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Recovery of Nickel from Spent Hydrogenation Catalyst Using Chelating Resin

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Abstract: Spent catalyst samples from hydrogenation of palm and palm kernel oils were subjected to soxhlet extraction to remove oil residue, digestion with concentrated sulfuric acid and nickel extraction using chelating ion exchange resin. The results showed that the spent catalysts contained oil residue (42.2-54.0%), nickel (11.32-15.63%), Mg (1.65-2.51%), Ca (3.84-5.68%). Other metals, Fe, K, Na, K, Al, Zn, Cu, Cr and Mn are minor components (<0.1%). The Amberlite IRC-718 resin has extracted more than 90% Ni in the spent catalysts (as nickel nitrate) with purity of higher than 90% with regards to the amount of Mg and Ca in the sample. The Amberlite resin showed the highest sorption capacity for Ni(II) (56.8 mg/g) at pH 5.

Key words: spent catalyst, nickel, chelating resin

1 Introduction

Hydrogenation of oils and fats is a chemical reaction in which hydrogen is added to a double bond of unsaturated acids present in the oils. The reaction is best performed using a silica support nickel catalyst (1). In Malaysia, hydrogenation process is carried out on palm oil, palm stearin, palm kernel oil and fatty acids to produce confectionary fats, saturated fatty acids for oleochemical industries or to produce fats with low iodine value for industrial applications. This process generates large amounts of spent catalyst which is considered as a solid waste. Reuse the spent catalyst is not advisable due to variation in catalyst selectivity, and the accumulated impurities might affect the product uniformity. Attempts have been made to recover nickel metal from the spent catalyst using acid digestion, followed by selective precipitation (2), leaching in sulfuric acid

solution (3) and direct crystallization method (4). In this study, a nickel from spent catalysts used to hydrogenate palm and palm kernel oils was extracted using an Amberlite IRC-718 resin. The method was relatively simple, involved only acid digestion and column separation. The Amberlite IRC-718 resin with iminodiacetatic acid funtional group shows high selectivity towards Ni(II) than other metal ions (5). This study is aimed to prevent the accumulation of spent hydrogenation catalyst and thus, solves the disposal problem face by the oil palm industries.

2 Materials and Method

2·1 Materials

Samples of spent nickel catalyst from hydrogenation of palm (SC1) and palm kernel oils (SC2), were obtained from a local oleochemical company. All metal

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salts for preparing standard solutions, and n-hexane were purchased from Fluka Chemical with purities more 90%. An ion exchange resin, Amberlite IRC-718 was purchased from Sigma Chemical.

2·2　Metal Content

Oil residue from the spent catalysts was removed by soxhlet extraction for 36 hours using n-hexane. The completion of extraction was monitored by FT-IR for the disappearence of palm oil's carbonyl peak at 1740 cm^{-1} using a Perkin Elmer FT-IR 1650 spectrometer. The spent catalysts (5.0 g) were digested with 20.0 ml HNO_3 (conc.) until completely dissolved (5 hours). The clear green solution was filtered and diluted to the mark with distilled water in a 50 ml volumetric flask. Metal content was determined by atomic absorption spectrometry (AAS model GBC-903). Aluminium ion was determined by ICP-AES (Perkin Elmer Plasma 1000).

2·3　Recovery of Nickel

Sorption capacities of the Amberlite IRC-718 for Ni(II), Mg(II) and Ca(II) were determined by mixing 1.0 g of resin with 1.0 ml of 0.1M standard solution of either Ni(II), Mg(II) or Ca(II), 15.0 ml of sodium acetate buffer of pH 1-6 and 9.0 ml of distilled water. After shaking for 24 hours, the solution was filtered and the metal content was determined by AAS. The pH of the solutions were determined before and after equilibration. Column separation of metal ions was carried out using a glass column (30 cm length $\times$ 1 cm i.d). The column was packed with slurry of resin to 10 cm

high and conditioned with HNO_3 at pH 5 and 10 ml of spent catalyst sample solution (digested and adjusted with HNO_3 to pH 5) was loaded on to the resin column and first, eluted with HNO_3 solution at pH 5 (1×10^{-5} M). Ten fractions of eluate of 10 ml each were collected. The Ni(II) retained in the column was then eluted with 100 ml of 1M HNO_3 solution where again, ten fractions of 10 ml each were collected. The flow rate was maintained at 0.5 ml/min. The quantity of the metal ions Ni(II), Mg(II) and Ca(II) in the eluate was determined by AAS.

3　Results and Discussion

The results showed that the spent catalysts contained oil residue (42.2%-54.0%), nickel (11.3-15.6%), Mg (1.7-2.5%) and Ca (3.8-5.7%). Other metals detected, Fe, K, Na, K, Al, Zn, Cu, Cr and Mn presented at low concentration (<0.1%). Amberlite IRC-718 resin showed highest sorption capacity for Ni at pH 5 (56.8 mg/g), followed by Mg (30.4 mg/g) and Ca (16.5 mg/g. This shows that Ni(II) will be sorbed efficiently by the resin at pH 5 than other two metals ions. Chelating resins with iminodiacetic acid functional group are known to have high sorption capacities for transition metal (5) compared to alkaline earth ions (6).

3·1　Column Separation

Spent catalyst sample (SC1 or SC2) was digested and adjusted to pH 5 prior to column separation. About 10 ml of each sample solution was loaded onto the resin column and first, eluted with HNO_3 solution at pH 5
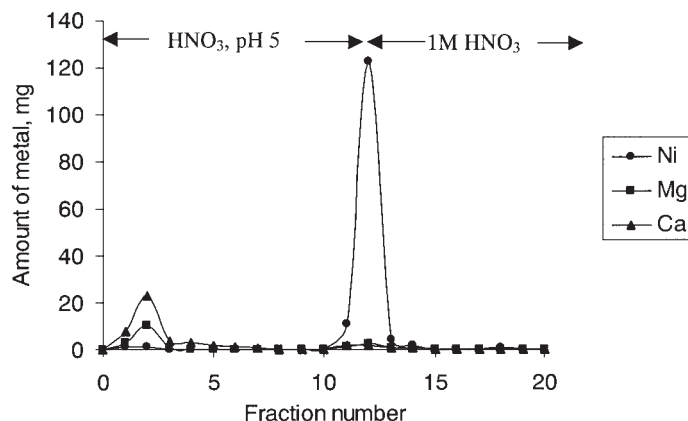
Fig. 1　Nickel-magnesium-calcium Separation from Spent Catalyst Sample (SC1) Using Amberlite Chelating Resin Column.

Table 1 Recovery of Ni(II) from Spent Catalyst Solution (1 g/10 ml) loaded on to Resin Column and Eluted with 1M HNO$_3$ Solution; n=3.

Catalyst sample	Amount of Ni in catalyst (mg)	Amount of Ni recovered by 1M HNO$_3$ mg($\pm$ SD)	Recovery % ($\pm$ SD)
SC1	156.3	141.1 (1.5)	90.2 (0.9)
SC2	113.2	103.7 (0.9)	91.6 (0.8)

Table 2 Purity of Ni(II) Separated from Spent Catalyst in 1M HNO$_3$ Eluate from Resin.

Catalyst sample	Amount of metal in 1M HNO$_3$ eluate (mg)			% Ni
	Ni(II)	Mg(II)	Ca(II)	
SC1	140.8	4.9	5.2	93.3
SC2	102.4	4.3	6.2	90.7

(1×10^{-5} M). At this stage most of the Mg(II) and Ca(II) were eluted. The Ni(II) retained in the column was then recovered by eluting with 100 ml HNO$_3$ (1M) solution. The column separation of Ni(II), Mg (II) and Ca(II) is represented graphically in **Fig. 1** for spent catalyst sample SC1. From the total amount of Ni(II), Mg(II) and Ca(II), recovered by eluting with 1M HNO$_3$, the percentages of recovery of Ni(II) was calculated and found to be more than 90% (**Table 1**) with the purity of more than 90% with respect to the amount of Mg and Ca in the eluate collected (**Table 2**). Other metals were not eluted or recovered since they are present at trace amount or very low concentration. The efficiency of recovery of nickel by Amberlite IRC-718 is, therefore high (>90%). Ni(II) solution was evaporated to give a light green nickel nitrate (NiNO$_3$) salt. In summary, it is possible to recover, with high yield and purity, nickel from spent hydrogenation catalyst using an ion exchange resin. The nickel nitrate salt can be reuse either in the production of a fresh hydrogenation catalyst or in other uses.

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