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Recovery of Nickel and Oil from Spent Nickel Hydrogenation Catalyst

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Abstract

Many industries make extensive use of hydrogenation nickel catalyst for conversion of fats into oil which creates large amount of spent catalysts containing environmentally hazardous and economically valuable metals. In the present study, a simple recovery process for nickel and oil from spent hydrogenation catalyst using hydrochloric acid leaching was described. Simultaneous recovery of nickel and oil varies with acid concentration, time, temperature and solid-liquid ratio. Under the optimum condition of leaching Viz. 4 N hydrochloric acid, 90^0C temperature, 1.10 gm/ml solid liquid ratio and 2 hrs reaction time, it was possible to recover 98.5% nickel along with 99.8% oil. Purification of this recovered leaching liquor was performed by adjusting pH of leach liquor containing nickel, iron, aluminium and calcium to 5.5 with sodium carbonate followed by addition of hydrogen peroxide for removal of iron and aluminium. Then ammonium oxalate was added, followed by dilute ammonia solution to neutralize the acid which precipitates calcium oxalate. To this resulting solution, required quantity of sodium carbonate was added to recover nickel as nickel carbonate which was found to be 99% pure.

Keywords: Nickel, oil, spent nickel catalyst, hydrochloric acid, recovery.

Introduction

Nickel is cheap, sufficiently active, and allows suitable catalysts to be economically produced[1]. Large quantity of spent nickel catalysts is available from fertilizer, petrochemical, pharmaceuticals vegetables oil and other industries and disposal of spent catalyst is a problem as it falls under category of hazardous industrial wastes. Nickel can cause skin rash called nickel dermatitis on exposure to nickel through direct contact[2]. The recovery of metals from such catalysts is an important economical aspect. Hydrogenation spent nickel catalyst is a solid catalyst composed of lumps of nickel and oil and is used for hydrogenation of vegetable oil, conversion of oils to fats. Some other nickel based catalysts are also widely used for hydrodesulphurization, hydro processing ($NiMo/Al_2O_3$), hydro raking ($NiS/WS_3/SiO_2$ Al_2O_3), methanation of carbon oxide form hydrogen and ammonium synthesis gas (NiO/Al_2O_3, Ni/SiO_2)[3]. After the usage of catalysts for certain period of time, its activity reduces and it is consider as a spent. Spent catalysts are harmful to the environmental due to the presence of soluble/ leachable organic and inorganic compounds. Moreover, Nickel is considered as one of the most important metal in the preparations of many metal-ligand complexes as they show potential microbial activity[4-8].

There are numerous studies reporting on the extraction of nickel from spent catalyst resulting from industrial processes using mineral acids. Most of these studies reported on the optimum conditions for maximum recovery of nickel. Numerous acid leaching studies that involved nickel-based catalyst and other metal-based catalysts are comprehensively reviewed[9].

The possibility of recovering nickel from the spent catalyst (NiO/Al_2O_3) resulting from the steam reforming process has been investigated[10]. Ivascanu and Roman studied extraction of nickel from a spent nickel catalyst by leaching with sulphuric acid and they recovered 99% of the nickel as nickel sulfate under the following conditions: particle size: 0.09mm, acid concentration: 80%, time: 50 min, and temperature: 70^0C[11]. Method for nickel extraction with yield of about 18% from the low grade spent catalyst from smelting industry by leaching with hydrochloric acid has been reported[12]. Recovery with 98.6% nickel from spent raneynickel catalyst through dilute sulfuric acid leaching and soda ash precipitation was also reported[13]. Some researcher examined the dissolution of spent commercial $NiMo/Al_2O_3$ and $CoMo/Al_2O_3–SiO_2$ catalysts in aqueous solutions containing fluoride ions under mild experimental conditions[14]. Recovery of nickel from spent catalyst from palm oil hydrogenation process was also carried out via extractive leaching process using sulfuric and hydrochloric acids[15]. Certain fundamental aspects of leaching of nickel with sulfuric acid solutions from spent catalysts for steam conversion of methane under static and dynamic conditions have been also reported[16].

Many researchers have paid considerable attention towards kinetic study of nickel recovery from spent catalyst. The kinetics of spent nickel oxide catalyst (NiO/Al_2O_3) leaching in sulphuric acid solutions was investigated[17]. Kinetics of nickel leaching from spent NiO/Al_2O_3 catalyst using sulfuric acid as leaching reagent also investigated[18]. Leaching kinetics study of spent nickel oxide catalyst with sulfuric acid has been investigated[19]. The kinetics of leaching of pure nickel powder in aqueous chlorine solution is also reported[20].

Some micro-organism based processes have been also adopted for nickel recovery from spent catalyst. *Aspergillus Niger* has been used for bioleaching of spent refinery processing catalyst[21]. Integrated biological processes using *Acidithiobacillus Thiooxidans* involving the dissolution and subsequent precipitation have been used for the treatment of the spent material from the hydrogenation of vegetable oil containing a high-level of nickel[22].

Spent hydro processing catalysts are considered as potential secondary sources for the recovery of valuable metals such as Ni, V, Mo, and Co. Alkali leaching, and two stages leaching with acid and alkaline solutions were also reported in the literature[23,24].

The aim of this work is to develop a simple process to recover nickel and oil from the spent hydrogenation catalyst, which is generated during hydrogenation reaction in soap industry. The study mainly focused on hydrometallurgical leaching of spent catalyst with hydrochloric acid to produce nickel chloride solution with negligible impurities followed by purification to produce nickel carbonate.

Material and Methods

Reagent and Apparatus: Nickel hydrogenation catalyst is used in industry for the conversion of oil into fats by hydrogenation reaction under specified temperature and pressure conditions. The catalysts after 1-5 runs of catalytic reactions became inactive and consider as spent catalysts. A spent catalyst used in this study was obtained from local soap company and was received as it is. The chemical used in this study were analytical grade HCl, H_2SO_4, HNO_3, Na_2CO_3, H_2O_2, ammonium oxalate, ammonia. The pH values were measured with a pH meter Elico LI-127 digital pH meter (Elico India Ltd., India) supplied with a combined glass electrode. A GB 400 model AAS was used to determine Ni, Al, Fe and Ca concentration.

Leaching Studies: Initially, spent catalyst received from soap industry was ground and powdered. Chemical analysis shows that the washed catalyst contains 20-21% Ni, 2% Al, 15% Fe and 1% Ca. Leaching experiment was conducted in 4 N HCl within two litres round bottom flask fitted with mechanical stirrer and immersed in the oil bath maintained at 90^0C $\pm 1^0$C. As soon temperature of flask reached 90^0C $\pm 1^0$C, 100 gm of the given sample (S/L ratio 1:2-1:15 gm/ml) was added. Aliqouts from sample solution were withdrawn at different time interval (0.5-2.5 hr). Analysis of nickel metal and oil content were determined after proper dilution.

Processing of leach liquor: Removal of impurities: H_2O_2 and Na_2CO_3 were added to oxidize Fe^{+2} to Fe^{+3} and pH was adjusted at 5.0-5.5 which precipitates Al and Fe as their hydroxides. To this solution NaF/HF were added accordingly to adjust the pH 6.5 which precipitates Mg as MgF.

Removal of impurities: *Stoichiometric* quantity of Na_2CO_3 is added to purify (impurity free) leach liquor to precipitate nickel as Nickel carbonate. The obtained precipitate was washed with distilled water to neutralize pH and then converted into $NiCl_2$. The solution was evaporated to obtain $NiCl_2$ with 99% purity.

Results and Discussion

Selection of acid: Figure-1 shows that effect of various acids on the leaching efficiency of metals for 1:10 g/ml solid/liquid ratio. Temperature maintained at 90^0C for time interval of 2 hrs. It was observed that Leaching efficiency of metal and oil increase with increasing acid concentration. Results clearly suggest that maximum leaching efficiency of metal and oil can achieve with 4 N HCl acid and further increase in acid concentration had no adverse effect on leaching of metals and oil. Comparison of leaching efficiency at 2 hrs reaction time with 4 N HCl and 1:10 g/ml Solid/Liquid ratio indicates increase nickel and oil leaching from 89.5 to 93% and 82.8 to 99.8% respectively.

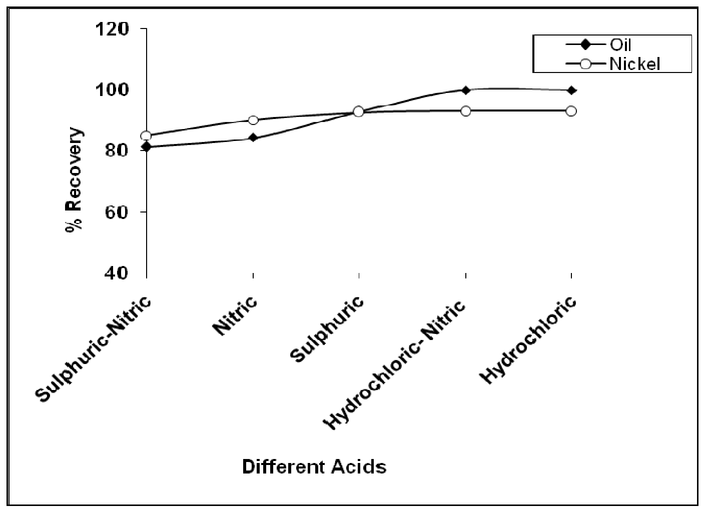

Figure-1
Effect of different acids on extraction of oil and nickel

Effect of time: Effect of time on extraction of nickel has been studied for time interval of 0.5 to 2.5 hrs with other optimum conditions. It was observed in figure-2 that initially leaching efficiency increases with time and after 1.5 hrs it remains steady indicating complete leaching of nickel. Therefore 2 hrs time was considered as optimum time to ensure complete leaching of nickel.

Effect of Temperature: The temperature variation studies were carried out between 60-100^{0}C on the leaching efficiency of metal at S/L ratio of 1:10 g/ml using 4 N hydrochloric acid and results were shown in figure-3. Temperature had marginal effect on the leaching efficiency of metals with time interval from 0.5-5 hrs. Based on the leaching result the optimum leaching conditions are 1:10 g/ml S/L, 4N HCl and 80^0C under these conditions sufficient quantity of leach liquor was regenerated with 98% nickel.

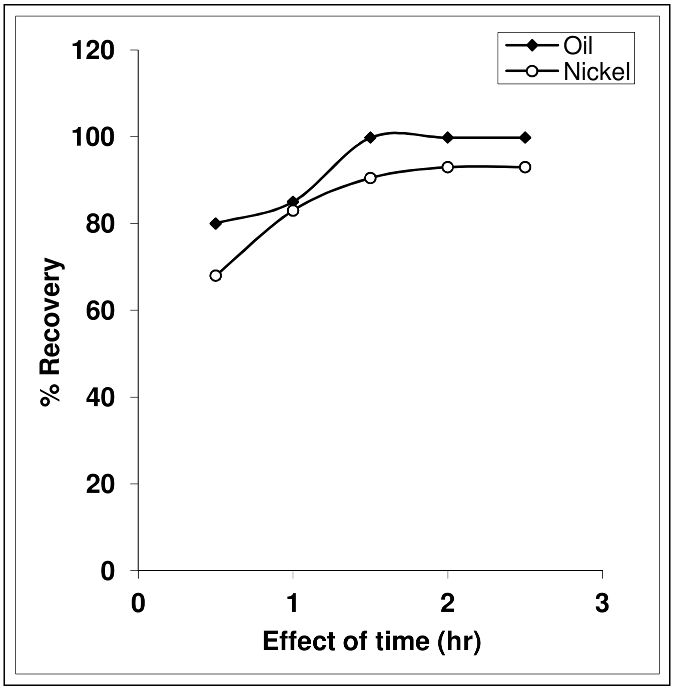

Figure-2
Effect of time on extraction of oil and nickel

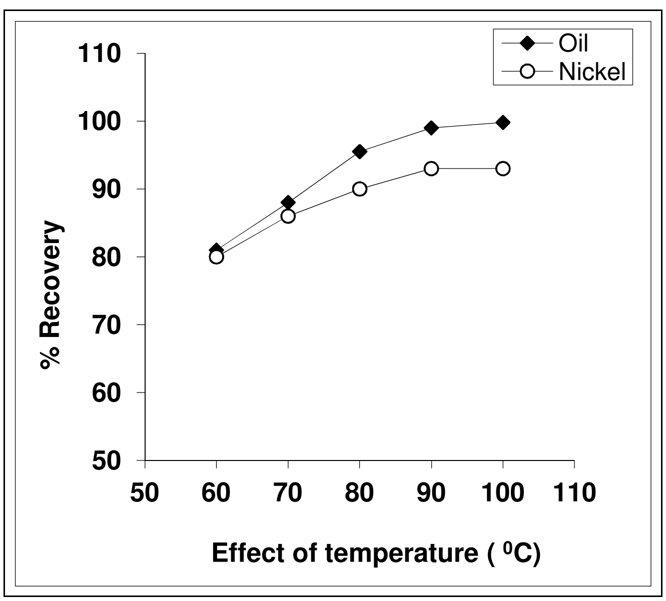

Figure-3
Effect of temperature on extraction of oil and nickel

Effect of Hydrochloric Acid: Figure-4 shows the effect of hydrochloric acid concentration in the range 1-4 N as a function of time from 0.5-5 hrs on the leaching efficiency of metals maintained at 80^0C and at solid /liquid ratio 1:10 g/ml. The acid concentration increases result clearly suggest that maximum leaching efficiency of metals is attained with about 4 N of hydrochloric acid concentration and further increase of acid concentration had marginal effect on leaching of metals.

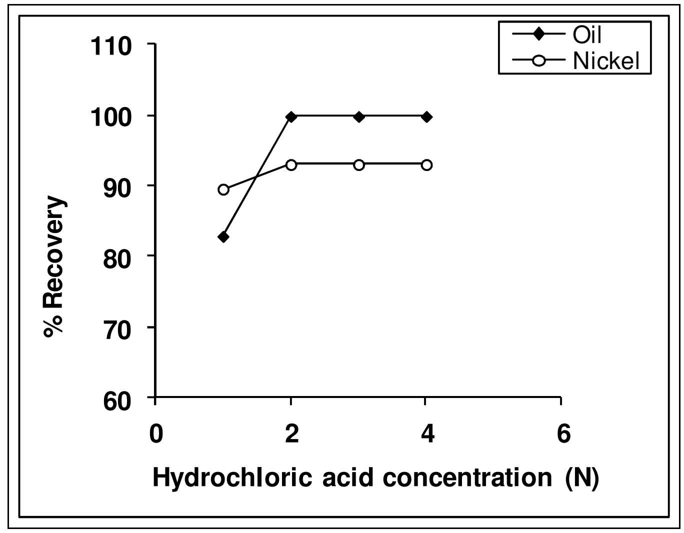

Figure-4
Effect of hydrochloric acid on extraction of oil and nickel

Effect of Solid to Liquid Ratio: Experiments were carried out at 1:1 to 1:15 S/L ratios using 4 N HCl at 80^0C and time 2 hrs are shown in figure-5. Leaching efficiency of nickel was 98% at 1:10 S/L ratio, while Increase in S/L ratio had no adverse effect on leaching of nickel. So it can be concluded from the leaching efficiency of nickel, S/L ratio 1:10 g/ml is advantageous in terms of high nickel recovery at 80^0C.

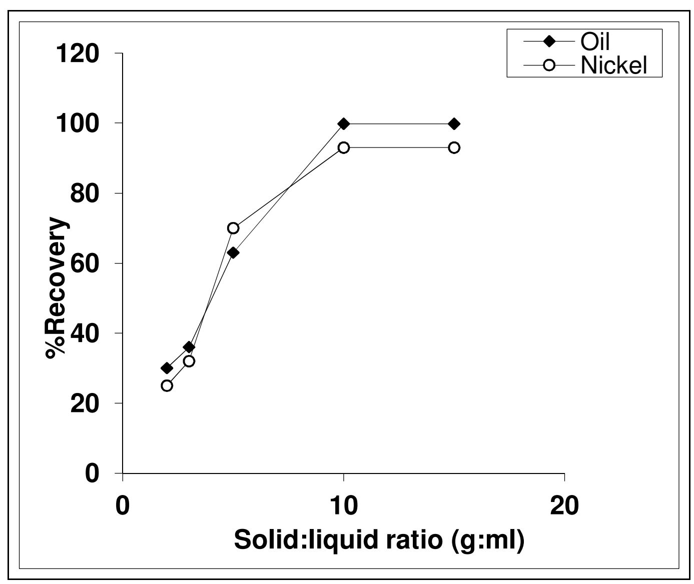

Figure-5
Effect of solid: liquid ratio on extraction of oil and nickel

Conclusion

A simple environmental friendly hydrometallurgical process developed to recover oil and Ni from spent hydrogenation catalysts reported in this paper. Optimum conditions for leaching of nickel and oil are 4 N hydrochloric acid, 90^0C temperature, 1.10 gm/ml solid liquid ratio and 2 hrs reaction time. With this simple and economical method, it was possible to recover 98.5 % nickel along with 99.8% oil. Initially, spent nickel catalyst sample was treated with 4 N HCl to leach out nickel and oil along with other metals. Then pH of leach liquor containing nickel, iron, aluminium and calcium was adjusted to 5.5 with sodium carbonate followed by addition of hydrogen peroxide for removal of iron and aluminium. Then ammonium oxalate was added, followed by dilute ammonia solution to neutralize the acid which precipitates calcium oxalate. To this resulting solution, required quantity of sodium carbonate was added to recover nickel.

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