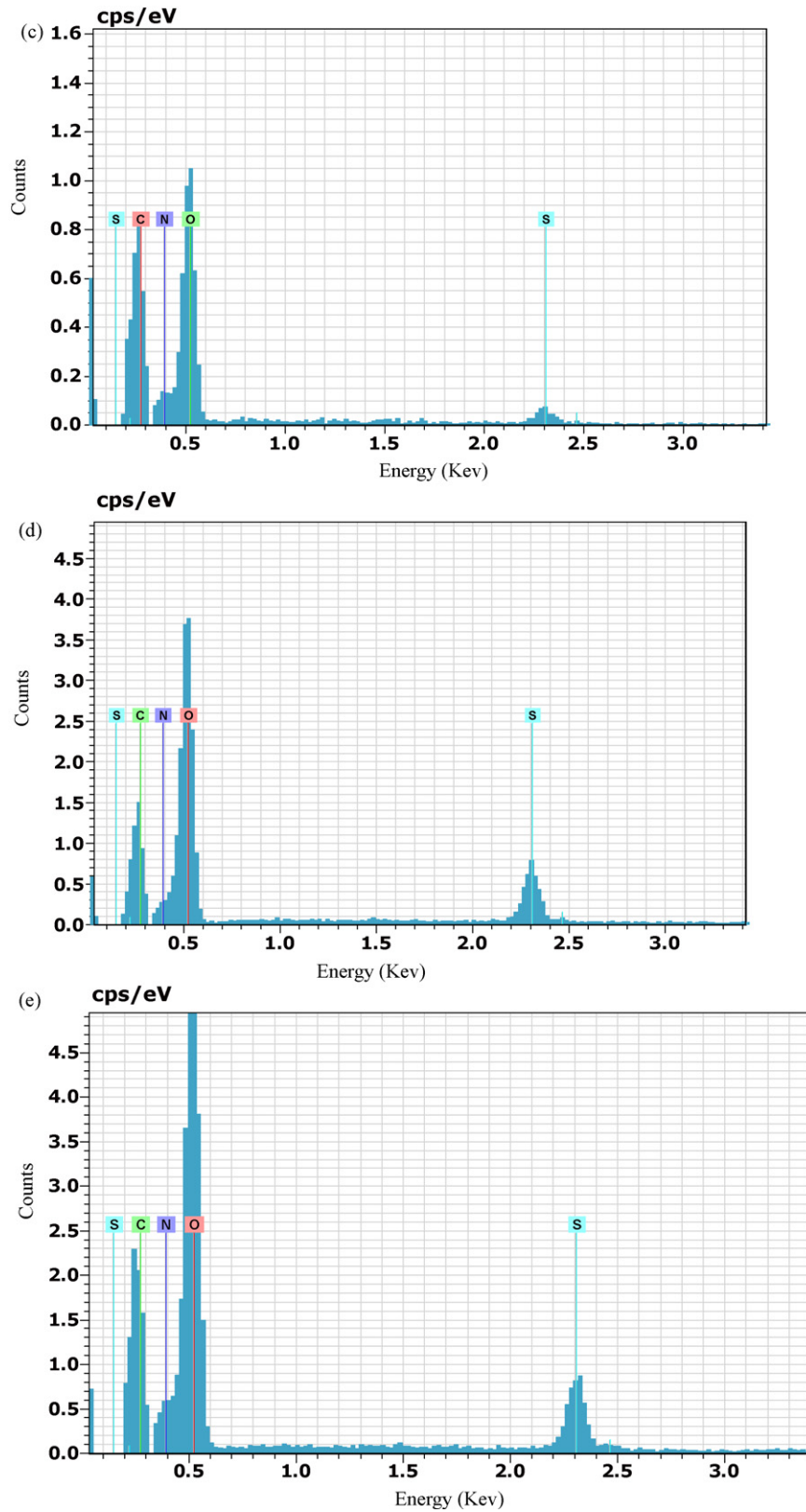
Fig. 13. (*Continued*).

underneath the peaks of fresh EDTA is 18.42 and 37.4 in Fig. 11(a). For the fourth recycle of EDTA the area is 0.0438 and 0.0238 in Fig. 11(e). Thus the ratio is maintained at 1:2 up to the fourth cycle of EDTA. There is no dissociation of the structure of the hydrogen atoms.

3.8.2. Fourier transform infrared spectroscopy (FTIR)

Infrared spectroscopy has long been used to identify structural characteristics of metal–ligands. EDTA salt compounds and recovered EDTA have previously been analyzed by traditional transmission methods. The spectrum is shown in Fig. 12(a–c). The

solid salt of EDTA was mixed with KBr and pellets were made for analysis.

3.8.2.1. Region 3600–3000 cm^{-1}. The region between 3600 and 3200 cm^{-1} is generally attributed to O–H and N–H stretching vibrations. For hydrogen bonded dimeric carboxylic acids, a downward shift of the O–H stretching band to near 3000 cm^{-1} is typical, this is shown by fresh and recycled EDTA. Bands between 3600 and 3000 cm^{-1} indicate the presence of hydroxyl groups as a result of hydrogen bonding and complexed water molecules as well as N–H stretching. All three of these stretching vibrations are observed in each of the spectrums shown Fig. 12(a–c).

3.8.2.2. Region 3000–2500 cm^{-1}. Broad vibrational bands found between 2700 and 2500 cm^{-1} are characteristic of carboxylic acid dimmers and are assigned to overtone and combination bands of C–O stretching and O–H bending.

3.8.2.3. Region 1700–1500 cm^{-1}. Intermolecular interactions make the crystalline spectra more complicated than the aqueous spectra and the spectrum was taken in crystalline form of KBr pellets. Hydrogen bonding tends to decrease the frequency of the carboxyl groups and the carbonyl vibration of free carboxylic acid groups. It also increases the frequency of the antisymmetric carboxylate stretching vibration. The typical range for saturated aliphatic carboxylic acids is 1725–1705 cm^{-1}. The band at 1711 cm^{-1} is likely the result of fresh and recovered EDTA acid groups.

3.8.2.4. Region 1500–1900 cm^{-1}. For carboxylic acids and carboxylates, this region includes bands for O–H bending, C–O stretching, and C–H bending vibrations. These bands tend to have weaker intensities compared to the carboxyl group bands. In the region that have strong absorption can enhance the band intensity for other functional groups [16].

The bands are assigned in Table 2.

3.8.3. Energy dispersive X-ray analysis (EDX)

Energy dispersive X-ray studies of the EDTA were performed on the EVO 50 apparatus. The samples were placed onto a metallic support and covered with a thin silver film. The electron micrographs were obtained at 15 kV. Elemental dot maps of sections were made by scanning the surface of EDTA with an electron beam to generate characteristic X-ray radiation from elements excited in the sample.

The scanned graphs show the different elements present in EDTA. Fig. 13(a) shows the fresh EDTA elements in the graph and shows carbon, oxygen, nitrogen and sodium of the di sodium salt, sulfur is also present in traces. Fig. 13(b–e) shows an increasing amount of sulfur present as the EDTA is further recycled. The sulfur in repeated cycles of EDTA is increased because the sulfuric acid was used for the dechelation to break the complex of EDTA and Ni metal.

3.8.4. Thermogravimetry analysis (TGA)

Thermogravimetry analysis was carried out in the range of 50–450 °C using a Standard Deviation Thermogravimetry analyzer, model Q600 from TA instruments. During TGA the purge gas used was air. Fig. 14(a) shows the weight loss up to 250 °C, after that no more losses occur in the fresh EDTA sample because the melting point of EDTA is 251 °C. Further losses occurring are likely due to be associated with the EDTA salt.

Fig. 14(b) shows the weight loss with increasing temperature of the first time recovered EDTA. The figure shows higher weight losses than the fresh EDTA. As identified from EDX analysis a small amount of sulfur is present in the recovered EDTA. It is therefore expected that a higher weight loss occurred due to the formation of the sulfur oxide during the combustion of EDTA (due to dechelation
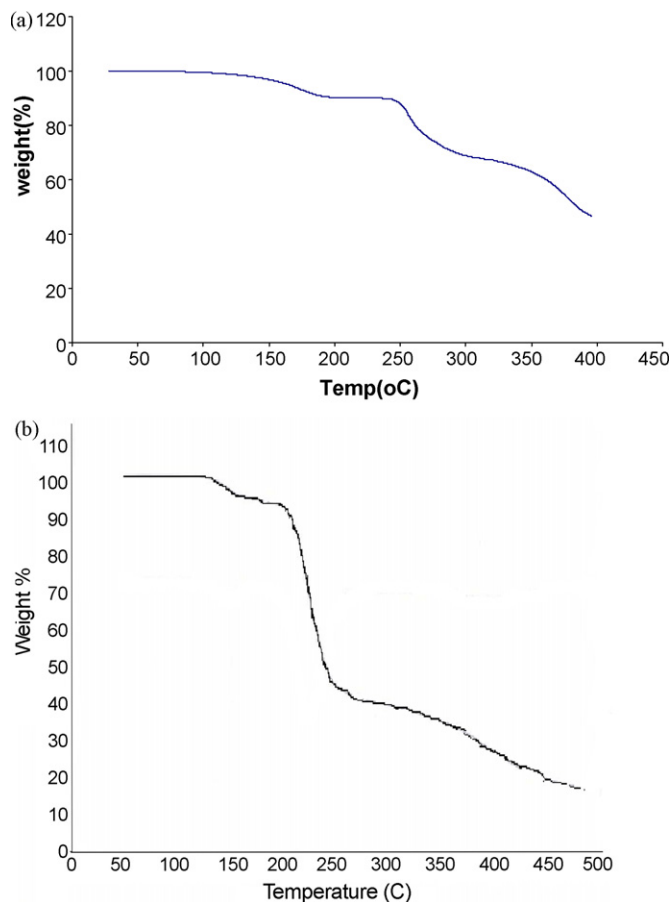

Fig. 14. TGA of (a) TGA of fresh EDTA and (b) first time recycled EDTA.

with H$_2$SO$_4$). Therefore the combined loss of water and sulfur is much higher than in the fresh EDTA sample.

4. Conclusion

Recovery of Ni from spent catalyst was carried out using a chelating agent and the process for the recovery of EDTA from the catalyst solution was verified. Also the optimum parameters for the extraction of nickel were found.

EDTA recovery from the extracted solution was achieved by acidification of the chelated solution and filtration to recover more than 95% of used EDTA. This EDTA was reused in the experiments.

Nickel as nickel sulfate was achieved with fresh EDTA giving 96.1% Ni under the following conditions: EDTA concentration 0.8 M, solid to liquid ratio 1:50, time of digestion 10 h, particle size 100 μm, 700 rpm, pH 10 and 100 °C.

For first time recovered EDTA, extraction was 91.3% under the same conditions. When using the recovered EDTA for further extraction 95% Ni was recovered. Each time EDTA was recycled, 96–98% of EDTA could be recovered from solution.

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