DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

INVESTIGATION OF Ni AND Co RECOVERY FROM LEACH SOLUTIONS BY SOLID ION EXCHANGE RESINS

by
Özge SOLAK

July, 2006
İZMİR

INVESTIGATION OF Ni AND Co RECOVERY FROM LEACH SOLUTIONS BY SOLID ION EXCHANGE RESINS

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We have read the thesis entitled **"INVESTIGATION OF Ni AND Co RECOVERY FROM LEACH SOLUTIONS BY SOLID ION EXCHANGE RESINS"** completed by **Özge SOLAK** under supervision of **Assist. Prof. Dr. Abdullah SEYRANKAYA** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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INVESTIGATION OF Ni AND Co RECOVERY FROM LEACH SOLUTIONS BY SOLID ION EXCHANGE RESINS

ABSTRACT

Traditional pyrometallurgical processing of nickel and cobalt ores is no longer environmentally acceptable nor economically viable with the increasingly important proportion of low-grade and "dirty" concentrates. Hydrometallurgical alternatives are increasingly being considered unless carried out under extreme conditions.

This study includes the resin-in-leach (RIL) technology which will enable more efficient and selective removal and recovery process to be developed, optimized and controlled.

In this study, commercial resins Purolite S-930 and Purolite S-950 was used. Recovery of nickel and cobalt from aqueous solutions by chelating resins was investigated by batch and continuous processes. Optimum pH range and resin amount were investigated by several batch studies for two type chelating resins. Selectivity tests were done in the presence of manganese, aluminium, iron competing ions. The performance of nickel removal was effected by competing ions.

Kinetic test were performed by both Purolite S-930 and Purolite S-950. The data obtained from kinetic studies were applied to the various kinetic models.

Column performance of the Purolite S-950 was investigated with continuous studies. Breakthrough capacity of Purolite S-950 for nickel was found beter than cobalt removal. The complete elution of nickel and cobalt were performed by using 4 molar sulphuric acid solution.

Keywords: Chelating resin, Cobalt, Ion Exchange, Nickel

KATI İYON DEĞİŞTİRİCİ REÇİNELER KULLANARAK LİÇ ÇÖZELTİLERİNDEN Ni VE Co KAZANIMININ İNCELENMESİ

ÖZ

Düşük tenörlü cevherlerin ve proses açısından empürite içeren konsantrelerin önemli oranda artmasıyla nikel ve kobalt cevherlerinin klasik pirometalurjik yöntemlerle işlenmesi hem ekonomik hem de çevresel açıdan artık mümkün olmamaktadır. Alternatif olarak hidrometalurjik yöntemler de kullanılmaktadır.

Bu çalışma, daha seçimli ve verimi yüksek kazanım ve giderim işlemlerinin yapılabildiği reçine-liç teknolojisini içermektedir.

Bu çalışmada Purolite S-930 ve Purolite S-950 ticari reçineleri kullanılmıştır. Sulu çözeltilerden şelatlayıcı reçineler yardımıyla nikel ve kobalt kazanımı kesikli ve sürekli çalışmalar ile incelenmiştir. Her iki reçine ile yapılan kesikli çalışmalar ile optimum pH aralığı ve reçine miktarı bulunmuştur. Seçimlilik çalışmaları mangan, aluminyum, demir iyonları varlığında gerçekleştirilmiştir. Nikel giderim performansının ortamda bulunan iyonlardan etkilendiği görülmüştür.

Kinetik çalışmalar Purolite S-930 ve S-950 ile gerçekleştirilmiştir. Kinetik çalışmalardan elde edilen veriler çeşitli kinetik modellere uygulanmıştır.

Purolite S-950 reçinesinin kolon performansı sürekli çalışmalar ile incelenmiştir. Nikel için Purolite S-950 ile elde edilen salıverme kapasitesinin, Kobalt ile elde edilenden daha iyi olduğu görülmüştür. Nikel ve kobalt iyonlarının reçineden tamamıyla sıyrılması 4 molar sülfürik asit çözeltisi ile gerçekleştirilmiştir.

Anahtar Sözcükler: Kobalt, İyon değiştirme, Nikel, Şelatlayıcı reçine

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CHAPTER ONE
INTRODUCTION

1.1 Nickel

1.1.1 Identity, Physical and Chemical Properties of Nickel

Nickel, symbol Ni, is a silvery white, magnetic metallic element used chiefly in making alloys. The name nickel comes from the German word "kupfernickel" meaning Devil's copper or St Nicholas's copper (World Health Organization [WHO], 1991). The Nickeline ore can be seen in Figure 1.1.

Nickel is a metallic element belonging to group VIIIB of the periodic table. It is resistant to alkalis, but generally dissolves in dilute oxidizing acids. Nickel carbonate, nickel sulfide, and nickel oxide are insoluble in water, whereas nickel chloride, nickel sulfate, and nickel nitrate are water soluble. Nickel carbonyl is a volatile colourless liquid that decomposes at temperatures above 50 °C. The prevalent ionic form is nickel (II). In biological systems, dissolved nickel may form complex components with various ligands and bind to organic material (WHO, 1991). General properties of nickel are summarized in Table 1.1.

Table 1.1 General properties of nickel

Atomic Number	28
Symbol	Ni
Atomic Weight	58.71
Discovery	Cronstedt 1751
Electron Configuration	$[Ar]4s^2 3d^8$
Isotopes	There are 14 known isotopes of nickel, 5 stable and 9 unstable. Natural nickel is a mixture of the 5 stable isotopes.
Properties	The melting point of nickel is 1453°C, boiling point is 2732°C, specific gravity is 8.902 (25°C), with a valence of 0, 1, 2, or 3. Nickel is hard, ductile, malleable, and somewhat ferromagnetic. It is a fair conductor of heat and electricity. Nickel is a member of the iron-cobalt group of metals. Exposure to nickel metal and soluble compounds should not exceed 1 mg/M^3 (8 hour time weighted average for a 40 hour week). Some nickel compounds (nickel carbonyl, nickel sulfide) are considered to be highly toxic or carcinogenic.

Figure 1.1 Picture of nickeline ore

The most commonly used methods for the analysis of biological and environmental materials are atomic absorption spectroscopy and voltammetry. (WHO, 1991).

1.1.2 Sources

Nickel occurs in nature as oxides and sulphides. Sulphide ores are typically found at depths of hundreds of meters in a hard rock geological environment. The minerology of the ore generally comprises pyrhotite ($Fe_{1-x}S$), pentlandite $(FeNi)_9S_8$, chalcopyrite ($CuFeS_2$), and magnetite (Fe_3O_4). Of those four, pentlandite is the major commercial primary nickel mineral. Sulphide bearing nickel ore is being economicallly mined with gardes of 1.5% to 4% in Russia, Canada and Australia. Nickel laterite ores are formed through the weathering of nickel-bearing olivine-rich ultramafic bedrock such as peridotite or serpentine. This occurs when the acidic surface water attacks the bedrock and releases iron, nickel, magnesium and silica into solution. In particular, the most soluble portions are washed away, thus increasing the relative concentration of the remaining components. In this process the magnesium oxide migrates downward while the iron oxides are less mobile, and hence become more dominant near the surface. Significant deposits have been discovered in Australia, Cuba, Indonesia, New Caledonia, Papua New Guinea and the Philippines. Economic nickel are limonit (nickel mixed with hydrated iron oxide) and garnierite/saprolite ((Ni, Mg) $SiO_3.nH_2O$). The limonite has a distinct, rusty reddish colour fading to Brown with depth with economic grades of 1% to 2% Ni.

Saprolite is less weathered and tends to be harder tahn limonite. It contains high magnesia and less iron with grades of 1.5% to 3.5% Ni. This difference in minerology is the major factor controlling the choise of the treatment process (Zainol & Nicol, 2003).

1.1.3 Intermediate Products and End-use of Nickel

Most of the nickel is used for the production of stainless steel and other nickel alloys with high corrosion and temperature resistance. In the production of nickel steel alloys, steel scrap, limestone, iron oxide ore, and nickel are charged into a furnace (open-hearth furnace, electric arc furnace and cupola) where the steel and iron alloys are melted. After final adjustment of the carbon and alloy contents, the steel is cast into moulds. Non-ferrous melting is commonly performed in a reverberatory furnace (Norton & Leahy, 2006).

Nickel alloys and nickel platings are used in vehicles, processing machinery, armaments, tools, electrical equipment, household appliances, and coinage. Nickel compounds are also used as catalysts, pigments, and in batteries (Norton & Leahy, 2006).

Table 1.2 Consumption of nickel by intermediate product and end-use industry in 1985 in the USA

Index	***Consumption (% of total)***
Intermediate product	
Stainless and alloy steels	42
Nonferrous alloys	36
Electroplating	18
End-use industry	
Transportation	23
Chemical industry	15
Electrical equipment	12
Construction	10
Fabricating metal products	9
Petroleum	8
Household appliances	8
Machinery	8
Other	7

The addition of nickel to steel and cast iron yields an alloy with increased strength and toughness and resistance to corrosion. Stainless steel is used in the chemical and food-processing industries. Because of their ferromagnetic properties, iron-nickel alloys are important materials for the electrical industry. Various medical devices, such as prostheses or orthopaedic implants, are made from stainless steel (Norton & Leahy, 2006).

Nickel-copper alloys exhibit the highest mechanical strength and resistance to corrosion and are used in the chemical and machine industries (pipes, nozzles, machine parts for the food and textile industries). Their high resistance to corrosion makes these alloys a valuable material for the shipbuilding industry (Norton & Leahy, 2006).

Other important uses of nickel are in nickel-cadmium batteries, electronic equipment, and computers. Nickel compounds are used as catalysts in the manufacture of organic chemicals, petroleum refining, and edible oil hardening. They are also constituents of pigments and colours for ceramics and glassware, and of marine anti-fouling paint. In the glass industry, nickel is used in moulds for bottles (WHO, 1991).

The production of secondary nickel in the form of scrap recovery is a major source of nickel. Recycled scrap is generally melted and refined and subsequently used for the production of steels and alloys, similar in composition to those in which it entered the recycling process. Thus, scrap recycling processes are analogous with those used in primary production (WHO, 1991).

1.1.4 World Production Levels and Trends of Nickel

The development of global mine production during this decade is shown in Table 1.3.

Table 1.3 Mine production and reserves of nickel (Norton & Leahy, 2006)

Salient Statistics-United States:	**2001**	**2002**	**2003**	**2004**	**2005**
Production, refinery byproduct	W	W	W	W	W
Shipments of purchased scrap	121.000	114.000	119.000	113.000	121.000
Imports : Primary	136.000	121.000	125.000	136.000	148.000
Secondary	8.760	9.110	11.500	18.800	16.500
Exports : Primary	8.450	6.520	6.330	8.000	10.900
Secondary	48.600	39.400	47.300	48.300	51.900
Consumption: Reported, primary	98.800	88.200	87.400	98.800	105.000
Reported, secondary	81.200	83.900	83.500	83.300	85.200
Apparent, primary	129.000	121.000	117.000	129.000	136.000
Total	210.000	205.000	200.000	212.000	221.000
Price, average annual, London Metal Exchange					
Cash, dollars per metric ton	5.945	6.772	9.629	13.823	14.538
Cash, dollars per pound	2.696	3.072	4.368	6.270	6.594
Stocks: Consumer, yearend	12.500	11.600	10.900	10.600	11.500
Producer, yearend	12.600	6.150	8.040	6.580	7.310
Net import reliance as a percentage of apparent consumption	52	52	50		54

	Mine Production		**Reserves**	**Reserve base**
	2004	**2005**	**(1000 ton)**	**(1000 ton)**
United States	-	-	-	-
Australia	178.000	210.000	22,000.000	27,000.000
Botswana	33.000	37.100	490.000	920.000
Brazil	45.200	46.000	4,500.000	8,300.000
Canada	187.000	196.000	4,900.000	15,000.000
China	64.000	71.000	1,100.000	7,600.000
Colombia	75.000	72.500	830.000	1,100.000
Cuba	72.400	75.000	5,600.000	23,000.000
Dominican Republic	47.000	47.000	720.000	1,000.000
Greece	21.700	22.100	490.000	900.000
Indonesia	133.000	140.000	3,200.000	13,000.000
New Caledonia	118.000	122.000	4,400.000	12,000.000
Philippines	17.000	22.000	940.000	5,200.000
Russia	315.000	315.000	6,600.000	9,200.000
South Africa	39.900	41.700	3,700.000	12,000.000
Venezuela	20.500	22.000	560.000	630.000
Zimbabwe	9.520	9.800	15.000	260.000
Other countries	11.000	26.000	2,100.000	5,900.000
World total (rounded)	1,440.000	1,500.000	62,000.000	140,000.000

1.1.5 Nickel Reserves in Turkey

Nickel total reserve in Turkey is 40 million tones. 39.5 million tones of total, places in Manisa-Turgutlu-Çaldağ, the rest locates in Bursa-Yapköydere and Bitlis-Pancarlı. Nickel reserves in Turkey is shown in Table 1.4.

Table 1.4 Nickel reserves in Turkey (Norton & Leahy, 2006)

Location	**Type**	**Grade (%)**	**Reserve(1000 ton)**
Manisa-Çaldağ	Laterite	0.93-1.95 Ni; 0.042-0.060 Co	39.500
Bursa-Yapköy	Sulfide	1.4 Ni	163
Bitlis-Pancarlı	Sulfide	1.4 Ni	15.5

1.2 Cobalt

Cobalt, symbol Co, is a hard, lustrous, silver-gray metal, a chemical element. The name cobalt comes from the German word "Kobald" meaning evil spirit or Greek word “Cobalos” meaning mine (Shedd, 2006). The Cobalt ore can be seen in Figure 1.2.

Cobalt is a metallic element belonging to group VIII B of the periodic table. It is resistant to alkalis, but generally dissolves in dilute oxidizing acids. Cobalt sulfide, and cobalt oxide are insoluble in water, whereas cobalt chloride, cobalt sulfate, and cobalt nitrate are water soluble. There is a wide variety of cobalt compounds. The +2 and +3 oxidation states are most prevalent, however cobalt(I) complexes are also fairly common. Cobalt(II) salts form the red-pink $[Co(OH_2)_6]^{2+}$ complex in aqueous solution. Adding excess chloride will also change the colour from pink to blue, due to the formation of $[CoCl_4]^{2-}$. Cobalt oxides are antiferromagnetic at low temperature: CoO (temperature 291 K) and Co_3O_4 (temperature: 40 K). General properties of cobalt are summarized in Table 1.5 (Shedd, 2006).

Table 1.5 General properties of cobalt

Atomic Number	27
Symbol	Co
Atomic Weight	58.9332
Discovery	Brandt, circa 1735
Electron Configuration	$[Ar]4s^2 3d^7$
Isotopes	Twenty-six isotopes of cobalt have been identified. Cobalt-59 occurs naturally and is stable. Cobalt-48, cobalt-49, and cobalt-51 are not radioactive; the other sythesized isotopes are.
Properties	Cobalt has a melting point of 1495°C, boiling point of 2870°C, specific gravity of 8.9 (20°C), with a valence of 2 or 3. Cobalt is a hard, brittle metal. It is similar in appearance to iron and nickel. Cobalt has a magnetic permeability around 2/3 that of iron. Cobalt is found as a mixture of two allotropes over a wide temperature range. The β-form is dominant at temperatures under 400°C, while the α-form predominates at higher temperatures.

Figure 1.2 Picture of cobalt ore

1.2.1 Sources

Cobalt is not found as a free metal and is generally found in the form of ores. Cobalt is a fairly rare metal, comprising only 0.001 percent of the earth's crust, but is widely dispersed and commonly found and obtained in association with other mining activities.

Cobalt is usually not mined alone, and tends to be produced as a by-product of nickel and copper mining activities. The main ores of cobalt are cobaltite, erythrite, glaucodot, and skutterudite. Cobalt is also found in meteorites. The world's major producers of cobalt are the Democratic Republic of the Congo, China, Zambia,

Russia and Australia. It is also found in Finland, Azerbaijan, and Kazakhstan. It is also produced in the town of Cobalt, Ontario as a byproduct of the silver mining (Norton & Leahy, 2006).

1.2.2 Intermediate Products and End-use of Cobalt

Cobalt is a strategic and critical metal used in many diverse commercial, industrial, and military applications. The largest use of cobalt is in superalloys, which are used to make parts for gas turbine aircraft engines. Cobalt is also used to make magnets; corrosion- and wear-resistant alloys; high-speed steels; cemented carbides (also called hardmetals) and diamond tools; catalysts for the petroleum and chemical industries; drying agents for paints, varnishes, and inks; ground coats for porcelain enamels; pigments; battery electrodes; steel-belted radial tires; and magnetic recording media. Cobalt metal is used in electroplating because of its appearance, hardness, and resistance to oxidation. It is alloyed with iron, nickel and other metals to make Alnico, an alloy of unusual magnetic strength with many important uses. Stellite alloys, containing cobalt, chromium and tungsten, are used for high-speed, heavy-duty, high temperature cutting tools, and for dies. Cobalt salts have been used for centuries to produce brilliant and permanent blue colours in porcelain, glass, pottery, tiles, and enamels. Cobalt carefully used in the form of the chloride, sulphate, acetate, or nitrate has been found effective in correcting a certain mineral deficiency disease in animals. As an element in the diet of sheep, cobalt prevents a disease called swayback and improves the quality of the wool. Cobalt compounds have been used for centuries to colour porcelain, glass, pottery, tile and enamel. Some of these compounds are known as: cobalt blue, cerulean, new blue, cobalt yellow and cobalt green. In addition to being used as a dye, cobalt is also important to human nutrition as it is an essential part of vitamin B (Norton & Leahy, 2006).

1.2.3 World Production Levels and Trends of Cobalt

The development of global mine production during this decade is shown in Table 1.6.

Table 1.6 Mine production and reserves of cobalt (Norton & Leahy, 2006)

Salient Statistics-United States:	**2001**	**2002**	**2003**	**2004**	**2005**
Production					
Mine	-	-	-	-	-
Secondary	2,810	2,750	2,130	2,300	2,400
Imports for consumption	9,410	8,450	8,080	8,720	10,500
Exports	3,210	2,080	2,710	2,510	2,700
Shipments from Government stockpile excesses	3,050	524	2,380	1,630	1,000
Consumption					
Reported (includes secondary)	9,540	7,880	7,590	8,450	9,000
Apparent (includes secondary)	11,800	9,830	10,000	9,920	11,000
Price, average annual spot for cathodes, dollars per pound	10.55	6.91	10.60	23.93	15.80
Stocks, industry, yearend	1,330	1,140	1,010	1,240	1,440
Net import reliance as a percentage of apparent consumption	76	72	79	77	78

	Mine Production		**Reserves**	**Reserve base**
	2004	**2005**	**(1000 ton)**	**(1000 ton)**
United States	-	-	NA	860,000
Australia	6,700	6,600	1,300,000	1,600,000
Brazil	1,400	1,400	35,000	40,000
Canada	5,200	5,700	130,000	350,000
Congo (Kinshasa)	16,000	16,000	3,400,000	4,700,000
Cuba	3,600	3,600	1,000,000	1,800,000
Morocco	1,600	1,600	20,000	NA
New Caledonia[6]	1,400	1,400	230,000	860,000
Russia	4,700	5,000	250,000	350,000
Zambia	10,000	9,000	270,000	680,000
Other countries	1,800	2,100	200,000	1,500,000
World total (rounded)	52,400	52,400	7,000,000	13,000,000

1.3 Production of Nickel and Cobalt

Nickel ore deposits are accumulations of nickel sulfide minerals (mostly entlandite) and laterites. Dissemination of Nickel in Laterite and sulphide ores can be seen in Figure 1.3. Laterite type ores placed in soft surface deposits and have easy low mining costs because the nickel is dissolved all of the ore must be processed. Sulphide type ores are deep underground mines and hard rock but in this type minerals of value can be concentrated by lower costs (Falconbridge Technology Centre Investors Presentation, 2004).

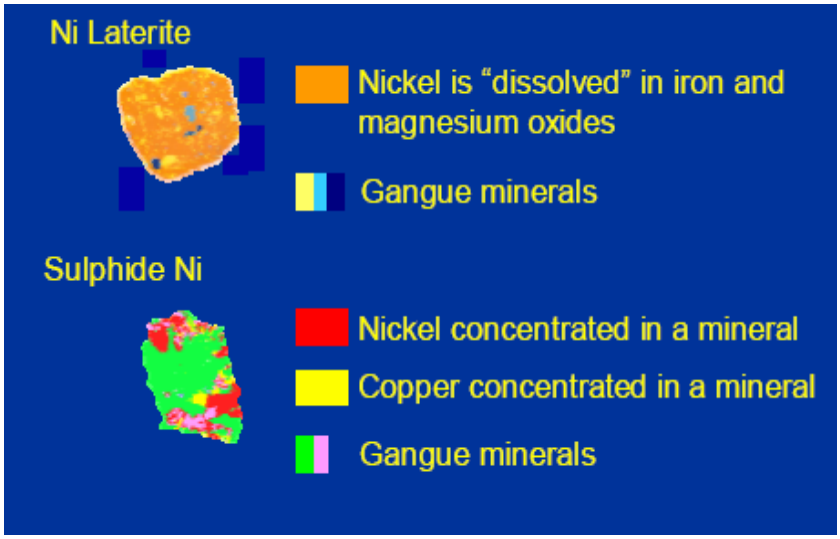

Figure 1.3 Dissemination of nickel in laterite and sulphide ores

Cobalt is usually mined as a by-product of either nickel, copper, or other more abundant metals. Most cobalt production is ultimately dependent on the production of copper and nickel. The mined ore often contains only 0.1% elemental cobalt. The ore is processed and the cobalt is extracted and converted to 99.9% cobalt metal. The metal is sold to a cobalt chemical manufacturer who converts the metal to cobalt carbonate, cobalt sulphate, or other cobalt salt derivatives (Middleton, 2002).

The methods for the extraction and refining of nickel and cobalt minerals depend on the mineralogical and geological characteristics of the ore. To date, nickel and cobalt have mainly been extracted from sulfide and laterite ores (Middleton, 2002).

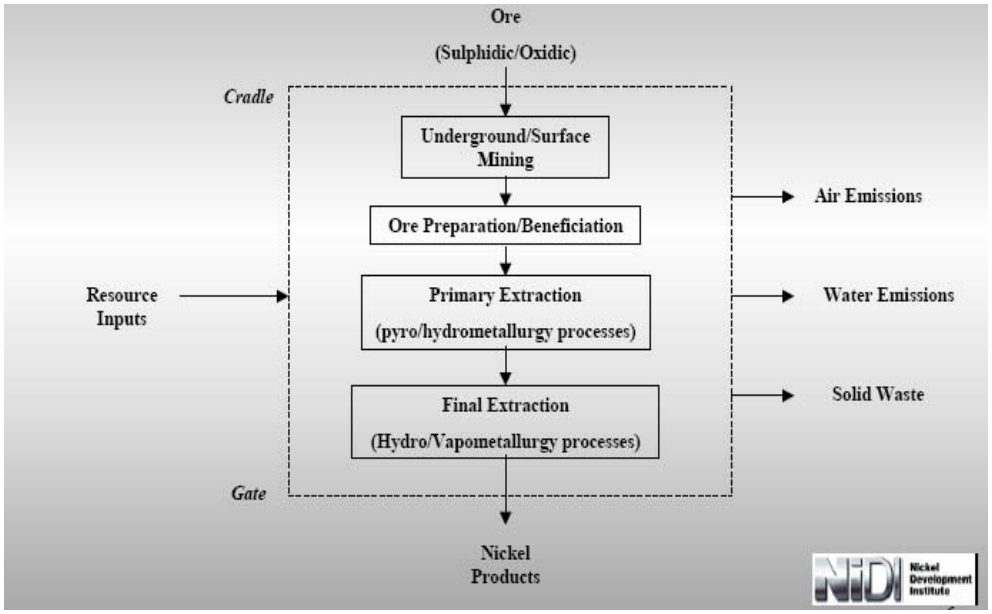

Figure 1.4 Basic flowsheet of sulphidic and oxidic ore processing

Both sulfide ore concentrates and laterite ores are subjected to pyro- and hydrometallurgical processes. The basic steps of nickel ore processing can be seen in Figure 1.4. The pyrometallurgical processing basically involves three operations, i.e., roasting, smelting, and converting. During roasting, the concentrate is oxidized by hot air. Most of the iron is oxidized, while nickel, copper, and cobalt remain combined with sulfur. Part of the sulfur is removed as gaseous sulfur dioxide. The roasted product is smelted in a furnace together with a siliceous flux to obtain two immiscible phases, an iron-rich silicate slag and a nickel-rich sulfide matte, which also contains iron, copper, and cobalt (Taylor, 2000).

The matte is treated in a "converter" where more sulfur is driven off and the remaining iron is oxidized and removed as slag. The matte is allowed to cool and treated in different ways. It may be, for example, cast into anodes for electrolytic refining or cooled slowly to facilitate crystallization to nickel sulfide, copper sulfide and a nickel-copper alloy containing the desired metals. These three phases can then be separated by flotation and magnetic separation. The species of nickel likely to be present during roasting, smelting, and converting include the ore, nickel subsulfides, nickel copper sulfides, nickel oxides, nickel-copper oxides, arsenides, and anhydrous nickel sulfate. The extraction of nickel from laterite ores is similar to the extraction of nickel from sulfide ores with the exception that sulfur by pyrometallurgical

processes (commonly gypsum) has to be added. The molten matte is charged into a converter where the iron is oxidized and the sulfur combines with nickel to form Ni_3S_2 (Taylor, 2000).

Smelting to ferronickel is essentially the same as matte smelting, except that no sulfur is added. It is often applied to laterite ores. The resulting iron-nickel alloy contains 20-50% nickel. Most of the nickel matte obtained from sulfide or laterite ore smelting undergoes further refining techniques, such as electro-, vapo-, or hydrometallurgical refining, but a part of the matte is roasted to marketable nickel oxide sinter (WHO, 1991).

During vapometallurgical refining, impure metal obtained by the reduction of nickel oxide is subjected to the action of carbon monoxide forming volatile nickel carbonyl [$Ni(CO)_4$] (carbonyl or Mond process). This reaction is reversed by heat and the nickel carbonyl decomposes to pure nickel metal and carbon monoxide. The carbonyl process produces the purest nickel (99.97% or more) (WHO, 1991).

The smelting and refining processes yield various marketable forms of nickel of different purities. Commercial forms of primary nickel are summarized in Table 1.7.

Table 1.7 Commercial forms of primary nickel (WHO, 1991)

Type	***Composition (%)***								
	Nickel	**Carbon**	**Copper**	**Iron**	**Sulfur**	**Cobalt**	**Oxygen**	**Silicon**	**Chromium**
Pure unwrought nickel									
Cathode	>99.9	0.01	0.005	0.002	0.001	-	-	-	-
Pellets	>99.97	<0.1	0.001	0.0015	0.0003	$5x10^{-5}$	-	-	-
Powder	99.74	<0.1	-	<0.1	<0.01	-	<0.15	-	-
Briquettes	99.9	0.01	0.001	0.002	0.0035	0.03	-	-	-
Rondelles	99.25	0.022	0.046	0.087	0.004	0.37	0.042	-	-
Ferronickel*	20-50[a]	1.5_1.8	-	Rest	<0.3	-	-	1.8-4	1.2-1.8
Nickel oxide	76.0	-	0.75	0.3	0.006	1.0	Rest	-	-

* Ranges used to denote variable grades produced.

[a] Cobalt included with nickel (1-2%).

Hydrometallurgical refining can be applied both to laterite ore and sulfide ore or sulfide ore concentrates. Soluble nickel amines are formed during pressure leaching

of the sulfide ore concentrate with strong ammoniacal solution at a moderately elevated temperature. The saturated solution is boiled to drive off ammonia and precipitate copper as sulfide. Sulfur is oxidized. Nickel and cobalt are recovered as pure metal powders by reduction with hydrogen under pressure. Laterite ores must first be reduced. The reduced ore is leached with an ammonia-ammonium carbonate solution. Nickel dissolves as nickel amine. The saturated solution is heated by steam, ammonia is driven off, and nickel is precipitated as a basic carbonate. Pure nickel (99.9%) can be produced by electrolytic refining. Generally, an impure metal anode (produced by reducing nickel oxide) and a cathode starting sheet are placed in an acidic electrolytic solution. When a current flows, nickel and other metals are dissolved from the anode. The electrolyte is then removed, purified and returned to the cathode compartment, where nickel is deposited on the cathode (Taylor, 2000).

Forty years after the construction of the first pressure acid leaching plant (PAL) for nickel laterites by Freeport at Moa Bay, Cuba, three new PAL plants are now in operation in Western Australia. Although modern designs of autoclaves and heat recovery systems have been adopted, the basic pressure leaching concept at the heart of the Bulong, Cawse and Murrin Murrin plants is, in fact, largely unchanged from Moa Bay. The main differences lie in how the nickel and cobalt are recovered and refined, for which each operation varies from each other as well as from Moa Bay. Murrin Murrin is the closest to Moa Bay with mixed sulphide precipitation, a strategy which was prudent in view of the large throughput and capital investment. Bulong, adopted a direct solvent extraction approach to reduce capital cost, in which cobalt and nickel are extracted sequentially from the pressure leach solution. Cawse, on the other hand, selected mixed hydroxide precipitation followed by ammonia releach, which allowed use of the nickel solvent extraction step commercially proven at Queensland Nickel. This strategy enabled Cawse to catch up with the other two, despite being a later starter (Taylor, 2000). Abbreviated flowsheets are illustrated in Figures 1.5-1.7.

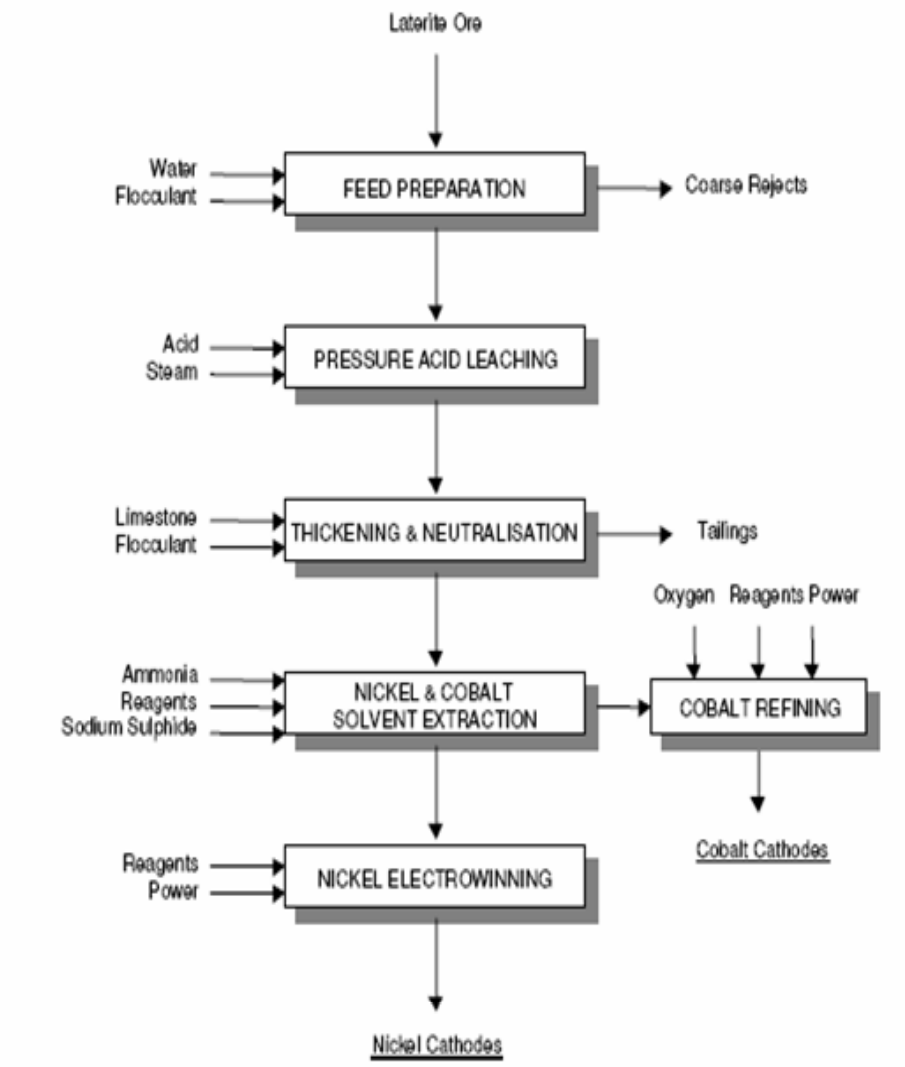

Figure 1.5 Simplified flowsheet of Bulong

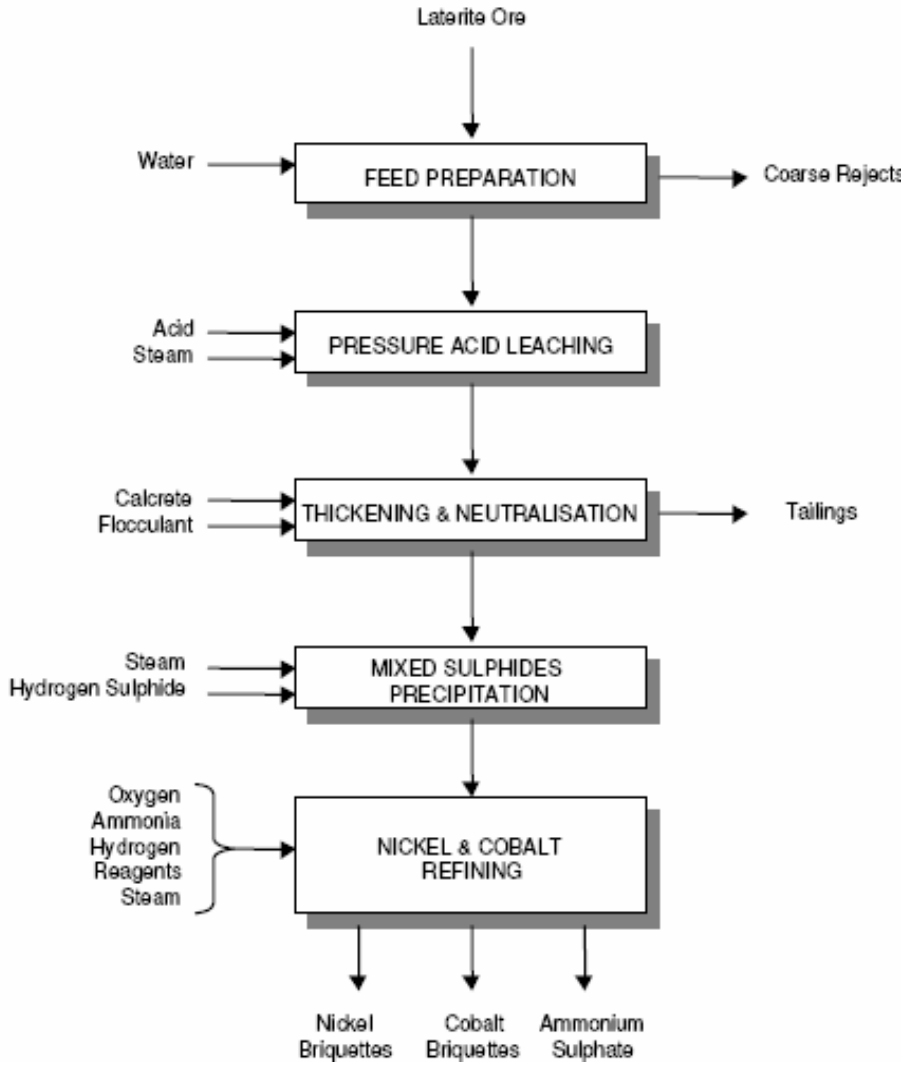

Figure 1.6 Simplified flowsheet of Murrin-Murrin

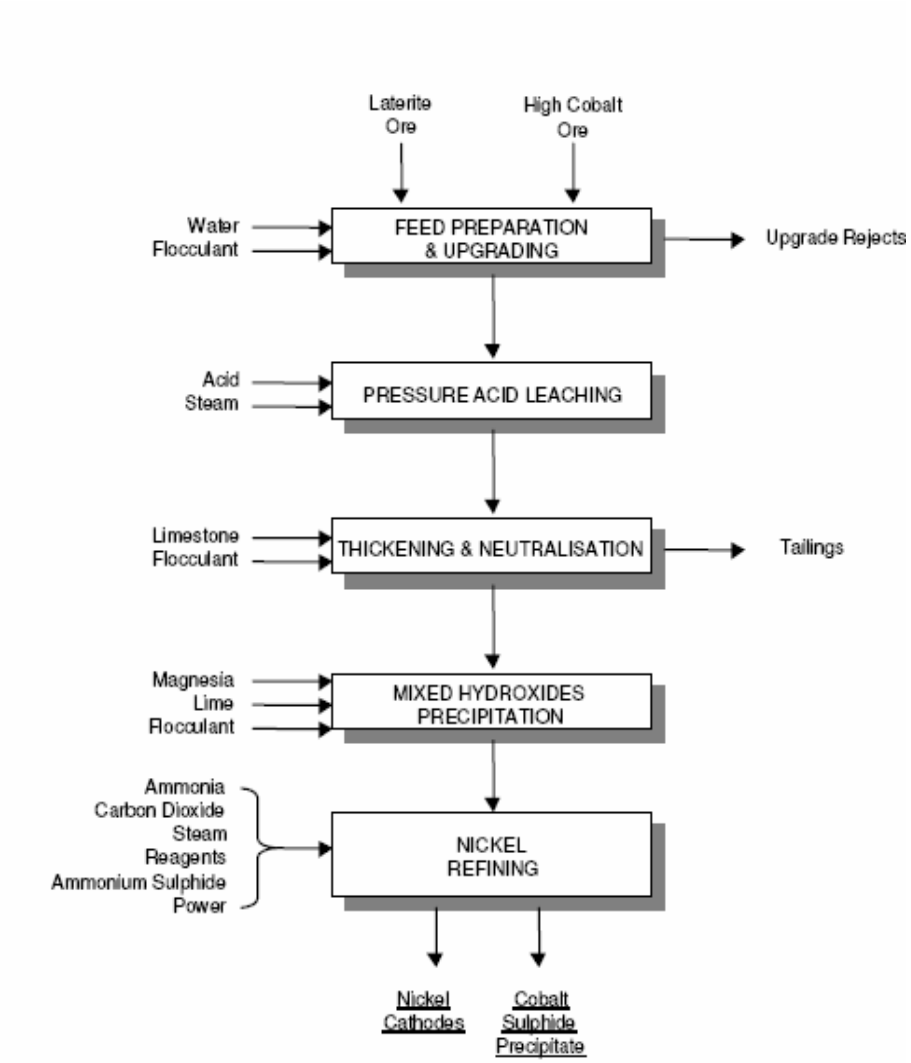

Figure 1.7 Simplified flowsheet of Cawse

These include process steps applied in other operations, emerging technology and innovations previously considered for PAL plants but not yet commercially applied (Taylor, 2000).

All current PAL plants, including Moa Bay, operate at around 250 ^{o}C in the autoclaves. They reported that benefits of higher temperature included faster leach kinetics, reduced retention time and therefore smaller autoclaves, lower acid consumption and improved purity of the resulting leach solution. On the debit side, the operating pressure rises significantly, requiring increased autoclave wall thickness (Taylor, 2000).

In this arrangement, high acid consuming ore is used in place of all or part of the limestone to neutralise residual leach acid at atmospheric pressure. The partially leached ore then joins the feed to the autoclaves. This improves the economics of treating the high acid consuming ore and, in some cases, may significantly add to the economic ore reserves. The requirement for limestone will be eliminated or significantly reduced with resulting cost savings. A typical flowsheet is depicted in Figure 1.8. In an alternative concept, the use low grade ore for neutralisation could be considered (Taylor, 2000).

A potential lower cost alternative is to use lime in place of magnesia, combined with releaching in an ammonia/ammonium sulphate medium instead of ammonia/ammonium carbonate. One disadvantage is reduced releach efficiencies, requiring further leaching of the residue with, for example, sulphuric acid and sulphur dioxide to recover and recycle nickel and cobalt. Others include a higher mass of releach residue due to the presence of gypsum, the need for a lime boil circuit in lieu of steam stripping to recuperate ammonia from releach residue and bleed streams, and slower stripping kinetics in the subsequent nickel solvent extraction circuit leading to the requirement for an additional stage. The cost benefits of the lime precipitation route will depend on the relative cost and availability of the reagents (Taylor, 2000).

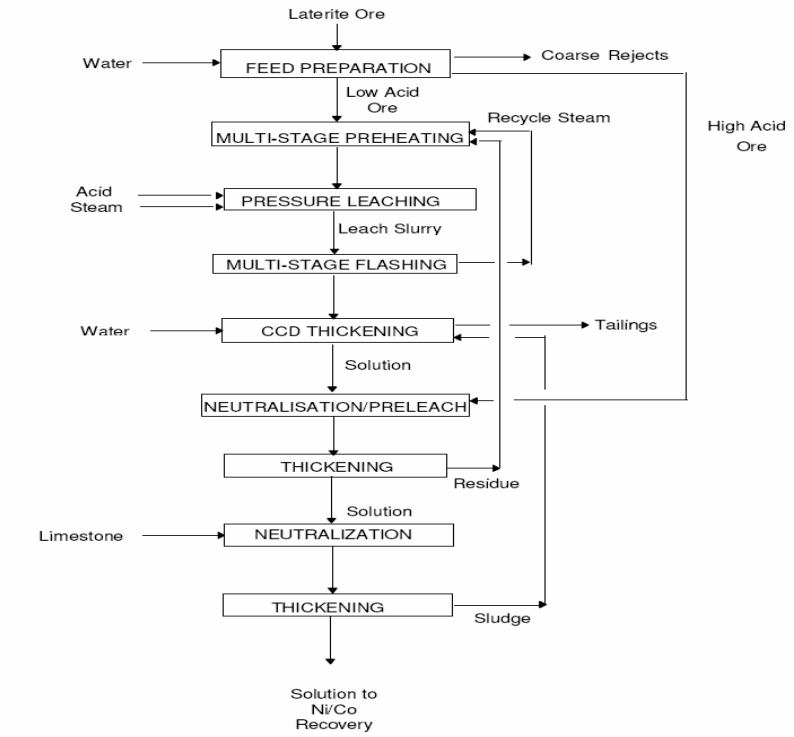

Figure 1.8 Flowsheet of neutralisation with high acid consuming ore

In the longer term, other new technical developments will be considered in the quest to achieve process improvements and reductions in capital and operating costs (Taylor, 2000).

Membrane technology is well established for wastewater treatment and environmental remediation applications, which can offer the possibility of reagent recovery and reuse. However, there is a growing trend to develop applications for process enhancements such as solution concentration, purification, selective ionic separation and acid recovery. The technology could also offer opportunities for cost savings, process improvement and simplification in PAL flowsheets. Another area of development is molecular recognition technology (MRT), which involves the use of chemical ligands to selectively complex with ions in solution. Ligands are already in use for the purification of nickel electrolytes. Opportunities for Ni/Co PAL applications include electrolyte purification and treatment of low grade solutions (Taylor, 2000).

Some laterites have already been shown to be amenable to simple upgrading by removal of low grade coarser material by screening or cycloning. Nickel sulfide ores

are mostly mined underground using drilling, blasting, and other techniques. Milling procedures include liberation, flotation, and magnetic separation. Liberation of the sulfides from the gangue includes grinding of the rock material. The commonly fine nature of most laterites means that grinding may not be needed, thus rendering flotation relatively inexpensive. Therefore, it may be an economic proposition even if there are significant metal losses with the tailings.Then the sulfides are concentrated by flotation processes. Flotation, which has given some encouragement in the past, though not enough to lead to commercial application. Flotation involves streaming air bubbles through an aqueous slurry of the ore particles in a flotation cell. The particles that are not wetted by the liquid adhere to the air bubbles, rise to the surface of the slurry, and can be removed. The addition of different chemicals to the flotation medium allows the selective flotation of nickel- and copper-rich fractions. Most of the pyrohotite (both lump ore and ground ore) can be separated magnetically, because of its magnetic properties (Taylor, 2000).

Bulong is the only operating PAL plant employing direct Solvent Extraction. In principle, the direct approach offers relative simplicity and reduced capital cost, especially if more selective extractants are developed. Thus, further development can be expected. Another opportunity for a more selective extractant is for the recovery of cobalt from the cobalt Solvent Extraction strip solution in the current Bulong flowsheet to reduce capital and operating costs (Taylor, 2000).

All four operating PAL plants include a series of large diameter corrosion resistant thickeners. These circuits involve significant capital and operating costs, occupy large footprint area, and require a significant quantity of wash water which dilutes the feed to the associated Ni/Co recovery facilities. A possible option is to use a resin-in-pulp (RIP) system, which employs a resin to recover the nickel and cobalt values from the leach pulp without thickening. The widely used, and highly successful, CIP process for gold is a similar concept, in which carbon plays the role of the resin. It is interesting to note the current interest in the use of resins for gold recovery. For the potential PAL plant application, the best approach may be to extract the nickel and cobalt together in a single CIL circuit, then separate and purify them for individual recovery from the resulting concentrated eluate solution. Final

recovery could be by Electrowinning, hydrogen reduction etc. The eluate solution could be either sulphate or chloride based. The challenge for PAL plants is to find an existing resin or develop a new one capable of extracting the nickel and cobalt with a reasonable degree of selectivity, so that the resin loading is not dominated by another element. It may be preferable to drop out elements such as iron ahead of RIP to alleviate the task of the resin. A notional flowsheet is shown in Figure 1.9 (Taylor, 2000).

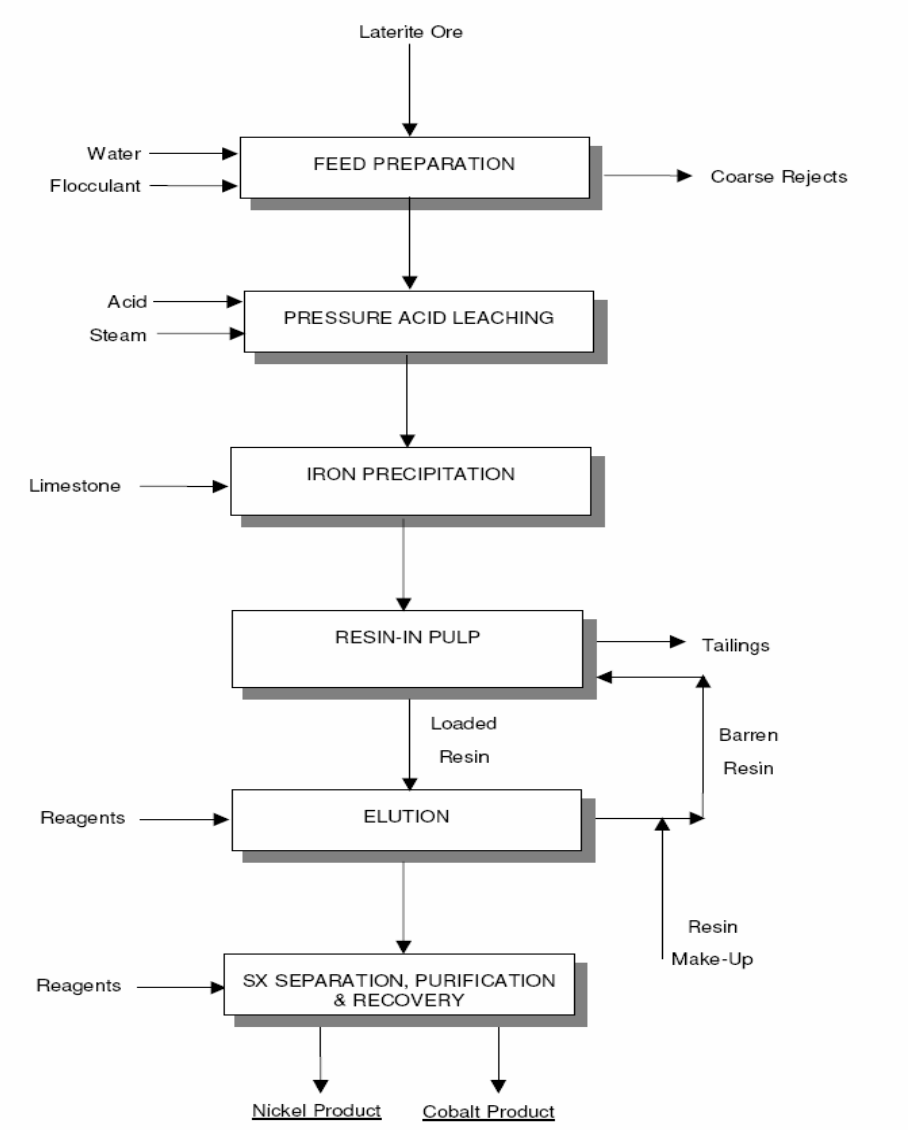

Figure 1.9 Notional RIP flowsheet

The focus on direct hydrometallurgical treatment of sulfide ores and concentrates has continued unabated in research groups around the world. This is reflected in the

number of leaching plants (for conventional, pressure, bacterial and heap leaching) which are either under construction or at various stages of planning (Taylor, 2000).

Diniz et al. (2002) investigated the effect of pH on the adsorption of nickel (II), copper (II), cobalt (II), lead (II), manganese (II), and iron (III) from concentrated chloride solutions onto Dowex M-4195. This chelating resin had an unusual ability to adsorb many of these metals, most notably copper, even at very low pH. The selectivity for many of these metals made this resin particularly attractive for detoxifying concentrated acidic chloride solutions generated during the processing of many manganese ores and minerals.

The pressure acid leach (PAL) process has been applied in three recent new plants which recover nickel and cobalt from lateritic ores in Western Australia. This process was first developed and implemented at Moa Bay in Cuba and there are several new plants at the feasibility, planning and construction phases in Australia and elsewhere (Kuck, 2001).

The PAL process involves the leaching of the ore with sulfuric acid at temperatures in the range 250– 270 ^{o}C followed by a number of stages of countercurrent decantation (CCD) in which the pregnant liquor is separated from the unleached residue and passed as overflow to neutralisation and metal recovery while the underflow (typically 35% solids) is removed as residue to the tailing dam. Due to washing inefficiencies with the fine laterite leach residue, an economically significant fraction of soluble nickel and cobalt passes unrecovered to the tails. Ion exchange processes are generally more suitable for treating dilute solutions of metal ions such as those in the tailings. The major advantage of ion exchange is the ability to recover metals from slurries directly in a resin-in-pulp (RIP) process. (Zainol & Nicol, 2003) Cation chelating resins such as those with the iminodiacetate functional group have the advantage of operating in the low pH region with high capacity and high selectivity for the metals of interest and they are also relatively easily eluted with dilute acid (Rohm and Haas, 1998)

According to Zontov et al. (2001), resin-in-pulp technology can be applied to (1) existing operations with CCD processes or (2) process design under consideration for

replacing CCD conventional technology. A resin in pulp process can be designed so that the adsorbent recovers significant amounts of the dissolved product before it is screened from the pulp, avoiding losses of valuable product that occurs during a solid–liquid separation step. In addition, their application is able to provide a more effective and straightforward purification compared to purification by precipitation or solvent extraction, which are the most commonly used techniques at present for these purpose (Kononova et al., 2000; Mendes & Martins, 2005; Grinstead, 1984).

In Mendes and Martins' studies four chelating ion exchange polymeric resins were tested to remove Ni and Co from synthetic solutions simulating pressure acid leach liquor. These four commercially available ion exchange polymeric resins, Dowex M4195R, Amberlite IRC748R, Ionac SR-5R and Purolite S930R, presented very peculiar features concerning selectivity and each of them seemed to be efficient on nickel and cobalt sorption under certain experimental conditions. Dowex M4195R showed the best results for nickel and cobalt selective sorption from acid liquors, since nickel and cobalt were equally recovered, in all pH range, with small influence of other elements. Even in lower pH, such as pH = 1, Dowex M4195R had the best performance for nickel and cobalt sorption. Amberlite IRC 748R also presented very promising results (Mendes & Martins, 2005).

Mendes and Martins (2005) investigated the developments and results that have been obtained in recent studies done by using the resin in pulp (RIP) technology in the extraction of nickel and cobalt. In their experiments Amberlite IRC 748 was used and it appeared to be more selective for nickel over other metals. They proved that the increase in pH value was able to provide a better nickel recovery from pulp and also other parameters such as temperature, stirring speed, time and resin to pulp ratio had some influence on nickel adsorption and the best values for maximizing nickel recovery could be defined. The resin had a strong affinity for iron and copper, which should be removed from the solution by the addition of lime or limestone prior to RIP process.

The adsorption of cobalt, chromium and nickel from aqueous solutions on IRN77 cation-exchange resin has been studied comparatively by Rengaraj et al. (2002). The percentage removal of cobalt, chromium and nickel was examined by varying

experimental conditions, viz. dosage of adsorbent, pH of the solution and contact time. It was found that more than 95% removal was achieved under optimal conditions.

Kononova et al. (2000) researched the ion exchange recovery of nickel from the system $Mn(NO_3)_2$–H_2O by aminocarboxylic amphoteric ion exchangers AMF-1T, AMF-2T, AMF-2M, ANKB-35 as well as on carboxylic cation exchanger KB-2T by means of sorption–desorption method. The ion exchanger AMF-2T possesses the best selectivity to Ni(II) ions, therefore the nickel separation and the pure $Mn(NO_3)_2$ salt production are possible under dynamic conditions.

In Lehto et al. (1996) studies chelating resins have shown better performance with respect to transition metal ions compared to ordinary organic ion exchangers. Since chelating resins form strong complexing chelates with transition metals, they can strip complexes present in the solution that are weaker than those in the resin (Koivula et al., 2000). In the same way, since alkali and alkaline earth metals do not form complexes, these metals are not loaded (Lehto et al., 1999).

Grinstead et al. (1979) studied on nickel and cobalt sorption according to some experimental parameters, such as pH. The pH influence was evaluated during the kinetics sorption studies, which is the most important variable governing metal ion sorption. In its simplest form, the sorption of a metal ion by the resin can be expressed as follows:

$$M^{+m} + \overline{R \cdot nH^{+}} \rightarrow \overline{MR^{+m}} + nH^{+} \qquad \textbf{(1.1)}$$

$$K' = \frac{\overline{(MR^{+m})}(H^{+})^{n}}{\overline{(R \cdot nH^{+})}(M^{+m})}$$

where R represents the resin structure, and barred species are in the resin phase. This is not a complete expression of the sorption process, since if m≠n, then some sulfate species must transfer into or out of the resin to maintain electrical neutrality. In such a situation, K' will not be a constant, but will depend upon the sulfate concentrations in both the resin and solution phases (Grinstead et al., 1979).

As it can be seen in various examples ion exchange polymeric resins have found increasing application over the last decade and are available commercially for almost any separation process (Grinstead et al., 1979).

Ion exchange is a hydrometallurgical process for recovering, upgrading, separating and purifying metals and minerals using resins to transfer the target species from one solution to another via a solid substrate. Resins are functionalised synthetic polymers that have the ability to exchange ions with those present in an aqueous solution. With this process, dilute solutions can be treated effectively, and the metal of interest can be removed or recovered selectively while rejecting others. Ion exchange also has the potential to treat poorly clarified liquors and pulps, thus avoiding the need for costly solid / liquid separations. As an example, RIP technology can be used to clean up effluent (solution or slurry) streams and produce an environmentally friendlier effluent, whilst at the same time recovering trace elements of valuable metals.

1.4 Ion Exchange Technology

1.4.1 Historical Review

The widespread interest in ion exchange and its general utility during the past decade are direct results of the development and commercial availability of stable and high capacity ion-exchange resins (Kunin, 1960):

1850-1854: Discovery of ion exchange by Thompson and Way in England.

1905: Development of commercial use of ion exchange developed by Gans in Germany.

1935: Synthesis of synthetic ion-exchange resins by Adams and Holmes.

1939: Introducing patents of Adams and Holmes to U.S. industry.

1940: Development of first commercial phenol formaldehyde-based cation and anion exchange resins.

1946: Development of anion exchange resins for ulcer therapy.

1948: Development of styrene-based ion-exchange resins and first unifunctional carboxylic cation exchange and first strong base anion exchange resins.
1950: Development of resins for sodium reduction.

1952: Construction of first commercial ion-exchange uranium recovery plant.
1955: Construction of first commercial uranium resin-in-pulp plant and first atomic-powered submarine with an ion exchange deionizing Monobed.
1956: Development of first large-scale commercial ion-exchange rare earth separation plant.
1957: Processing of first commercial liquid ion-exchange operation.

Since then, many adaptations of the process and variations of the properties of the original products have been made to suit the applications of these materials. Today, numerous ion exchange resins are available commercially and are widely used in water treatment, separation and purification in hydrometallurgy, etc. (Zainol & Nicol, 2003)

1.4.2 Ion Exchange Phenomenon

Ion exchange describes the physical-chemical process which can be defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase, the ion exchanger being insoluble in the medium in which the ion exchange is carried out. Ions held by electrostatic forces to charged functional groups on the surfaces of a solid are exchanged for ions of like charge in a solution in which the solid is being contacted. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign. If an ion exchanger M^-A^+, carrying cations A^+ as the exchanger ions, is placed in an aqueous solution phase containing B^+ cations, an ion exchange reaction takes place which may be represented by the following equation (Harland, 1994):

$$\underset{Solid}{\overline{M^-A^+}} + \underset{Solution}{B^+} \leftrightarrow \underset{Solid}{\overline{M^-B^+}} + \underset{Solution}{A^+} \qquad \textbf{(1.2)}$$

The equilibrium represented by the above equation is an example of cation exchange, where M^- is the insoluble fixed anionic complement of the ion exchanger

M^-A^+, often called simply the fixed anion. The cations A^+ and B^+ are referred to as counter-ions, whilst ions in the solution which bear the same charge as the fixed anion of the exchanger are called co-ions. In much the same way, anions can be exchanged provided that an anion-receptive medium is employed. An analogous representation of an anion exchange reaction may be written as follows (Harland, 1994):

$$\underset{Solid}{\overline{M^+C^-}} + \underset{Solution}{D^+} \leftrightarrow \underset{Solid}{\overline{M^+D^-}} + \underset{Solution}{C^-} \qquad \textbf{(1.3)}$$

Ion exchange is most useful for dilute wastewaters (less than 100 mg/L metals). It is effective at higher metal concentrations but the economics favor other technologies must be discussed (Nandy et al, 1990).

Ion exchange process used in;

- *Water treatment:* Softening and deionization, condensate treatment, process water treatment, drinking water treatment, effluent treatment, wastewaters treatment, brewing water treatment. The treatment of a variety of industrial wastes to recover valuable waste materials, such as the ionic forms of the gold, silver, platinum, chromium, and uranium.

- *Hydrometallurgy:* Recovery and concentration of precious metals, extraction and concentration of uranium and nickel from dilute leaching solutions, separation of rare earth metals and of heavy metals, purification of plutonium.

- *Food industry:* Sugar and sweetening agents; wine-making; fruit juices; citric acid and amino acid separation, protein recovery, sorbitol deionization.

- *Dairy industry:* Milk whey demineralization, purification of lactose, removal of calcium and sodium from milk, preparation of pure casein.

- *Medicine:* Reduction in serum cholesterol, bipolar resins for blood preservation.
- *Biochemistry and biotechnology:* Immobilized enzymes, immobilized microorganisms, virus and protein sorption, preparation of biologically active substances.

- *Analytical chemistry:* Ion exchange chromatography, ion chromatography.

- *Electronic Industry:* The production of ultra pure water for the electronic and pharmaceutical industries.

- *Photography:* Silver separation from photographic baths, recovery of color developers, removal of hexacyanoferrate.

- *Pollution control:* Detoxification, removal of toxic gases, stabilization of metallic pollutant in industrial wastes, treatment of waste gases and waste waters (Ekinci, 1996).

1.4.3 Ion Exchange Resins

Ion exchangers are insoluble materials carrying reversibly exchangeable ions. These ions can be stoichiometrically exchanged for other ions of the same sign when the ion exchanger is in contact with an electrolyte solution. They are polymers carrying fixed functional groups (see Figure 1.10) (Zagarodni, 1997).

The fixed groups are either permanently ionized so that they always possess a formal charge, or are capable of ionization or acceptance of protons to from the charged site. The resin interacts with mobile ions from an external solution. Ions of opposite charge to that on the resin, and which are exchanged by the resin, are known as counter-ions, while ions of the same charge as that of the exchange sites are known as co-ions. The polymeric network of the resin is known as the matrix (Bolto & Pawlowski, 1987).

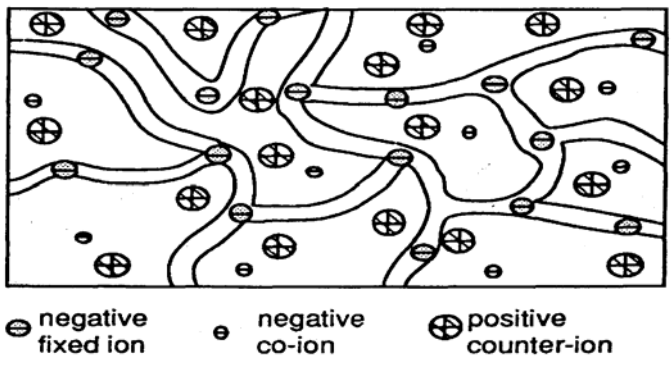

Figure 1.10 A cation exchange resin structure (Zagarodni, 1997).

Basic requirements of ion exchange resins are:

1. Resin must be highly polymeric and sufficiently crosslinked.
2. Resin must be of high exchange capacity.
3. Resin must be as stable as possibly chemically and physically.
4. Resin must be sufficiently hydrophilic.
5. Resin must be of granulation tuned to envisaged application.
6. Resin in swollen state should be denser than water (Bolto & Pawlowski, 1987).

The ionizable group attached to resin structure determines the functional capability of the exchanger. According to their functional groups, ion exchangers are divided into three groups:

1.4.3.1 Cation Exchange Resins

1.4.3.1.1Strongly Acid Type. The most important cation exchange resins are those of the sulfonic acid type ($-SO_3H$), which are used in acid, neutral, or alkaline solution . The resins are widely used for the uptake and chromatographic separation of ampholytic substances, e.g., amino acids (Samuelson, 1963).

1.4.3.1.2Weakly Acid Type. These cation exchange resins possess carboxylic acid groups (-COOH) as the functional species. Being of weak electrolyte character, the carboxylic acid groups dissociate to varying extents depending on the pH level. They are essentially undissociated at pH 3 and below, dissociation increases with increase in pH until by pH 10 until they are fully dissociated. Carboxylic acid resins are very stable thermally. This type of resin used for separation of basic amino acids and the separation of strong organic bases from weak ones (Samuelson, 1963).

1.4.3.2 Anion Exchange Resins

1.4.3.2.1Strongly Basic Type. In analytical chemistry, resins of the strong basic resin type are much more useful than weakly basic resins. Anion-exchange resins of the strong base type are usually based on quaternary ammonium groups ($-N^+R_3OH^-$), connected to the aromatic rings of styrene-DVB copolymers via a methylene group. In general, strong base resins are very much less stable than strong acid resins. This

type of resins used for the uptake and chromatographic separation of complex metal ions (Bolto & Pawlowski, 1987).

1.4.3.2.2Weakly Basic Type. Weak base resins can possess *tertiary* (-NR_2), *secondary* (-NHR) or *primary* (-NH_2) *amino groups*, or mixtures of the same. The matrix can be as for strong base resins, although there are other matrices employed specifically for weak base resins. In acid medium a weakly basic resin in the free-base form is a valuable tool for the removal of acids from solutions of various non-electrolytes. These resins are preffered when solutes which are unstable at high pH are present in solution (Samuelson, 1963).

1.4.3.3 Chelating Ion Exchangers

Compared with sulfonic acid resins the chelating resins show superior selectivity in their sorption of various metallic cations. The published data show that the affinities for alkali metals are low, whereas most multivalent cations are held very strongly by the chelating resins (Samuelson, 1963).

These are weak acid cation exchangers consisting of iminodiacetate, aminomethyl and phosphonic functional groups in sodium form. These groups impart to the resin properties similar to those of ethylenediaminetetra-acetic acid (EDTA), in that the resin can form strong complexes with heavy metal ions. These resins have optimum porosity and surface area that give excellent operating capacities (Samuelson, 1963).

Certain resins can exchange both cations and anions, and are termed as *amphoteric ion* exchangers (Bolto & Pawlowski, 1987).

According to their material, ion exchangers are divided into two groups:

1.4.3.3.1 Inorganic Ion Exchangers. Most inorganic materials are crystalline alumosilicates with cation exchange properties. Characteristic representatives of this group of materials are the zeolites which are the best known of these, and included the minerals: analcite ($Na[Si_2AlO_6]_2.6H_2O$), chabazite ($Ca,Na[Si_2AlO_6]_2.6H_2O$),

harmotome ($K,Ba[Si_5Al_2O_{10}].5H_2O$), heulandite ($Ca[Si_3AlO_8].5H_2O$), natrolite ($Na_2[Si_3Al_2O_{10}].2H_2O$) (Bolto & Pawlowski, 1987).

1.4.3.3.2Organic Ion Exchangers. The majority of organic resins have a matrix of an irregular, three-dimensional network of macromolecular hydrocarbon chains. In most cases, this consists of a copolymer of styrene and divinylbenzene (DVB), with the latter providing the crosslinking. The properties of the resins are determined all else by the ion-exchange groups present on the matrix. In general, these may be divided into three groups: cation exchangers (strong acid or weak acid groups); anion exchangers (strong base or weak base groups); specific ion exchangers (selective chelating groups) as mentioned before (Bolto & Pawlowski, 1987).

According to their physical structures, ion exchange resins are divided into five groups:

1.4.3.3.3Gel Resins. The organic ion exchangers first developed were so-called gel resins. They have an essentially homogeneous distribution of water throughout the resin matrix (Bolto & Pawlowski, 1987).

Gel resins are homogenous crosslinked polymers and are the most common resins available. Gel resins usually have higher operating efficiencies and cost less. There are no permanent pore structures for the gel type resins. These pores are generally considered to be quite small and are referred as gelular pores or molecular pores. The pore structures are determined by the distance between the polymer chains and crosslinks which vary with the crosslink level of the polymer, the polarity of the solvent and the operating conditions. The gel type resins are generally translucent (Desilva, 1999).

1.4.3.3.4 Macroporous Resins. Macroporous resins are made with large pores that permit access to interior exchange sites. Macroporous resins are manufactured by a process that leaves a network of pathways throughout the bead. This sponge like structure allows the active portion of the bead to contain a high level of DVB crosslinking without affecting the exchange kinetics. Unfortunately, it also means

that the resin has a lower capacity because the beads contain less exchange sites (Desilva, 1999).

Macroporous copolymers, being highly crosslinked, are generally tougher than their gel equivalents and are more resistant to physical breakdown through mechanical forces, osmotic volume changes, and chemical degradation of crosslinking through the action of oxidizing agents (Harland, 1994).

1.4.3.3.5Isoporous Resins. It is claimed that some of the disadvantages of macroporous resins can be overcome by the synthesis of isoporous resins, in which the matrix has a substantially uniform network, free of highly crosslinked regions (Bolto & Pawlowski, 1987).

1.4.3.3.6Microporous Resins. Microporous is the term used to describe polymer particles manufactured with a low level of cross-linker. Improved rates of exchange can be obtained by using smaller particles, which make a larger surface area available. Powdered ion exchangers are employed in what has been termed precoat filters. However, because they are very fine particles (even though they are present in a coagulated form) they cause a high pressure loss in operation. Because of the high pressure loss, they can not be employed in a column system (Bolto & Pawlowski, 1987).

1.4.3.3.7Magnetic Resins. The difficulties of handling small, rapidly reacting resin beads can be surmounted by incorporating a magnetic filler such as the iron oxide γ-Fe_2O_3 within the particles. The magnetized resin beads then flocculate strongly to give agglomerates, which have settling rates comparable to those of normal sized beads. The flocs, which are held together by magnetic forces, are readily broken up by agitation so that the fast exchange rates associated with the small size of the resin particles can be achieved. Magnetic resins therefore combine some of the handling characteristics of conventional resin beads with the reaction rates of small particles (Bolto & Pawlowski, 1987).

1.4.4 Synthesis of Ion Exchange Resins

The majority of ion exchange resins are made by the copolymerization of styrene and divinylbenzene (DVB) (see Figure 1.11). The styrene molecules provide the basic matrix of the resin, while the DVB is used to crosslink the polymers to allow for the general insolubility and toughness of the resin. The degree of crosslinking in the resin's three-dimensional array is important because it determines the internal pore structure, which will have a large effect on the internal movement of exchanging ions (Helfferich, 1962).

Typically a styrene and DVB mixture containing a polymerization initiator is dispersed as spherical liquid droplets in water. The styrene and DVB, both liquids at the start, are put into a chemical reactor with roughly the same amount of water. The suspension is continuously stirred and heated. A surfactant is also present to keep everything dispersed. The styrene/DVB begin to form large globules of material, and as the speed of agitation increases, the globules break up into smaller droplets until reaching the size of about a milimeter. At this point, the polymerization reaction is initiated by the addition of benzoyl peroxide, which causes styrene/DVB molecules to form the resultant small plastic beads. The divinylbenzene is a crosslinking agent that gives the beads their physical strength, and without which the styrene would be water-soluble. Higher DVB content gives the bead additional strength, but the additional crosslinking can hinder kinetics by making the bead too resistant to the shrinking and swelling necessary during normal operation (Desilva, 1999).

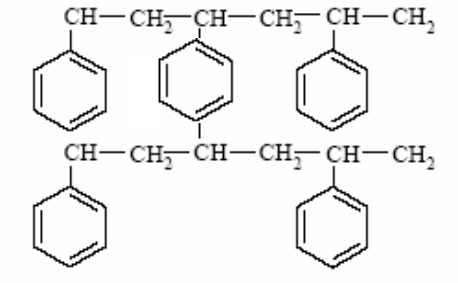

Figure 1.11 Styrene-divinylbenzene copolymer

There are three parameters defining the chemical structure of an ion-exchange resin (Marinsky, 1966):

1. The nature of the exchange grouping,
2. The degree of cross-linking, usually defined by the percentage of cross-linking agent used in the preparation of the cross-linked matrix,
3. The number of exchange groups per unit amount of exchanger.

Active groups are attached to provide chemical functionality to the bead. Each active group has a fixed electrical charge, which is balanced by an equivalent number of oppositely charged ions, which are free to exchange with other ions of the same charge. Strong acid cation resins are formed by treating the beads with concentrated sulphuric acid (process called sulphonation) to form permanent, negatively charged sulphonic-acid groups throughout the beads. Important here is the fact that the exchange sites thus formed are located throughout the bead. The ion exchange process is not a surface phenomenon; more than 99% of the capacity of anion exchange material is found in the interior of the bead (Desilva, 1999).

Strong base anion resins are activated in two steps process that consists of chloromethylation followed by amination. The two steps process begins with the same styrene/DVB material as is used for cation resins. The only difference is that the amount of DVB used is less to allow for a more porous bead. The first reaction step is the attachment of a chloromethyl group to each of the benzene rings in the bead structure (Desilva, 1999).

This intermediate chloromethylated plastic material needs to be reacted with an amine in a process called amination. The type of amine used determines the functionality of the resin (Desilva, 1999).

1.4.5 Properties and Characterization of Ion Exchange Resins

Discussion of the properties of ion exchangers is limited to capacity, equilibrium, and kinetic behavior. However, these properties are not sufficient for characterizing synthetic polymeric products, which are prepared either in a laboratory or by complex processes in which a large number of characteristics are controlled by small variations in production conditions. The prime objective of an ion exchanger is described by sufficiently high capacity, a rapid attainment of equilibrium, and a good

rate of exchange. But the question of selectivity, mechanical properties, physical and chemical stability etc. appears already at this stage, must taken into consideration (Samuelson, 1963).

1.4.5.1 Matrix

Framework of ion exchanger, the so-called matrix, consists of an irregular, macromolecular, three-dimensional network of hydrocarbon chains. The matrix of the resin is hydrophobic. However, hydrophilic components are introduced by the incorporation of ionic groups such as $–SO_3^-H^+$ (Helfferich, 1962).

The common choice is between "styrene-divinylbenzene" or "acrylic-divinylbenzene" copolymer. In the case of the cation exchange resins, selection is easily made since the acrylic products are weakly acidic whilst the styrenic resins are strongly acidic. Therefore for cation exchange the choice of copolymer is primarily decided by the process application and operating pH. The situation is very different with anion exchange resins since the two types of matrix pertain to products of both weak and strong functionality. Here anion exchange resins are concerned the choice between an acrylic resin and its styrenic equivalent is often made on considerations of operating exchange capacity, physical strength, and fouling resistance to complex high molecular weight organic anions (Harland, 1994).

1.4.5.2 Crosslinking

Crosslinking influences not only the solubility but the mechanical stability, exchange capacity, water uptake and swelling behavior, volume change in different forms of loading, selectivity, and chemical as well as oxidation resistance of ion exchangers. The amount of crosslinking depends on the proportions of different monomers used in the polymerization step. Practical ranges are 4% to 16%. Exchangers with low degree of crosslinking are soft and mechanically unstable (in the swollen state), while highly crosslinked products are hard and brittle with an increased sensitivity to osmotic influences. Properties that are interrelated with crosslinking are (Desilva, 1999):

1.4.5.3 Moisture Content

A physical property of the ion exchange resins that changes with changes in crosslinkage is the moisture content of the resin. For example sulfonic acid groups attract water, and this water is tenaciously held inside each resin particle. The quaternary ammonium groups of the anion resins behave in a similar manner. The Figure 1.12 shows a plot of moisture content change with changes in crosslinkage (Desilva, 1999).

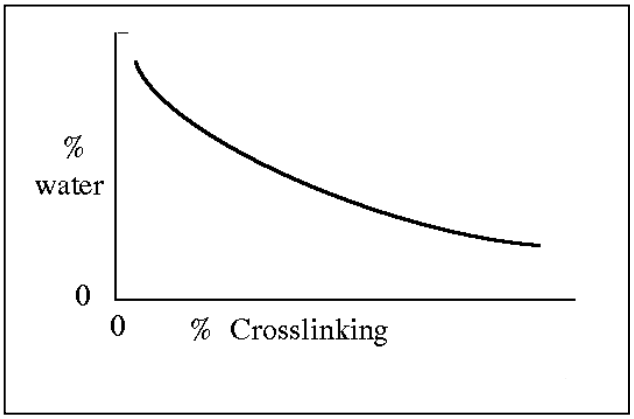

Figure 1.12 Relation between moisture content and crosslinkage (Desilva, 1999)

1.4.5.4 Capacity

The total capacity of an ion exchange resin is defined as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin. The capacity may be expressed in terms of milliequivalents per dry gram of resin or in terms of milliequivalents per dry gram of resin or in terms of millequivalents per milliliter of wet resin (Desilva, 1999).

The more highly crosslinked a resin, the more difficult it becomes to introduce additional funcitonal groups. Sulfonation is carried out after the crosslinking has been completed and the sulfonic acid groups are introduced inside the resin particle as well as over its surface. Likewise, the quaternary ammonium groups are introduced after the polymerization has been completed and they too are introduced both inside the particle as well as on its surface. Fewer functional groups can be

introduced inside the particles when they are highly crosslinked and hence the total capacity on a dry basis drops slightly (Desilva, 1999).

This situation is reversed when a wet volume basis is used to measure the capacity on a resin. Although fewer functional groups are introduced into a highly crosslinked resin, these groups are spaced closer together on a volume basis because the volume of water is reduced by the additional crosslinking. Thus the capacity on a wet volume basis increases as cross-linking increases. The Figure 1.13 describes the changes in capacity as crosslinking is changed (Desilva, 1999).

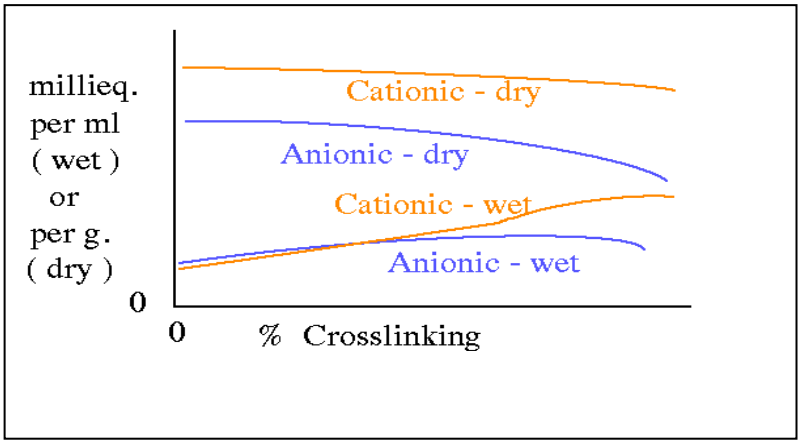

Figure 1.13 Relation between typical resin capacities and crosslinkage

1.4.5.5 Equilibration Rate

Ion exchange reactions are reversible reactions with equilibrium conditions being different for different ions. Crosslinkage has a definite influence on the time required for an ion to reach equilibrium. An ion exchange resin that is highly crosslinked is quite resistant to the diffusion of various ions through it and hence, the time required to reach equilibrium is much longer (Desilva, 1999).

1.4.5.6 Swelling

The volume change which takes place during transference from one medium to another is known as swelling. This swelling is produced by the osmotic pressure in the interior of the ion exchanger against the external, more dilute solution, so that the solvent uptake producing the swelling. Absolute swelling takes place when air-dried resin becomes wet. During absolute swelling a certain quantity of water is taken up

by the exchanger. Swelling is influenced by the matrix structure, i.e., the degree of crosslinking as discussed above. If the water contains an electrolyte, swelling depends also on the electrolyte concentration. When this concentration increases, the moisture uptake will increase, since the osmotic pressure difference between the external and internal solution is then smaller (Desilva, 1999).

1.4.5.7 Ionic Form

Most ionic forms may be prepared by passing a large excess of an appropriate acid, alkali, or salt solution through a column of resin over 20-30 minutes. The ease of resin conversion generally increases with decreasing particle size, decreasing crosslinking, and decreasing charge of the ion being displaced (Harland, 1994).

1.4.5.8 pH Range

The pH range is very much dependent upon the strength of the functional group, but the following guidelines could be applied (Harland, 1994):

1. Strong acid cation: any pH
2. Weak acid cation: > 4
3. Strong base anion: any pH
4. Weak base anion (tertiary): < 9

1.4.5.9 Chemical Stability

At the macroscopic level, the chemical stability of modern resins at normal ambient temperatures is excellent, being insoluble in all common organic solvents and electrolyte solutions. Two principle exceptions are resin breakdowns caused by sustained exposure to ionizing nuclear radiation and powerful chemical oxidizing agents such as nitric, chromic (VI) acid, chlorate (V) ions, halogens, and peroxy compound (Harland, 1994).

1.4.5.10 Thermal Stability

Over a temperature range, the stability characteristics of resins in common use may be summarized as follows (Harland, 1994):

1.4.5.10.1 Cation Exchange Resins. Cation exchange resins are generally quite stable, especially if they are in their salt forms.

1.4.5.10.2 Anion Exchange Resins. Strong base and weak base materials are also most stable in their salt forms compared with their hydroxide and free base forms, respectively. The effect of increased temperature is to accelerate the loss of exchange capacity, in which respect acrylic anion exchangers whether weak or strong base are significantly more unstable than their styrenic counterparts.

1.4.5.11 Physical Appearance

1.4.5.11.1 Gel Resins. Usually shiny beads, clear to transmitted light.

1.4.5.11.2 Macroporous Resins. Usually dull beads of opaque or translucent appearance.

1.4.5.12 Resin Particle Size

It is a major part of the fluid flow and effectiveness of separation of systems. For example, condensation type resins are generally broken granules. On the contrary, polymerization-type resins are small beads that are uniformally packed. To measure the grain size a mesh is used to keep out larger particles. In addition, for certain processes grain size is extremely important to efficiency. One such process is separations carried out by chromotography. The major point of study of grain size is that it determines the fluid resistance of an ion exchange column made from ion exchange resin. This can be the key to success of an industrial operation (Desilva, 1999).

The bead size range of conventional products is 300 μm to 1200 μm with a true mean value of approximately 700 μm (Harland, 1994).

1.4.5.13 Resin Density

The density of the any dry, water free resin is generally smaller for anion exchangers than cation exchangers. The density of water swollen resin depends on the type counter ion, swelling capacity and on the degree of crosslinking, besides the density of dry resin. Furthermore, it should be noted that bulk density is different

than the density of the swollen resin. These densities are important because operation is dependent upon the resins (Harland, 1994).

1.4.6 The Kinetics of Ion Exchange

An understanding of the kinetics of ion exchange reactions has application in two broad areas. Firstly, it helps to understand the nature of the various fundamental ionic transport mechanisms, which control or contribute to the overall exchange rate. Secondly, derived numerical parameters such as rate constants, mass transfer coefficients, or diffusion coefficients found from a rate investigation are of value when making projections concerning the dynamic behaviour of columns and process design (Harland, 1994).

In the general theory described by Boyd, Adamson and Myers the overall transport of mass may be divided into three steps (Samuelson, 1963);

1. Mass-transfer in the external solution up to the surface of the resin particles (film diffusion)
2. Diffusion inside the resin phase (particle diffusion)
3. Chemical exchange in the vicinity of the exchange groups

In the first two steps equivalent amounts of the exchanging and exchanged ions are moving counter to each other, except for the small transfer of ions caused by changes in penetration of the external electrolyte (Samuelson, 1963).

The chemical exchange is in general very rapid, and only few examples of a chemical rate determining step have been found. In general, the rate limiting step must either be the mass transfer in the external solution or the particle diffusion or these two steps combined (Atteberry and Boyd, 1950).

Figure 1.14 shows the radial concentration profiles of the exchanging species. The right sides of the diagrams show the profiles of species A (initially in the ion exchanger) and the left sides those of species B (initially in the solution). The various curves are for different contact times, t (Helfferich, 1962).

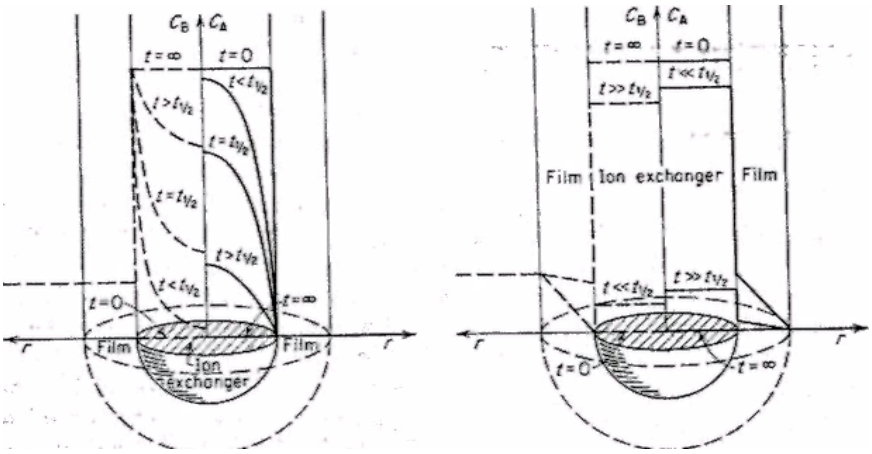

Figure 1.14 Radial concentration profiles for ideal particle diffusion control (Helfferich, 1962)

Two main rate–determining steps in kinetics of ion exchange could be given as:

$$\frac{X\bar{D}\delta}{CD_0 r_0}(5+2\alpha_B^A) \qquad << 1 \quad \text{particle diffusion control} \tag{1.4}$$

$$\frac{X\bar{D}\delta}{CD_0 r_0}(5+2\alpha_B^A) \qquad >> 1 \quad \text{film diffusion control} \tag{1.5}$$

X**:** concentration of fixed groups

C: solution concentration

$\bar{D}$: inter-diffusion coefficient in the ion exchange resin

D_0: inter-diffusion coefficient in the film

r_0: bead radius

δ: film thickness

α_B^A: separation factor

Rate laws can be derived by applying the diffusion equations to ion exchange systems. In general case, the differential equations and boundary conditions are nonlinear due to complications arising from diffusion-induced electric forces, selectivity, specific interactions and changes in swelling (Helfferich, 1962).

The following diffusion kinetic treatments are applicable for idealized ion exchange, i.e., they are only strictly true for isotropic exchange in a system which is in equilibrium expect for isotropic distribution. It is also assumed that all exchanger beads are spherical and have uniform size (Helfferich, 1962).

Diffusion processes are usually described in terms of Fick's first law:

$$J_i = -D \text{ grad } C_i \quad \textbf{(1.6)}$$

where J_i is the flux (in moles per unit time and unit cross section) of the diffusing species i, C_i is its concentration (in moles per unit volume), and D is the diffusion coefficient (Helfferich, 1962).

1.4.6.1 Particle Diffusion

In the case of particle diffusion control, concentration gradients will exist in the ion exchange bead. A quasi-homogenous model is assumed to derive the rate laws. The theoretical treatment of the diffusion within the solid phase is considered as occurring through a homogenous spherical electrolyte gel. The flux of the isotope A (J_A) in the ion exchanger is given by;

$$J_A = -\overline{D} \text{ grad } \overline{C_A} \quad \textbf{(1.7)}$$

where $\overline{D}$ is self diffusion coefficient of species and $\overline{C_A}$ is the concentration of species in the resin phase (Helfferich, 1962).

The time dependence of the concentration is interrelated with the flux by material balance (Fick's second law, termed the condition of continuity)

$$\frac{\partial \overline{C_A}}{\partial t} = -\text{div } J_A \quad \textbf{(1.8)}$$

where t is time.

The combination of Eqn. (1.7) and Eqn. (1.8) for systems with spherical geometry and with a constant diffusion coefficient gives

$$\frac{\partial \overline{C_A}}{\partial t} = \overline{D}\left(\frac{\partial^2 \overline{C_A}}{\partial r^2} + \frac{2}{r}\frac{\partial \overline{C_A}}{\partial r} \right) \tag{1.9}$$

where r is radial space coordinate (distance from the bead center) (Helfferich, 1962).

This equation must be solved under the appropriate initial condition, all ions A are in the ion exchanger at a uniform concentration $\overline{C_A}^{o}$, and no A is in the solution:

$$r > r_o,\ t = 0 \qquad \overline{C_A}(r) = 0$$

$$0 < r \le r_o,\ t = 0 \qquad \overline{C}_A(r) = \overline{C_A^o} = \text{const.} \tag{1.10}$$

The first and simpler condition applies when the concentration of A in the solution remains negligible throughout the process. This is true when a solution of constant composition is continuously passed through a thin layer of beads or in the case of batch operation if, the solution volume is so large (Helfferich, 1962).

$$\overline{C}\,\overline{V} << CV \tag{1.11}$$

where $\overline{V}$ and V are total volume of ion exchange material and solution respectively. This condition is called the “infinite solution volume”. The infinite solution volume condition thus is,

$$r = r_o,\ \ t > 0 \qquad \overline{C_A}(t) = 0 \tag{1.12}$$

Under this initial and infinite solution volume condition, the equation may be solved and integrated to give:

$$X = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{\overline{D}t\pi^2 n^2}{r_o^2} \right) \tag{1.13}$$

where X is the fractional attainment of equilibrium.

A simplified expression of this equation is given by the Vermeulen's approximation (Vermeulen, 1953).

$$X = \left(1 - \exp\left(-\frac{\overline{D}\pi^2}{r_o^2} t\right)\right)^{1/2} \quad \textbf{(1.14)}$$

The half time $t_{1/2}$ of ion exchange is readily calculated from Eqn. (1.11). The substitution X = 0.5 gives;

$$t_{1/2} = 0.03\frac{r_o^2}{\overline{D}} \quad \textbf{(1.15)}$$

Secondly, the "finite solution volume" condition which does not meet the condition (1.8). The solution obtained by Peterson is;

$$X = \frac{w+1}{w}\left[1 - \frac{1}{\alpha - \beta}\left[\alpha \exp(\alpha^2\tau)(1 + \text{erf } \alpha\ \tau^{1/2}) - \beta \exp(\beta^2\tau)(1 + \text{erf } \beta\ \tau^{1/2}\right]\right] \quad \textbf{(1.16)}$$

where α and β are the roots of the equation $X^2 + 3wX - 3w = 0$ (Helfferich, 1962).

1.4.6.2 Film Diffusion

The rate laws for film-diffusion controlled isotopic exchange are derived under the following assumptions:

1. Interdiffusion in the film is treated as quasi-stationary, i.e.; it is assumed that diffusion across the film is fast as compared with the concentration changes at the film boundaries.

2. The film is treated as a planar layer (one-dimensional diffusion).

This is admissible if the film thickness is much smaller than the bead radius. Under this condition, the momentary flux (J_A) constant throughout the film and from Eqn. (1.3) is given by

$$J_A = D\frac{\Delta C_A}{\delta} \quad \textbf{(1.17)}$$

where ΔC_A is concentration difference between the boundaries of the film and δ is the film thickness (Helfferich, 1962).

Time dependence is obtained from material balance;

$$-\frac{dQ_A}{dt} = FJ_A \qquad \textbf{(1.18)}$$

where F is the total surface area of the ion exchanger.

The equilibrium condition at the interface

$$\frac{\overline{C_A}}{C'_A} = \frac{\overline{C}}{C} \qquad \textbf{(1.19)}$$

Combination of Eqn. (1.15) and Eqn. (1.16) gives after substitution;

$$-\frac{dC'_A}{dt} = \frac{3C}{r_o \overline{C}} J_A \qquad \textbf{(1.20)}$$

Eqn. (1.17) and Eqn. (1.18) are solved under the appropriate initial and boundary conditions. The simple initial condition corresponding to uniform initial concentration $\overline{C_A}^o$ in the ion exchanger and no A in the solution is;

$$r = r_o,\ t = 0 \qquad C'_A = \frac{\overline{C_A}^o C}{\overline{C}}$$

$$r \geq r_o,\ t = 0 \qquad C_A(r, t) = 0 \qquad \textbf{(1.21)}$$

The boundary condition in the case of "infinite solution volume" condition

$$r \geq r_o + \delta,\ t \geq 0 \quad C_A(r, t) = 0 \qquad \textbf{(1.22)}$$

The mathematical solution under the conditions (1.17) to (1.18) is,

$$X = 1 - \exp\left(-\frac{3DCt}{r_o \delta \overline{C}}\right) \qquad \textbf{(1.23)}$$

with a half time of ion exchange :

$$t_{1/2} = 0.023\frac{r_o\delta\overline{C}}{DC} \qquad \textbf{(1.24)}$$

The rate thus is proportional to the diffusion coefficient in the film and to the concentration of the solution and is inversely proportional to the bead radius, the film thickness, and the counter-ion concentration in the ion exchanger (Helfferich, 1962).

In the case of "finite solution volume", the condition (1.19) replaces by;

$$r \geq r_o + \delta, \quad t > 0 \qquad C_A(r,t) = \frac{\overline{V}}{V}\left(\overline{C_A}^{o} - \overline{C_A}(t)\right) \qquad \textbf{(1.25)}$$

The solution to this case is given by:

$$X = 1 - \exp\left(-\frac{3D(\overline{V}\overline{C} + VC)}{r_o\delta\overline{C}V}t\right) \qquad \textbf{(1.26)}$$

1.4.6.3 Chemical Reaction Kinetics

Chemical reaction between the fixed ion exchange sites is one of the general ion exchange mechanisms. In certain cases, chemical reaction kinetics can control the ion exchange. This is seen to be the case in some chelating and solvent impregnated type ion exchange resins (Helfferich, 1962).

For non-catalytic reactions of solid particles with surrounding liquid, two basic models are considered; "continuous" or "homogenous" reaction model and heterogeneous "unreacted shrinking core" or "shell progressive" model (Levenspiel, 1962).

In the case of homogenous reaction the ion exchange reaction assumed to occur uniformly throughout the resin particle. This model fits well if the resin contains enough porosity to allow the fluid to pass through freely. Thus the concentration of the reacting ions is uniform throughout the resin. In the case of heterogeneous reaction, the porosity of the polymer is small and thus practically impervious to the

fluid reactant, the reaction may be explained by the "Shell Progressive", "Unreacted Shrinking Core" or "Ash Layer Models" (Levenspiel, 1962; Cortina 1997). Slicing a partly reacted bead and examining its cross-section, the unreacted core is found to be sharply distinguished form the layer of product as shown in Figure 1.15.

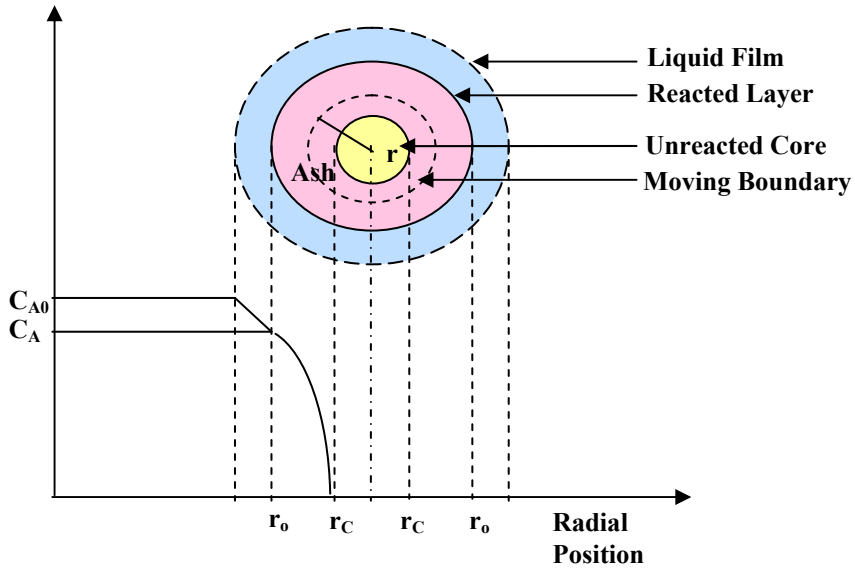

Figure 1.15 Concentration profile of a partially reacted ion exchange bead, C_{A0}; Concentration of species a in bulk solution and C_{As} ; Concentration of species A on the outer surface of the resin (Solak, 2004).

The rate at which counter ions A react with the unreacted core is controlled by the three consecutive processes:

1. Interface mass transfer of the reacting species A from the bulk solution to the outer surface of the solid bead,

2. Interparticle diffusion of the reacting species from the outer surface through the reacted portion of the solid bead to the zone of reaction and,

3. Chemical reaction of the reacting species with the ion exchange surface of the zone.

The kinetic concept of a "shell progressive" mechanism can be described in terms of the concentration profile of a liquid reactant containing a counter ion A advancing into a spherical bead of a partially substituted ion exchanger. As the reaction progresses in the bead, the material balance of counterion A follows Fick's diffusion

equation with spherical coordinates. In this case, the relationship between reaction time and degree of conversion gives the following expressions (Liberti, 1987).

When the fluid film is controlling

$$t = \frac{ar_o C_{so}}{3C_{Ao} K_{mA}} X \quad \textbf{(1.27)}$$

When the diffusion through the reacted layer control

$$t = \frac{ar_o^2 C_{so}}{6D_{e,r} C_{Ao}} \left[3 - 3(1-X)^{2/3} - 2X\right] \quad \textbf{(1.28)}$$

When the chemical reaction control

$$t = \frac{r_o}{k_s C_{Ao}} \left[1 - (1-X)^{1/3}\right] \quad \textbf{(1.29)}$$

1.4.7 Ion Exchange Operational Techniques

Ion exchange reaction starts when an ion exchanger is placed in an electrolyte solution contain a counter ion, which is different from the counter ion containing in the ion exchanger. During the ion exchange reaction the counter ion contained in the resin is partially or totally replaced by the counter ion contained in the solution (Zagorodni, 1997).

1.4.7.1 Batch Operation

The comparison of various ion-exchange resins with respect to their relative equilibrium and kinetic behaviour can be performed by batch techniques, i.e., by following the change in composition of an electrolyte solution in contact with an ion-exchange resin. The kinetic behaviour may be approximated by observing the change in composition of the solution as a function of time (Kunin, 1960).

In batch contact, a method with only slight usefulness, maximum removal (neutralization, etc.) is limited by the equilibrium relationship between resin and

solutes. When viscous solutions are being processed or when the equilibria are irreversible (neutralization, etc.), batch contact may offer some advantages (Kunin, 1960).

Since ion exchange is a form of sorption from a solution, it is possible to describe the equilibrium of ions between the solid and solute phases by different equations and isotherms which are *Langmuir* and *Freundlich isotherms* and related correlations are taken into account (Samuelson, 1963).

1.4.7.1.1Adsorption Isotherms. Adsorption is usually modeled by isotherms, which relate the amount adsorbed to the equilibrium concentration. Adsorption isotherms are measured by keeping solution environment conditions, such as temperature, pH and ionic strength, constant. The obtained equilibrium data described the capacity of the adsorbent for the adsorption of adsorbates and also the interaction of the adsorbate with adsorbent. Surface area and pore size of adsorbent, solubility of solute in aqueous solution, pH and temperature are the factors affecting the adsorption capacity (Helfferich, 1962).

Expressing the adsorption data using either a theoretical or empirical equation is essential for practical adsorption operation. The isotherm equation selected for the representation of the experimental data should provide a satisfactory fit over a wide range of concentration and have a small number of parameters. In addition, the equation must satisfy a necessary thermodynamic boundary condition: at very low surface coverage the equation must show that the adsorption of the solute per unit mass of adsorbent is proportional to the solute's concentration in the liquid. This boundary condition is Henry's law, which gives the simplest adsorption isotherm equation (Yılmaz, 2003).

1. Langmuir Model. In the Langmuir model for low concentrations adsorption is proportional to solute concentration, and hence, in this range this equation reduces to Henry's equation, and approaches a constant value at high concentrations. Langmuir model is based on the following assumptions (Yılmaz, 2003):

- Only monomolecular adsorption takes place
- Adsorption is localized, that is; the bonding to the adsorbent is sufficiently strong to prevent displacement of the adsorbed molecules along the surface.
- Heat of adsorption is independent of surface coverage because of homogeneous surfaces, whose adsorption sites are energetically equivalent.

Langmuir isotherm model is represented as (Yılmaz, 2003)**;**

$$\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad \textbf{(1.30)}$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of ion (such as Ni-II) sorbed on the resins (mg Ni(II)/g-dry resin), Q_o is a constant indicates the adsorption capacity of resins (mg Ni(II)/g-dry resin), b is a constant indicates energy of adsorption (L/mg).

2. Freundlich Model. The Freundlich model is an empirical isotherm equation and is suitable for highly heterogeneous surfaces. When this equation fits to data at high and moderate concentrations, it provides a poor fit for adsorption data at low concentrations. Since for highly heterogeneous surfaces, extremely low concentrations are required to attain the Henry's law region. Freundlich equation does not reduce to Henry's law at concentrations approaching zero (Yılmaz, 2003).

Freundlich isotherm implies a logarithmic decrease in the heat of adsorption with surface coverage. The dependence of heat of adsorption on surface coverage has its basis in the energetic heterogeneity of most solid surfaces. The first sites on a surface to be occupied are those, which attract adsorbate molecules most strongly and with the greatest release of energy. Thus the heat of adsorption decreases with surface coverage.

The equation for Freundlich isotherm model is as**;**

$$Q_e = K_f C_e^{(1/n)} \qquad \textbf{(1.31)}$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of ion (such as Ni-II) sorbed on the resins (mg Ni(II)/g-dry resin), K_f is a constant indicates the rate of adsorption, n is a constant indicates the degree of favorability of adsorption.

1.4.7.2 Column Operation

Ion-exchange materials are frequently tested for performance in a given application by small-scale column tests (Kunin, 1960). The solution is passed through a fixed bed of ion exchanger, which is packed in column, usually of glass. The solution which enters the column, is called the influent and the liquor leaving the column the effluent. Three types of column operations are; *down flow, up flow and counter flow.* Most beds operate with down flow operation (Samuelson, 1963).

Column operation conveniently suffices for complete removal. In equilibrium operation, the solution continuously contacts with resin and consequently there is a high driving force for the removal of solute from solution. In order to achieve maximum removal, the resin in the column must be most highly regenerated (Kunin, 1960).

A solution is passed through a bed of ion exchanger beads where its composition is changed by ion exchange reaction. The composition of the effluent and its change with time (or volume passed) depends on (Samuelson, 1963):

- The properties of the ion exchanger
- Composition of the feed solution
- Operating conditions

A typical breakthrough curve during a column operation and column experimental set-up are given in Figure 1.16 and Figure 1.17, respectively.

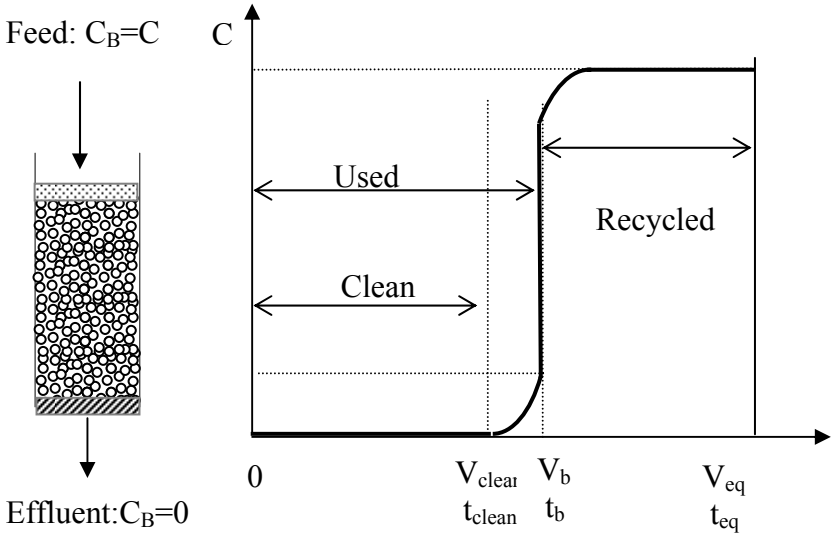

Figure 1.16 Breakthrough curve of column operation (Zagorodni, 1997)

1.4.8 Ion Exchange Capacity

Capacity and related data are primarily used for two purposes: lon characterizing of ion-exchange materials and for use in the numerical calculation of ion-exchange operations (Helfferich, 1962).

Ion exchange capacity could be defined as concentration of fixed functional groups per specified amount of ion exchanger (Zagarodni, 1997).

Ion exchange capacities can be classified as (Kunin, 1960):

1. Anion exchange capacity
2. Cation exchange capacity
3. Breakthrough capacity
4. Saturation column capacity

Taking into consideration the breakthrough curve given in Figure 1.16 and types of capacities given above, the following equations could be formulated:

Breakthrough Capacity = $\int_{0}^{Vb} (C_0 - C)dV$

Total Capacity = $\int_{0}^{V_{eq}} (C_0 - C)dV$ **(1.32)**

Degree of the Column Utilization = $\frac{\int_{0}^{V_b} (C_0 - C)dV}{\int_{0}^{V_{eq}} (C_0 - C)dV}$

CHAPTER TWO
EXPERIMENTAL

2.1 Materials

2.1.1 Resins

Chelating resin based macroporous polystyrene with iminodiacetic groups *Purolite S-930* and macroporous aminophosphonic acid chelating resin *Purolite S-950* were used. These resins were supplied by Purolite International Ltd., USA. Their characteristics are summarized in Tables 2.1 and 2.2.

Purolite S-930 designed for the removal of cations of heavy metals from industrial effluents. These cations may be separated from high concentrations of univalent cations (typically sodium) and also from common divalent cations (such as calcium). Removal can be achieved both from weakly acidic and weakly basic solutions depending on the metals to be removed.

Purolite S-950 designed for the removal of cations of toxic metals such as lead, copper and zinc from industrial effluents at low pH. At somewhat higher pH values, calcium, magnesium and barium, as well as the toxic metals cadmium, nickel, and cobalt are strongly complexed and may be separated from quite high concentrations of univalent cations.

Table 2.1 Physical and chemical properties of Purolite S-930 (MDS of Purolite S-930)

Ionic Form	Sodium
Shipping Weight, g/L	710-745
Specific Gravity	1.17
Moisture Content,%	55-65
Total Exchange Capacity	0.94 meq/mL (wet) min
Screen Size Range, mesh	14-52 (wet)
Effective Size, mm	+1.0<10%, -0.3<1%
Temperature Limitations, ^{o}C	70
pH Limitations	6-11

Table 2.2 Physical and chemical properties of Purolite S-950 (MDS of Purolite S-950)

Ionic Form	Sodium
Shipping Weight, g/L	710-745
Specific Gravity	1.13
Moisture Content,%	60-68
Total Exchange Capacity	2.0 meq/mL (wet) min 5.5 meq/g (dry) min
Screen Size Range, mesh	14-52 (wet)
Effective Size, mm	+1.2<5%, -0.3<1%
Temperature Limitations, ^{o}C	90
pH Limitations	6-11

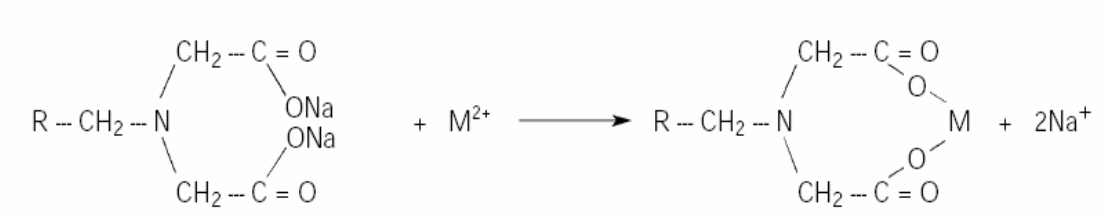

Figure 2.1 Principle of ion exchange reaction by chelating resins

The resins after air drying, were dried in vacuum oven below 40^{o}C. Then, the resins were used after swelling over 24 h in distilled water. Swelling volume of resins was calculated. For the swelling volume of resins, 1.0 g resin was swollen in 100 mL deionized water. The volume of 1.0 g Purolite S-930 resin found as 3.1 mL and Purolite S-950 volume found as 3 mL. Swollen resin was taken in a graduated column and volume of the resin was mesured as 0.5 mL for both Purolite S-930 and Purolite S-950 .

2.1.2 Reagents and Solutions

- $NiSO_4.6H_2O$, Merck
- $CoSO_4.7H_2O$, Merck
- NaOH, 99 %, (solid-pulp), J.T. Baker
- PLS (Pregnant Leach Solution) supplied by Bosphorous Nickel Madencilik in Manisa-Çaldağ and it is obtained from heap acid leach and contains Ni (1310 ppm), Co (56.3 ppm), Mn (400 ppm), Fe (6260 ppm) and Al (606 ppm).
- pH=4 and pH=7 buffer, Metrohm

2.1.3 Preparation of Model Solutions

Model solutions prepared to compare the experimental data with the results of experiments done with PLS.

- **10^{-1} M $NiSO_4.6H_2O$ solution:** 26.28 g nickel nitrate is dissolved in deionized water and diluted to 1 L.

- **10^{-1} M $CoSO_4.7H_2O$ solution:** 28 g nickel nitrate is dissolved in deionized water and diluted to 1 L.
- **1 M NaOH solution:** 40 g sodium hydroxide dissolved with and diluted to 1 L with deionized water.
- **1 M HCl solution:** 8.33 mL from concentrated hydrochloric acid (12 M HCl) is diluted to 100 mL with deionized water.

- **1000 mg/L Ni and Co solution: (**Merck) Ni and Co standarts were used.

- **Standard Ni(II) solutions (references):** Standard solutions of 0.5 – 1.0 – 3.0 – 5.0 – 10.0 – 20.0 – 50.0 – 100 – 250 – 500 mg Cr(VI) / L is prepared from 1000 mg Cr(VI) / L standart.

2.1.4 Equipments

- **Glass Column:** ID= 0.7cm
- **Vacuum oven:** Gallen Kamp
- **Shaker:** Memmert, Kotterman- D3165
- **Peristatic Pump:** ATTO- AC-2110
- **Fraction Collector:** Advantec SF-2100 W , ATTO- AC-5750
- **Atomic Absorption Spectrophotometer:** Analytik Jena-Nova 300, Atomic Absorption Spectrophotometer
- **pH meter:** WTW, pH/oksi 340İ/SET
- **Magnetic Stirrer:** IKA-Combimag- RCT
- **Balance:** Sartorius BP 210 S

2.2 Ni and Co Removal Studies

2.2.1 Batch-mode Sorption Studies

2.2.1.1 Optimum pH Range Selection Tests

In batch studies based on selection of optimum pH range, commercial resins Purolite S-930 and Purolite S-950 were used. 0.5 g dry resin of Purolite S-930 and Purolite S-950 (0.355-0.710 mm) were contacted with 4x 10^{-4} M 25 mL $NiSO_4.6H_2O$ and $CoSO_4.7H_2O$ model solutions at various pH (1, 2, 3, 4, 4.5, 5) at 30^oC for 24 h with continuous shaking in the shaker. pH of the solutions were adjusted by means of concentrated H_2SO_4.

2.2.1.2 Optimum Resin Amount Selection Tests

Optimum resin amounts for Ni(II) and Co(II) removal from aqueous solutions were determined using Purolite S-930 and Purolite S-950 (0.355-0.710 mm). Various dry resin amounts (0.1, 0.5, 1, 1.5 and 2.0 g) were contacted with 4x10^{-4}M 25 mL of $NiSO_4.6H_2O$ and $CoSO_4.7H_2O$ solutions at 30^oC for 24 h with continuous shaking in the shaker. Also same amount of dry resins were contacted with PLS (Pregnant Leach Solution) supplied from Bosphorus Nickel Madencilik and PLS solution obtained after Fe(III) precipitation.

2.2.1.3 Equilibrium Tests

Commercial resins Purolite S-930 and Purolite S-950 were used for removal of nickel and cobalt from aqueous solution. 0.5 g dry resin of Purolite S-930 and Purolite S-950 (0.355-0.710 mm) were contacted with 25 mL $NiSO_4.6H_2O$ and $CoSO_4.7H_2O$ model solutions (pH:2) at various nickel and cobalt concentrations (10^{-4}, 4 x 10^{-4}, 10^{-3}, 4 x 10^{-3}, 10^{-2}, 4 x 10^{-2}, 10^{-1}M) at 30^oC for 24 h with continuous shaking in the shaker.

2.2.1.4 Selectivity Tests

Selectivity studies were done by Purolite S-930 (aminophosphonic acid group) along with Purolite S-950 (iminodiacetic groups)chelating resin in a glass column. In

these studies the effect of nickel and cobalt ions on resin performances were investigated. For these tests, solutions containing $4x10^{-3}$ M Ni(II) along with $4x10^{-3}$ M, $2x10^{-4}$ M, $8x10^{-4}$M, $4x10^{-4}$M, $2x10^{-4}$Co(II) solutions have been used. Also the effect of concentrations of interfering ions on nickel and cobalt recovery was studied by using PLS (original pregnant leach solution) and PLS (after Fe precipitation) with 4 different resin amount (0.5 g, 1 g, 1.5 g, 2 g.).

2.2.1.5 Selection of Optimum pH Range of Eluting Agent Tests

Batch elution of Ni(II) and Co(II) from Purolite S-930 and S-950 were carried out by using H_2SO_4 at various concentrations (0.5, 1, 2, 4, 6 M). 0.5 g of resin was used at each batch elution test.

2.2.1.6 Kinetic Tests

Kinetic test was carried out in a 500 mL three neckled glass flask placed in a water bath at 25^{o}C. The solution in the flask was agitated on a mechanical stirrer with 200 rpm to prevent the resin particles from settling. Samples were withdrawn from the vessel at regular time intervals (5, 15, 30, 60, 90, 120, 180, 240, 360, 480, 1440 min.). Kinetic test was performed by using 4.0 g of dry Purolite S-930 and S-950 resins immersed in 400 mL 4 x 10^{-3} M processed PLS (Pregnant Leach Solution after Fe precipitation) at pH 2. The results kinetic tests were used to find the diffusion rate mechanism of Ni(II) and Co(II) removal.

2.2.1.7 Fe Precipitation Tests

In these studies PLS was used. Tests were carried in different pH (3, 3.2, 3.6, 4, 4.2, 4.3, 4.35, 4.8) to obtain maximum removal of Fe. Fe(III) was precipitated as $Fe(OH)_3$. pH of the solutions were adjusted by means of concentrated NaOH.

2.2.2 Column-mode Sorption–Elution Studies

In order to get some information about column performances of commercial resin on removal of nickel and cobalt from processed PLS solution, Purolite S-950 was used for column-mode sorption and elution tests.

In these studies, a glass column with an internal diameter of 0.7 cm was employed. The resin in the 0.355-0.710 mm of particle size range was used for the column studies. The resin beads were immersed into deionized water for 24 h before being packed into the column.

The column was packed with 1.5 mL wet-settled volume of resin. Processed PLS solution (pH 2) was delivered by down-flow to the column at room temperature using a peristaltic pump at SV 15 h^{-1}. Each successive 4 mL (~2.7 BV) fraction of the effluent was collected using a fraction collector.

Breakthrough curves were obtained by analysis of these successive fractions. Each fraction was analyzed by the Atomic Absorption Spectrometer in flame absorption mode at 232.0 nm (Ni) and 240.7 nm (Co) wavelength.

Resin packed into the column was washed with deionized water after sorption step. The nickel and cobalt loaded resin was eluted with 4 M H_2SO_4 solution at SV 5 h^{-1}. The column elution profiles were obtained by analysis of each successive 3 mL (2 BV) fractions of eluates.

CHAPTER THREE
RESULTS AND DISCUSSION

3.1 Batch-mode Sorption Studies

3.1.1 Optimum pH Range Selection Tests

Effect of pH on removal Ni(II) and Co(II) from model solutions (10^{-4} M 25 mL) for the pH range of 1-5 was studied using both Purolite S-930 and Purolite S-950.

Figures 3.2 -3.9, Tables 3.1 and 3.2 show that Ni(II) and Co(II) removal by Purolite S-930 and Purolite S-950 increases until pH 2. According to the results, pH decrease after pH:2 is indication of $Ni(OH)_2$ and $Co(OH)_2$ precipitation due to the resin type, final pH values increases (increase in OH^- concentration as seen in Figure 3.1) therefore the Ni(II) and Co(II) solubility product was exceeded. The decrease in the removal values after pH:2 can be explained by the precipitation of metals as hydroxide forms. This reaction prevents the adsorption of Ni and Co. As shown in Figure 3.1 final pH increased as equilibrium occured.

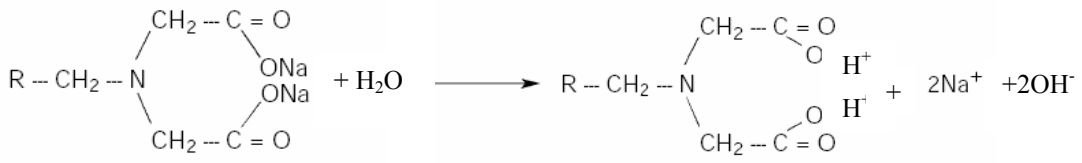

Figure 3.1 Principle of reaction in aqueous solution

$|Ni|.|OH|^2 = 2.10^{-15}$ → while $|Ni| = 4.10^{-3} M$ pH>7.85 $Ni(OH)_2$ precipitated.

$|Co|.|OH|^2 = 1.6.10^{-15}$ → while $|Co| = 4.10^{-3} M$ pH>7.80 $Co(OH)_2$ precipitated.

Table 3.1 Effect of pH on Ni(II) and Co(II) removal from aqueous solution by Purolite S-930

Nickel				Cobalt			
$pH_{initial}$	pH_{final}	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	$pH_{initial}$	pH_{final}	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)
1.0	1.12	96.45	13.35	1.0	1.10	97.21	14.14
2.0	7.80	98.86	13.53	2.0	7.40	99.34	14.73
3.0	10.46	96.66	12.90	3.0	10.30	97.30	14.25
4.0	10.5	96.38	12.68	4.0	10.44	97.31	14.14
4.5	10.59	96.31	12.75	4.5	10.52	97.31	14.09
5.0	10.67	96.26	12.92	5.0	10.54	97.32	14.18

Table 3.2 Effect of pH on Ni(II) and Co(II) removal from aqueous solution by Purolite S-950

Nickel				Cobalt			
$pH_{initial}$	pH_{final}	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	$pH_{initial}$	pH_{final}	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)
1.0	1.20	96.42	13.96	1.0	1.21	97.22	15.09
2.0	7.60	99.95	14.32	2.0	7.40	99.72	15.43
3.0	9.66	97.69	13.68	3.0	9.52	97.54	14.93
4.0	9.33	97.28	13.42	4.0	9.82	97.24	14.74
4.5	9.94	97.23	13.60	4.5	9.92	97.23	14.80
5.0	9.99	97.13	13.70	5.0	9.93	97.23	14.70

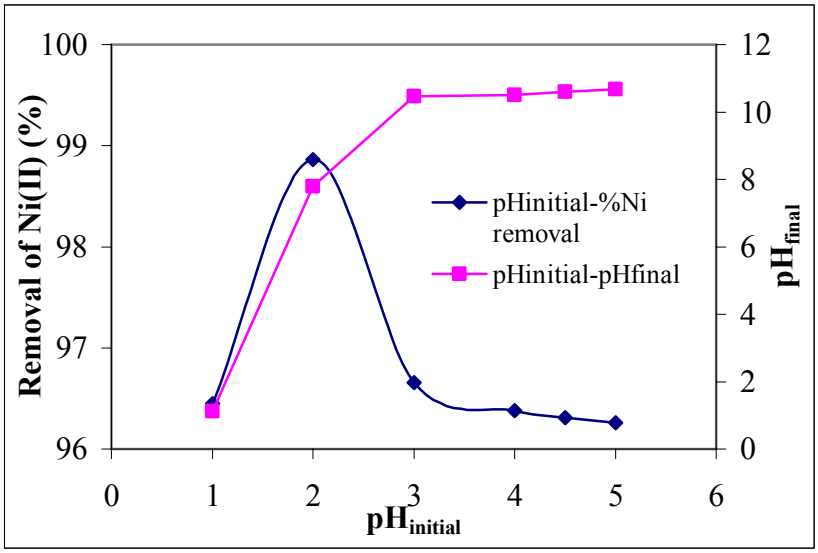

Figure 3.2 pH effect on removal of Ni(II) by Purolite S-930

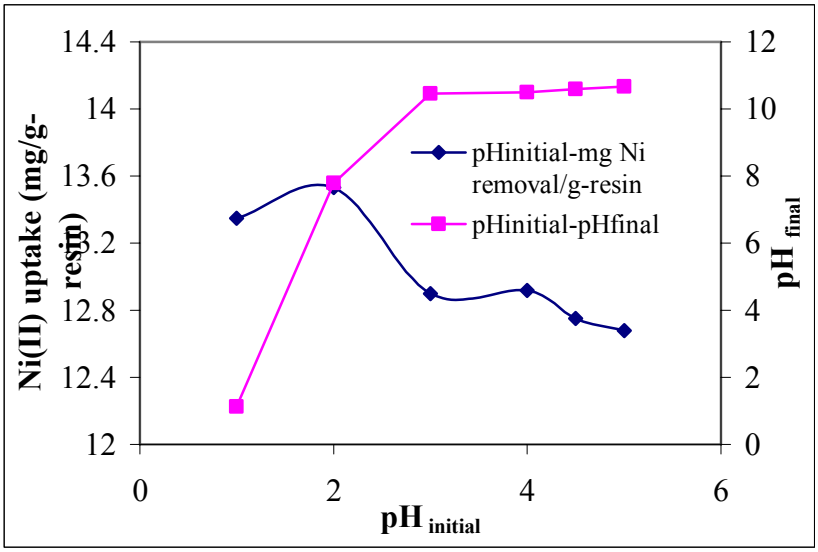

Figure 3.3 Ni(II) uptake by Purolite S-930 against pH

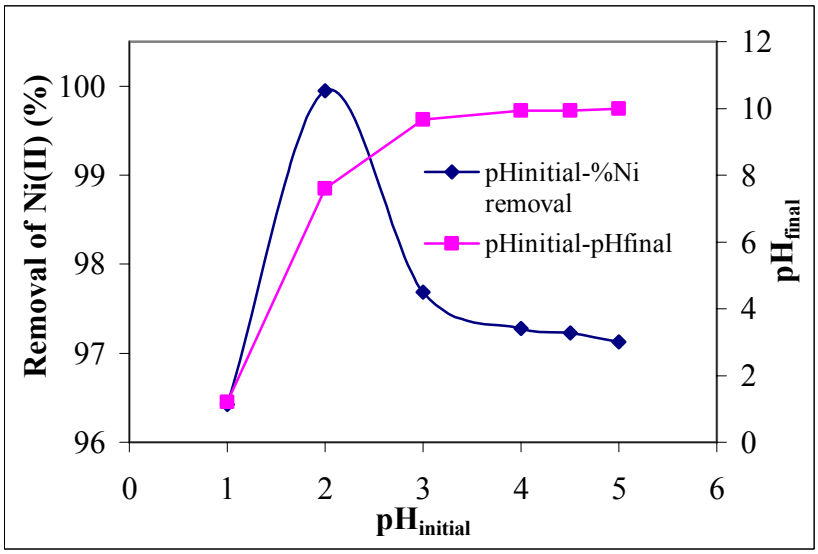

Figure 3.4 pH effect on removal of Ni(II) by Purolite S-950

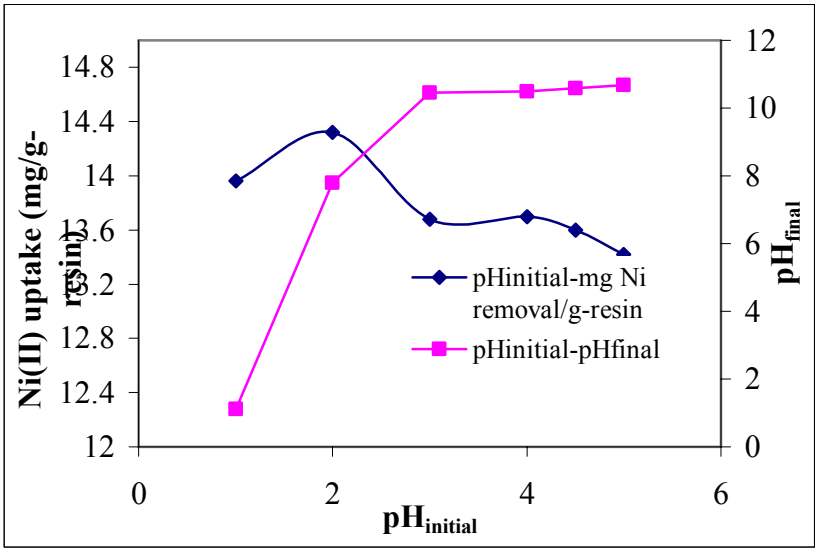

Figure 3.5 Ni(II) uptake by Purolite S-950 against pH

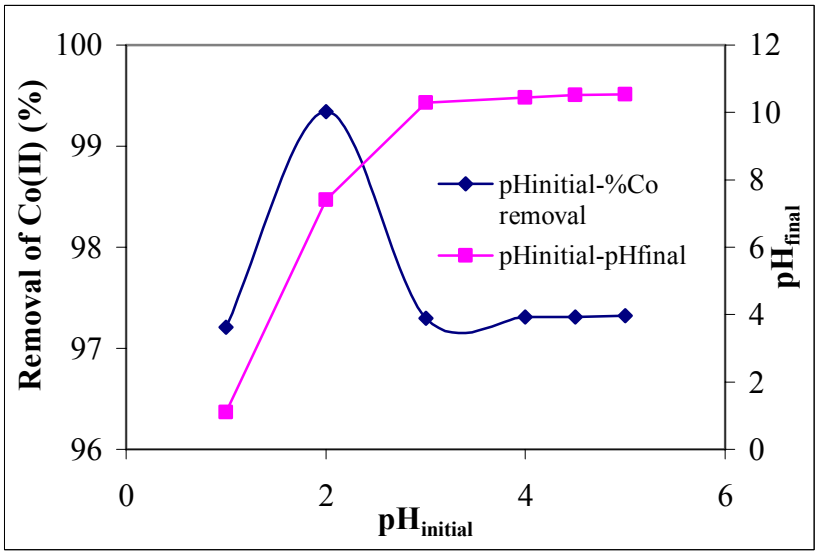

Figure 3.6 pH effect on removal of Co(II) by Purolite S-930

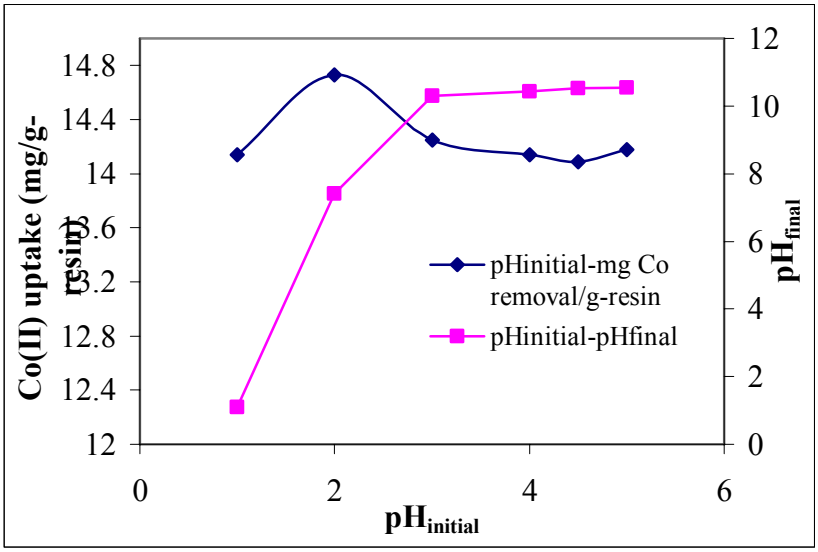

Figure 3.7 Co(II) uptake by Purolite S-930 against pH

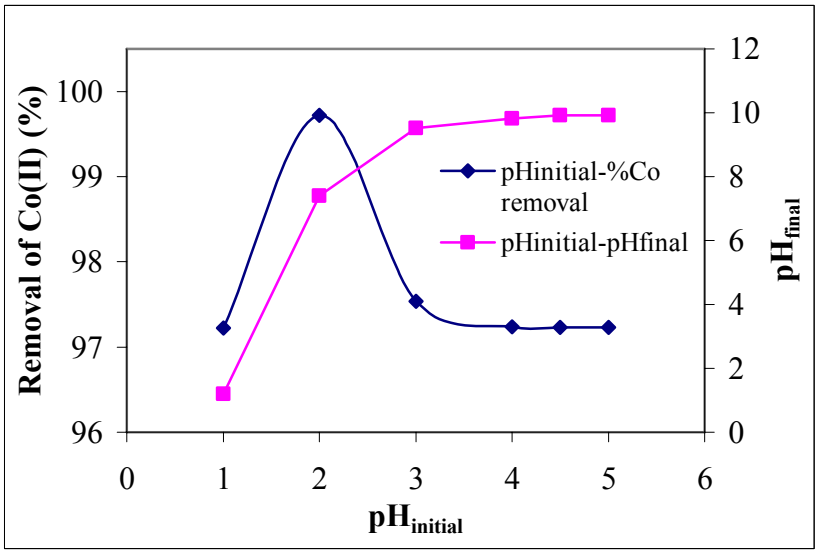

Figure 3.8 pH effect on removal of Co(II) by Purolite S-950

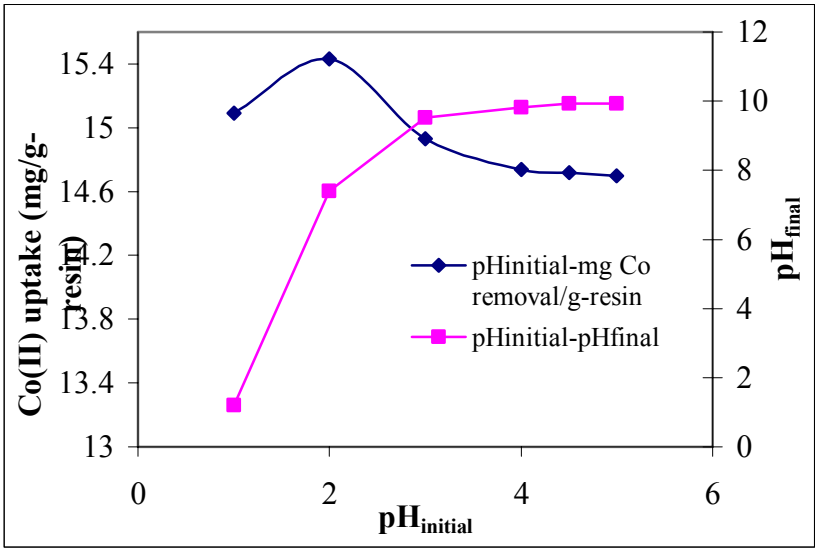

Figure 3.9 Co(II) uptake by Purolite S-950 against pH

3.1.2 Optimum Resin Amount Selection Tests

Optimum resin amounts for Ni(II) and Co(II) removal from aqueous solutions were determined using Purolite S-930 and Purolite S-950 (0.355-0.710 mm). Various amounts of resins were employed in batch-mode sorption tests. In these tests, 0.1, 0.5, 1, 1.5 and 2.0 g of resins of Purolite S-930 and Purolite S-950 were contacted with $4x10^{-4}$M 25 mL of $NiSO_4.6H_2O$ and $CoSO_4.7H_2O$ solutions at 30°C for 24 h with continuous shaking.

Tables 3.3 and 3.4 and Figures 3.10-3.13 show that nickel and cobalt removal increases with increasing resin amounts from 0.1 to 0.5 g by both Purolite S-930 and S-950. But nickel and cobalt removal had a plateau for the resin amounts between 0.5-2 g. There is no significant difference between the removal values obtained by 0.5 and 2 g resin. The economical reasons play important role in industrial processes, therefore the optimum resin amount is selested as 0.5 g resin/L for both Purolite S-930 and S-950 by which are more than %98 metal removal is found.

Table 3.3 Effect of resin amount on removal of nickel and cobalt by Purolite S-930

Nickel			**Cobalt**		
Resin amount (g)	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	Resin amount (g)	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)
0.1	93.03	59.43	0.1	97.39	76.56
0.5	98.83	13.50	0.5	99.40	15.83
1.0	98.99	6.70	1.0	99.53	7.90
1.5	99.78	4.57	1.5	99.80	5.30
2.0	99.83	3.43	2.0	99.82	3.98

Table 3.4 Effect of resin amount on removal of nickel and cobalt by Purolite S-950

Nickel			**Cobalt**		
Resin amount (g)	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	Resin amount (g)	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)
0.1	99.23	69.41	0.1	99.69	59.61
0.5	99.88	14.36	0.5	99.73	15.30
1.0	99.92	7.22	1.0	99.81	7.11
1.5	99.91	4.83	1.5	99.82	5.50
2.0	99.88	3.56	2.0	99.86	3.90

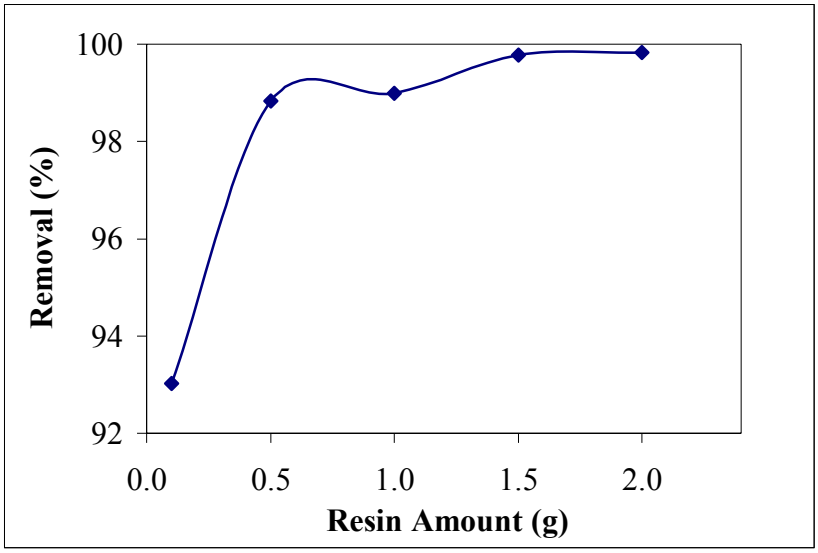

Figure 3.10 Effect of resin amount on removal of Ni(II) by Purolite S-930

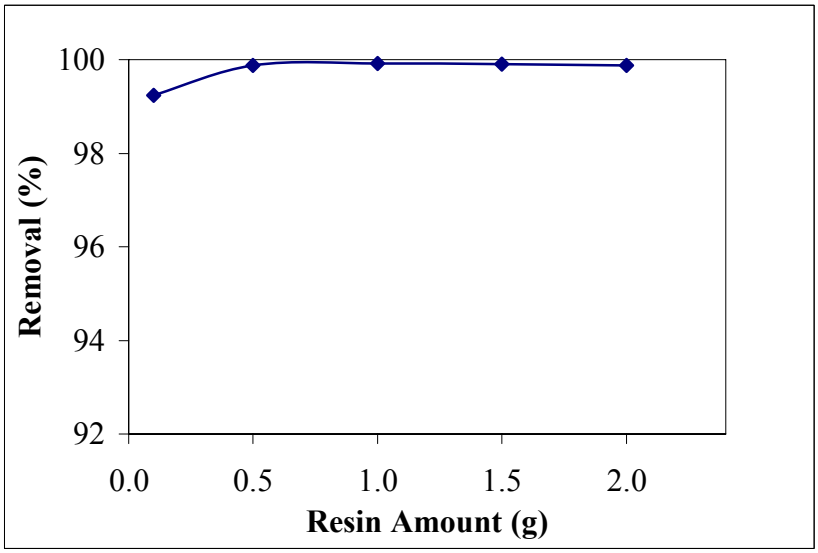

Figure 3.11 Effect of resin amount on removal of Ni(II) by Purolite S-950

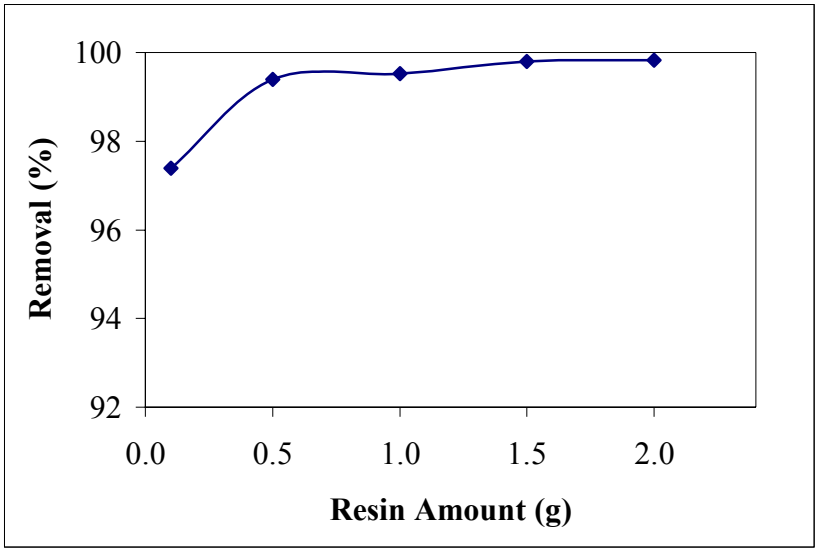

Figure 3.12 Effect of resin amount on removal of Co(II) by Purolite S-930

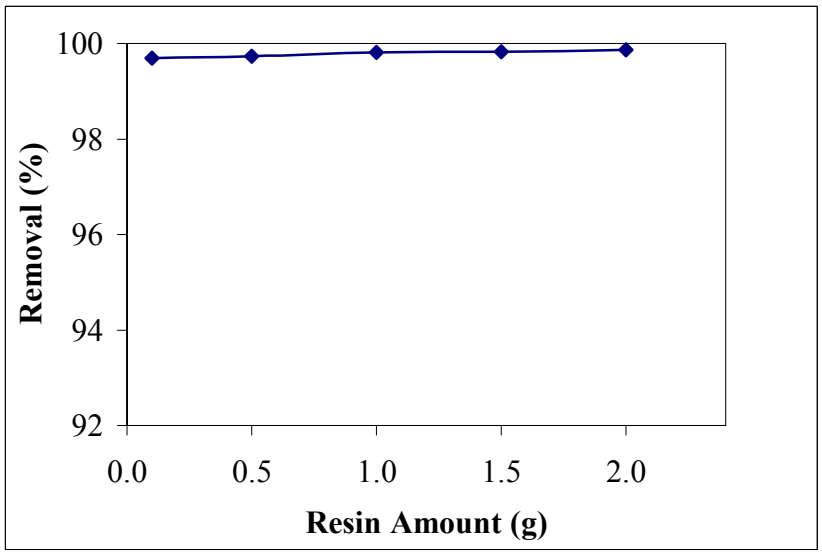

Figure 3.13 Effect of resin amount on removal of Co(II) by Purolite S-950

Same amount of dry resins were contacted with PLS and PLS solution obtained after Fe(III) precipitation.

Tables 3.5 and 3.6 and Figures 3.14-3.17 show that nickel and cobalt removal increases with increasing resin amounts from 0.1 to 1.5 g by both Purolite S-930 and S-950. But nickel and cobalt removal had a plateau for the resin amounts between 1.5-2 g. According to these results, the optimum resin amount should be 1.5 g resin/L

to obtain more than % 98 removal of Ni(II), Co(II), Mn(II) and Fe(III) by both Purolite S-930 and S-950. Presence of Fe(III) ions in the solution prevents the removal of Ni(II) and Co(II) ions effectively because as can be seen in Tables 3.5 and 3.6 both Purolite S-930 and S-950 is more selective for three valance ions than two valance ions.

Table 3.5 Effect of resin amount on removal of Ni(II), Co(II), Mn(II), Fe(III) by Purolite S-930 from PLS

	Nickel		**Cobalt**		**Manganese**		**Iron**	
Resin amount (g)	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)	Mn Removal (%)	Uptake of Mn(II) (mg Mn/g-resin)	Fe Removal (%)	Uptake of Fe(III) (mg Fe/g-resin)
0.5	39.29	6.02	4.00	0.01	23.75	1.61	88.01	53.96
1.0	86.02	6.57	40.43	0.08	28.50	1.32	97.50	32.88
1.5	99.37	5.06	77.43	0.10	90.34	1.26	98.19	22.26
2.0	99.59	3.79	95.43	0.09	99.18	0.76	98.51	16.73

Table 3.6 Effect of resin amount on removal of Ni(II), Co(II), Mn(II), Fe(III) by Purolite S-950 from PLS

	Nickel		**Cobalt**		**Manganese**		**Iron**	
Resin amount (g)	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)	Mn Removal (%)	Uptake of Mn(II) (mg Mn/g-resin)	Fe Removal (%)	Uptake of Fe(III) (mg Fe/g-resin)
0.5	38.07	6.08	0.00	0.00	51.00	2.86	58.73	41.88
1.0	51.78	4.14	41.43	0.08	85.75	2.40	78.77	28.04
1.5	96.98	5.18	67.71	0.09	98.33	1.84	97.64	23.25
2.0	99.21	3.99	83.14	0.08	99.62	1.40	98.03	17.52

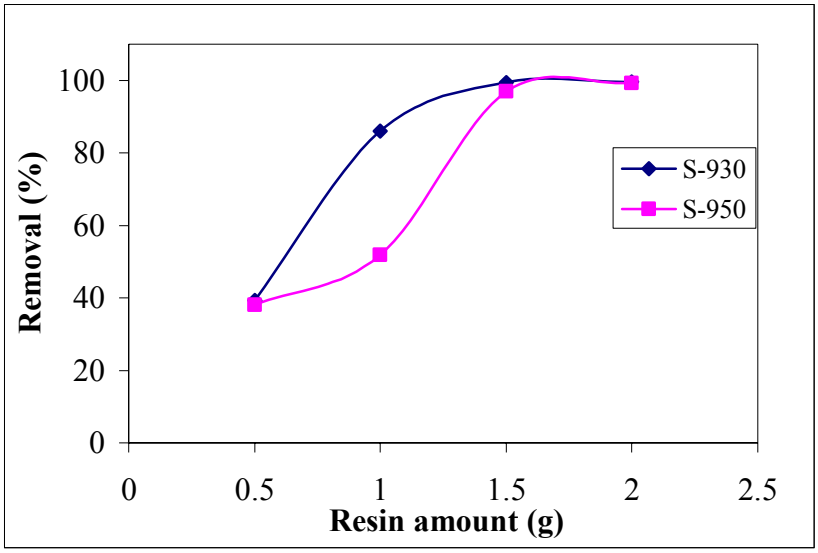

Figure 3.14 Effect of resin amount on removal of Ni(II) from PLS by Purolite S-930 and S-950

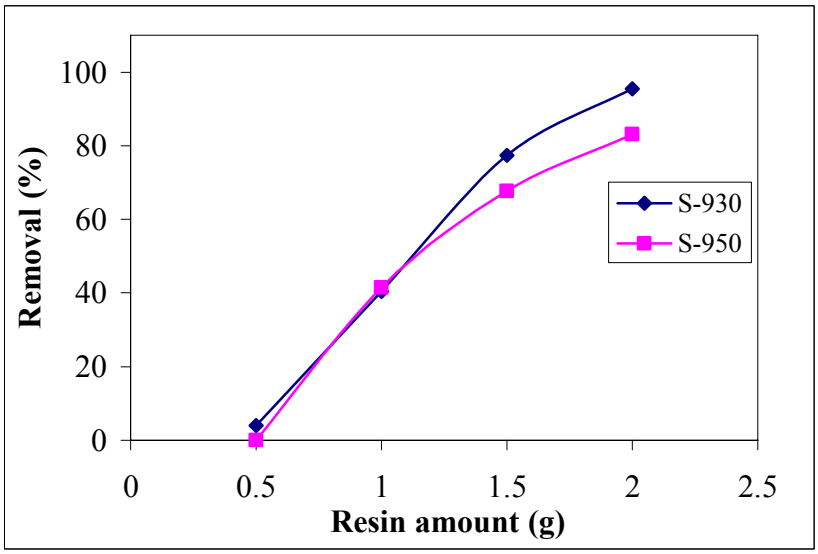

Figure 3.15 Effect of resin amount on removal of Co(II) from PLS by Purolite S-930 and S-950

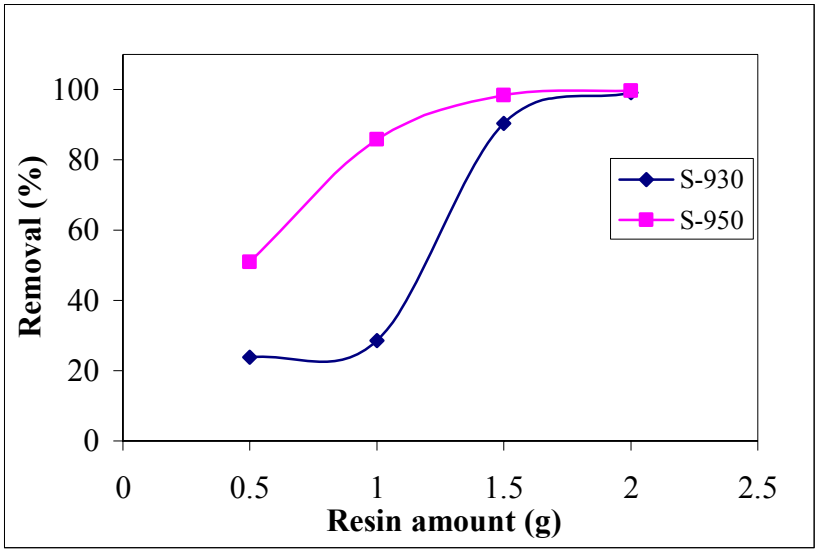

Figure 3.16 Effect of resin amount on removal of Mn(II) from PLS by Purolite S-930 and S-950

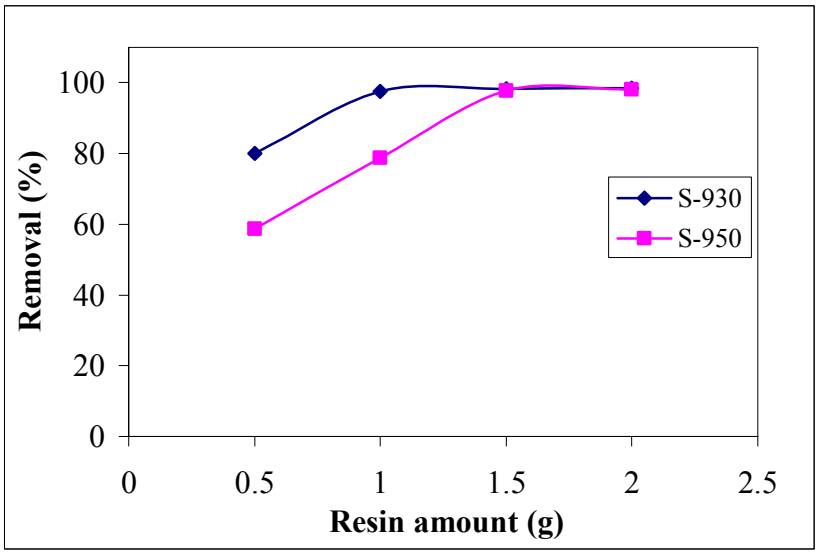

Figure 3.17 Effect of resin amount on removal of Fe(III) from PLS by Purolite S-930 and S-950

As discussed before, Fe(III) ions prevent the uptake of Ni(II) and Co(II) ions effectively by small amounts of resins. Therefore, PLS was processed and Fe was precipitated as $Fe(OH)_3$. The studies done after this process, Tables 3.7-3.8 and Figures 3.18-3.20 show that uptake values of Ni(II) and Co(II) almost same with studies done by using model solutions.

Table 3.7 Effect of resin amount on removal of Ni(II), Co(II), Mn(II) by Purolite S-930 from processed PLS

	Nickel		**Cobalt**		**Manganese**	
Resin amount (g)	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)	Mn Removal (%)	Uptake of Mn(II) (mg Mn/g-resin)
0.5	99.68	13.95	97.65	0.40	99.22	3.79
1.0	99.70	6.98	97.78	0.20	99.67	1.90
1.5	99.79	4.69	98.04	0.13	99.68	1.28
2.0	99.82	3.52	98.69	0.10	99.79	0.96

Table 3.8 Effect of resin amount on removal of Ni(II), Co(II), Mn(II) by Purolite S-950 from processed PLS

	Nickel		**Cobalt**		**Manganese**	
Resin amount (g)	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)	Mn Removal (%)	Uptake of Mn(II) (mg Mn/g-resin)
0.5	98.23	14.54	95.95	0.41	97.74	3.95
1.0	99.50	7.35	96.08	0.21	99.35	2.00
1.5	99.77	4.93	98.56	0.14	99.83	1.35
2.0	99.79	3.70	98.69	0.11	99.85	1.01

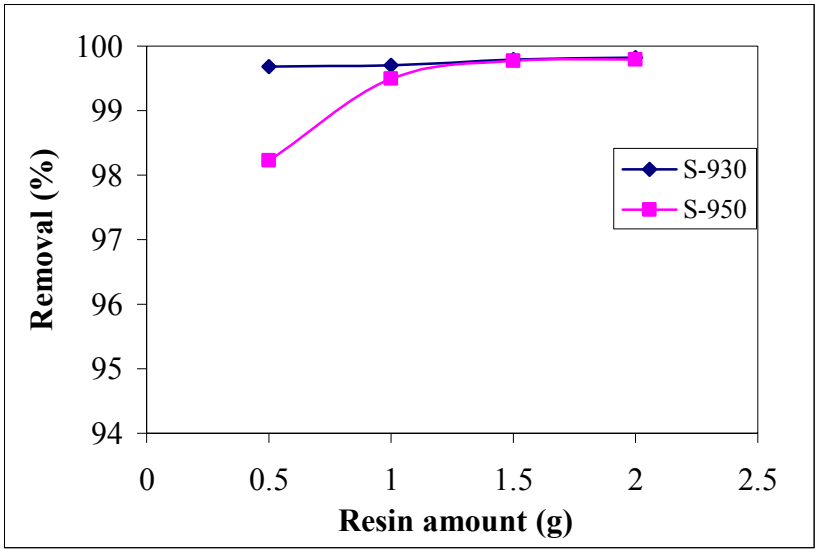

Figure 3.18 Effect of resin amount on removal of Ni(II) from processed PLS by Purolite S-930 and S-950

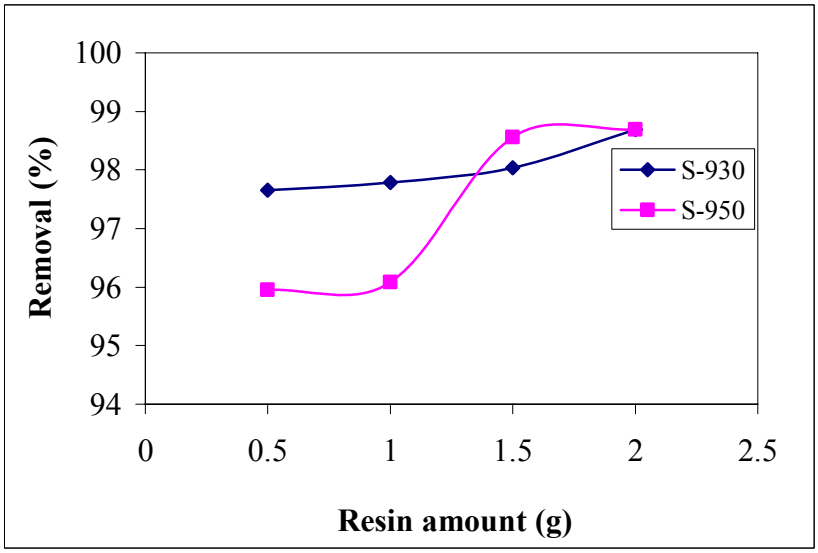

Figure 3.19 Effect of resin amount on removal of Co(II) from processed PLS by Purolite S-930 and S-950

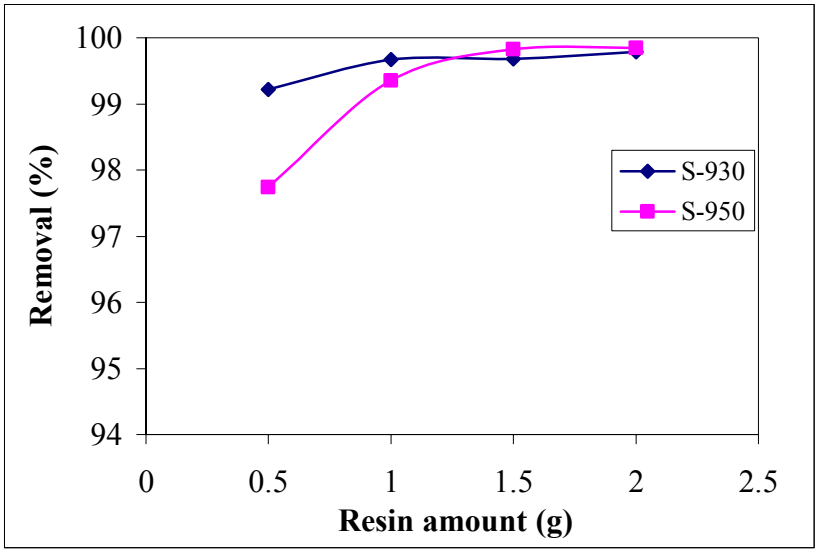

Figure 3.20 Effect of resin amount on removal of Mn(II) from processed PLS by Purolite S-930 and S-950

3.1.3 Equilibrium Tests

Equilibrium data were obtained for Ni(II) and Co(II) adsorption onto Purolite S-930 and Purolite S-950 resin at pH 2. The equilibrium relationships for Purolite S-930 and Purolite S-950 are shown in Tables 3.9-3.10 and Figures 3.21 and 3.24, respectively.

Table 3.9 Results of equilibrium studies by Purolite S-930

Samples (M)		**10^{-4}**	**$4x10^{-4}$**	**10^{-3}**	**$4x10^{-3}$**	**10^{-2}**	**$4x10^{-2}$**	**10^{-1}**
Ni	Ce (mg/L)	0.00	0.00	0.86	2.96	3.53	980	3550
	Qe (mg/g)	0.32	1.49	2.79	13.48	32.63	76.89	77.06
	Ce/Qe	0.00	0.00	0.31	0.22	0.11	12.74	46.07
	log Qe	0.00	0.17	0.44	1.12	1.51	1.88	1.88
	log Ce	0.00	0.00	0.00	0.47	0.54	2.99	3.55
Co	Ce (mg/L)	0.00	0.12	0.28	2.16	1.51	1230	4425
	Qe (mg/g)	0.35	1.56	3.04	15.11	35.41	74.25	74.85
	Ce/Qe	0.00	0.08	0.09	0.14	0.04	16.56	59.12
	log Qe	0.00	0.19	0.48	1.17	1.54	1.87	1.87
	log Ce	0.00	0.00	0.00	0.33	0.17	3.08	3.64

Table 3.10 Results of equilibrium studies by Purolite S-950

Samples (M)		10^{-4}	$4x10^{-4}$	10^{-3}	$4x10^{-3}$	10^{-2}	$4x10^{-2}$	10^{-1}
Ni	Ce (mg/L)	0.00	0.00	0.00	0.00	0.14	550	3130
	Qe (mg/g)	0.33	1.47	2.82	13.54	32.68	99.30	99.38
	Ce/Qe	0.00	0.00	0.00	0.00	0.00	5.54	31.50
	log Qe	0.00	0.16	0.45	1.13	1.51	1.99	1.99
	log Ce	0.00	0.00	0.00	0.00	0.00	2.74	3.49
Co	Ce (mg/L)	0.00	0.30	0.35	0.36	0.36	745	3310
	Qe (mg/g)	0.33	1.46	2.80	13.53	32.70	89.12	89.92
	Ce/Qe	0.00	0.21	0.13	0.03	0.01	8.36	36.81
	log Qe	0.00	0.16	0.44	1.13	1.51	1.95	1.95
	log Ce	0.00	0.00	0.00	0.00	0.00	2.87	3.51

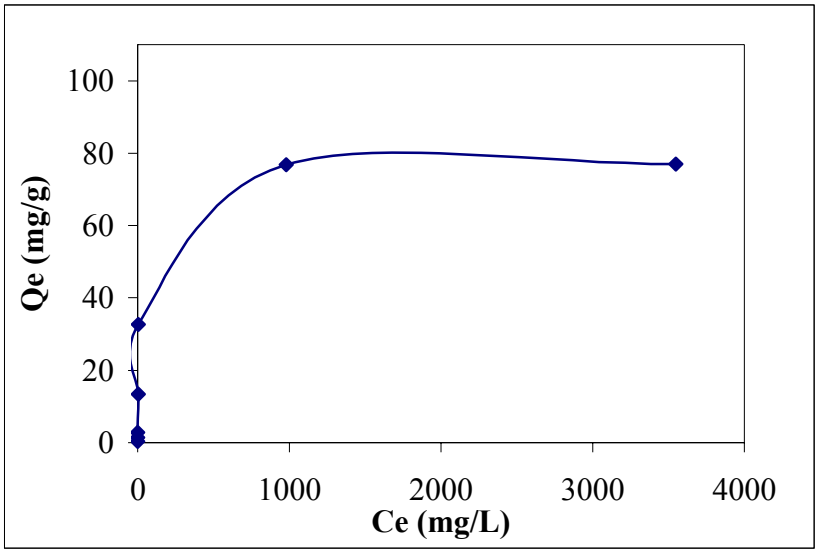

Figure 3.21 Equilibrium isotherm for loading Ni(II) onto Purolite S-930

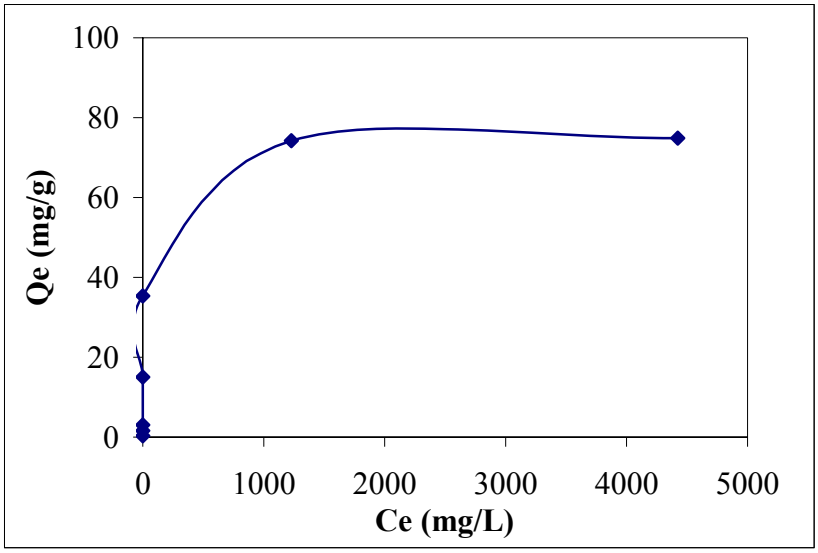

Figure 3.22 Equilibrium isotherm for loading Co(II) onto Purolite S-930

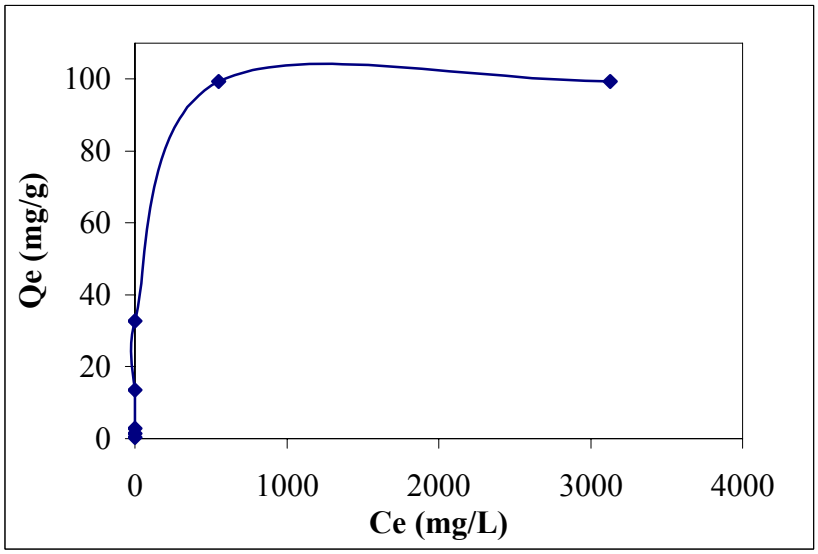

Figure 3.23 Equilibrium isotherm for loading Ni(II) onto Purolite S-950

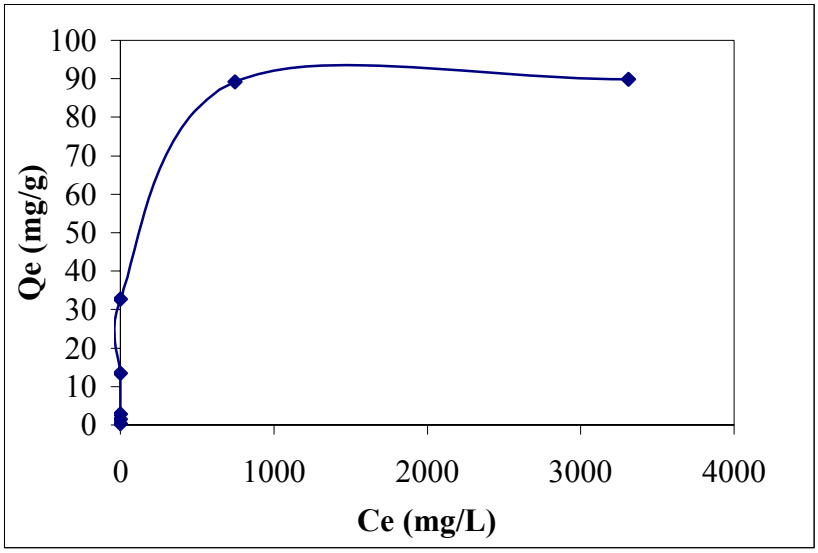

Figure 3.24 Equilibrium isotherm for loading Co(II) onto Purolite S-950

The maximum uptake was found as 77.06 mg Ni(II)/g-resin and mg 74.85 Co(II)/g-resin for Purolite S-930 and as 99.38 mg Ni(II)/g-resin and 89.92 mg Co(II)/g-resin for Purolite S-950. These results showed that macroporous aminophosphonic acid chelating resin *Purolite* S-950 has higher adsorption capacity than iminodiacetic groups chelating resin *Purolite S-930* for both Ni(II) and Co(II) removal.

The Langmuir isotherm (Eqn. 3.1) and Freundlich isotherm (Eqn. 3.2) models were applied for adsorption equilibrium of Purolite S-930 and Purolite S-950 (Figures 3.25- 3.28).

Langmuir isotherm model is represented as**;**

$$\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad \textbf{(3.1)}$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of ion (such as Ni(II)) sorbed on the resins (mg Ni(II)/g-dry resin), b is the energy of sorption (l / mg Ni(II)).

The equation for Freundlich isotherm model is as**;**

$$Q_e = K_f C_e^{(1/n)} \qquad \textbf{(3.2)}$$

where K_f and n is model constants for rate of adsorption and favorability of adsorption respectively. The linearized Freundlich fitting curves of Purolite S-930 and Purolite S-950 are given in Figures 3.29 -3.32, respectively.

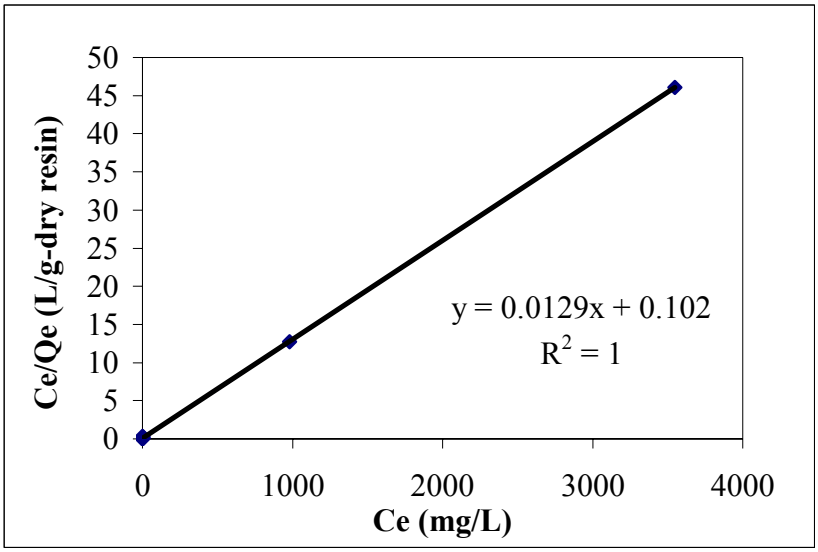

Figure 3.25 Linearized form of Langmuir fitting for Purolite S-930 in Ni(II) removal

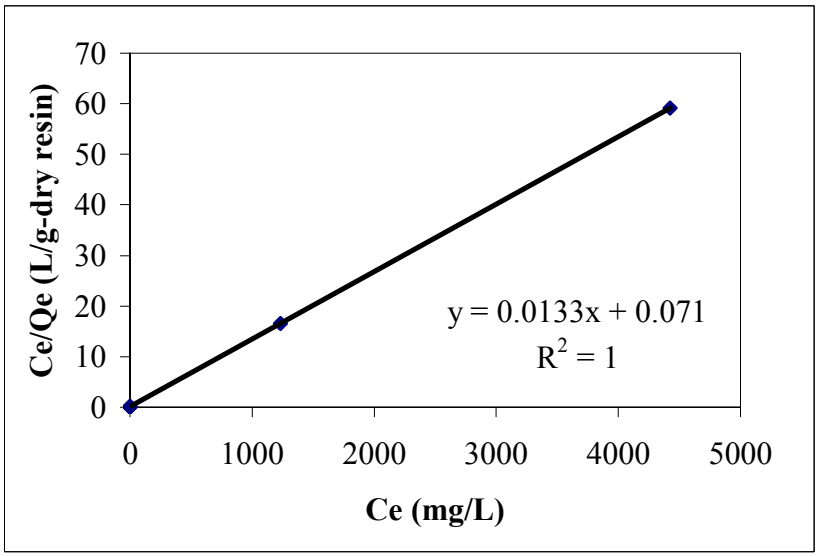

Figure 3.26 Linearized form of Langmuir for Purolite S-930 in Co(II) removal

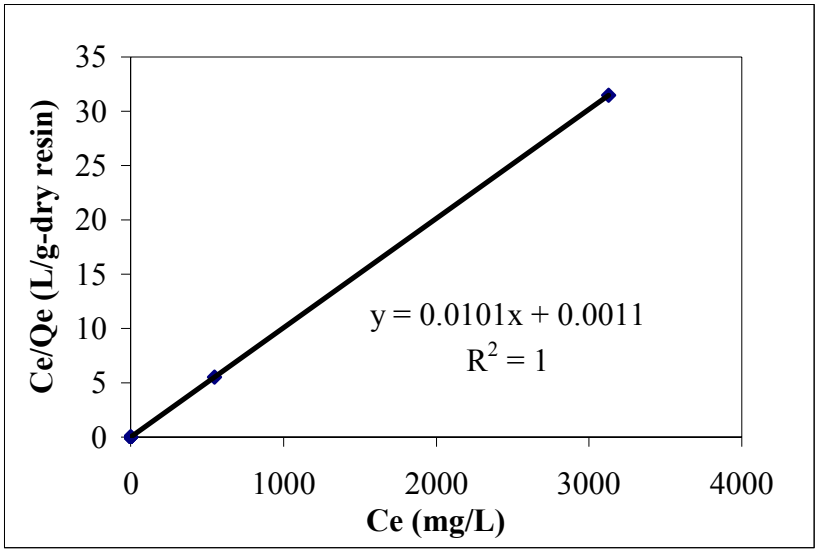

Figure 3.27 Linearized form of Langmuir fitting for Purolite S-950 in Ni(II) removal

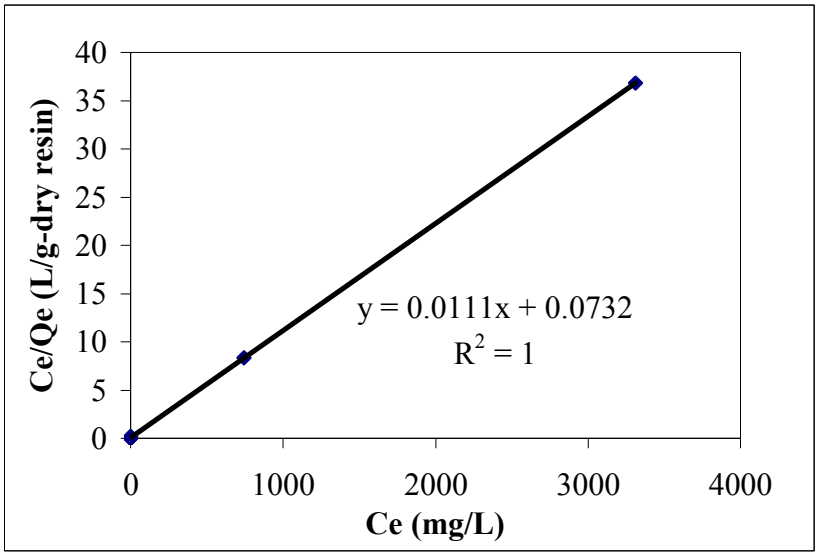

Figure 3.28 Linearized form of Langmuir fitting for Purolite S-950 in Co(II) removal

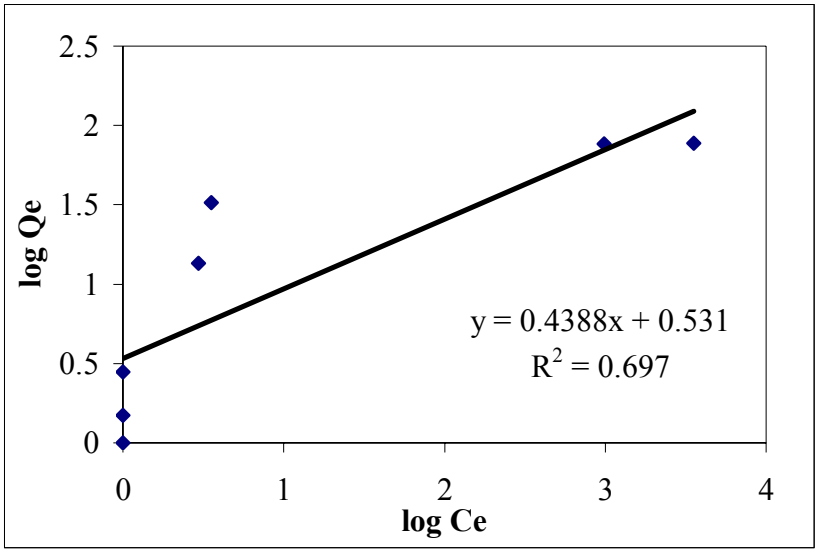

Figure 3.29 Linearized form of Freundlich fitting for Purolite S-930 in Ni(II) removal

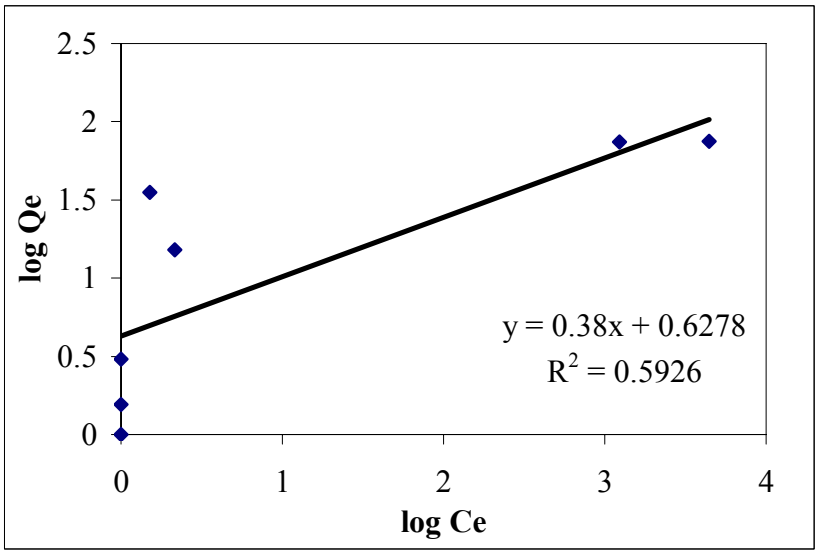

Figure 3.30 Linearized form of Freundlich fitting for Purolite S-930 in Co(II) removal

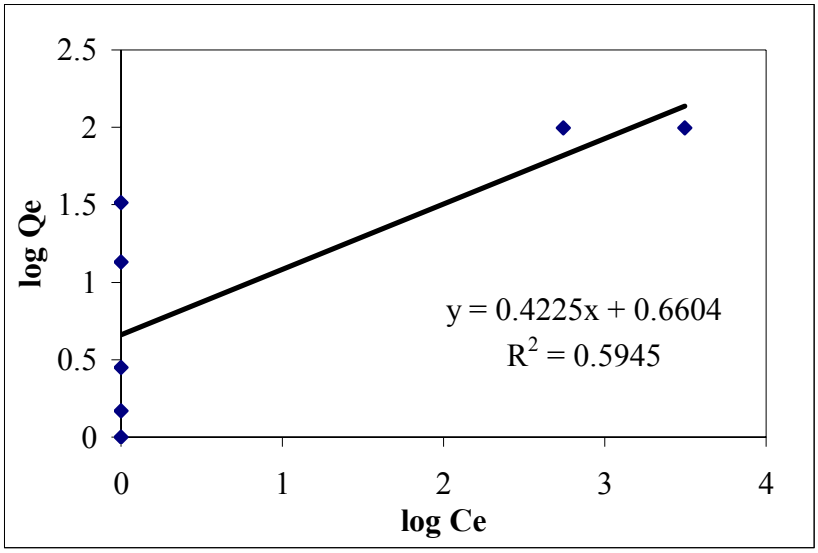

Figure 3.31 Linearized form of Freundlich fitting for Purolite S-950 in Ni(II) removal

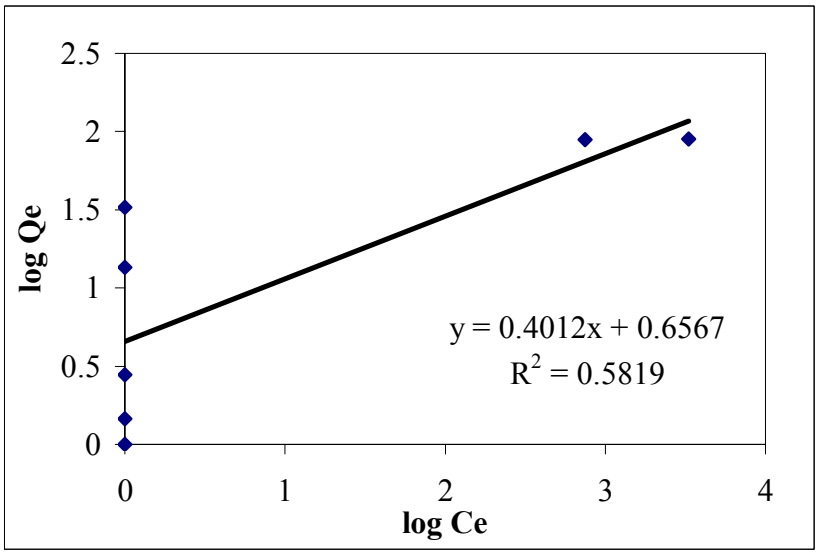

Figure 3.32 Linearized form of Freundlich fitting for Purolite S-950 in Ni(II) removal

The correlation coefficient for the linear regression fit of Langmuir isotherm equation was found to be 1 for both Ni(II) and Co(II) removal by Purolite S-930. The resin showed better fit for Langmuir isotherm than Freundlich isotherm.

The correlation coefficient for the linear regression fit of Freundlich isotherm equation was found to be 1 for both Ni(II) and Co(II) removal by Purolite S-950. The resin showed better fit for Langmuir isotherm than Freundlich isotherm.

Q_o, Langmuir isotherm constant, indicates the adsorption capacity of resins which was found as 77.52 mg Ni(II)/g-resin and 75.19 mg Co(II)/g-resin for Purolite S-930 and as 99.00 mg Ni(II)/g-resin and 90.10 mg Co(II)/g-resin for Purolite S-950. These results showed that Purolite S-950 has higher adsorption capacity than Purolite S-930.

b, Langmuir isotherm constant, indicates energy of adsorption which was found as 0.126 l/mg (Ni) and 0.187 l/mg (Co) for Purolite S-930 and as 9.18 l/mg and 0.15 l/mg for Purolite S-950. These result showed that Purolite S-950 has higher adsorption energy than that of Purolite S-930.

K_f, Freundlich isotherm constant, indicates rate of adsorption which was found as 3.39 (Ni) and 4.24 (Co) for Purolite S-930 and as 4.57 (Ni) and 4.54 (Co) for Purolite S-950 . These results showed that Purolite S-950 adsorption rate is higher than that of Purolite S-930.

n, Freundlich isotherm constant, indicates the degree of favorability of adsorption and should have values lying in the range of 1 to 10 for classification as favorable adsorption. The values of n were found as 2.28 (Ni) and 2.63 (Co) for Purolite S-930 and as 2.37 (Ni) and 2.49 (Co) for Purolite S-950. Both chelating resins showed favorable adsorption. All parameter values can be seen in Table 3.11.

Table 3.11 The values of the parameters in the Langmuir and Freundlich equation

Resin Type		**Q_o (mg/g-dry resin)**	**b (1/mg)**	**K_f**	**n**
Purolite S-930	Ni (II)	77.52	0.126	3.39	2.28
	Co(II)	75.19	0.187	4.24	2.63
Purolite S-950	Ni(II)	99.00	9.18	4.57	2.37
	Co(II)	90.10	0.15	4.54	2.49

3.1.4 Selectivity Tests

The selectivity of Purolite S-930 and Purolite S-950 for Ni(II) was studied in the presence of Co(II) ions. Selectivity tests have been carried out with 4 x 10^{-3} M Ni(II) solution in the presence of 4x10^{-3} M, 2x10^{-4} M, 8x10^{-4}M, 4x10^{-4}M, 2x10^{-4}Co(II) solutions. There is influence of Co(II) ions on removal of Ni(II) which is shown in Figure 3.33-3.34 As summarized in Table 3.12 and 3.13, removal of Ni(II) decreased 3.98% for Purolite S-930 and 0.35% for Purolite S-950 in the presence of same amount of Co(II) ions.

Table 3.12 Selectivity test on removal of nickel by Purolite S-930 in the presence of cobalt

Nickel			**Cobalt**		
Ni/Co	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	Ni/Co	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)
1/1	94.52	4.35	1/1	96.36	4.36
1/0.5	95.70	5.00	1/0.5	95.11	2.07
1/0.2	94.42	4.19	1/0.2	96.79	0.78
1/0.1	98.04	4.31	1/0.1	91.08	0.35
1/0.05	98.44	4.32	1/0.05	86.88	0.17

Table 3.13 Selectivity test on removal of nickel by Purolite S-950 in the presence of cobalt

Nickel			**Cobalt**		
Ni/Co	Ni Removal (%)	Uptake of Ni(II) (mg Ni/g-resin)	Ni/Co	Co Removal (%)	Uptake of Co(II) (mg Co/g-resin)
1/1	99.45	4.87	1/1	99.86	4.81
1/0.5	99.51	5.53	1/0.5	99.52	2.31
1/0.2	99.68	4.70	1/0.2	99.40	0.85
1/0.1	99.67	4.66	1/0.1	99.06	0.4
1/0.05	99.80	4.66	1/0.05	98.58	0.2

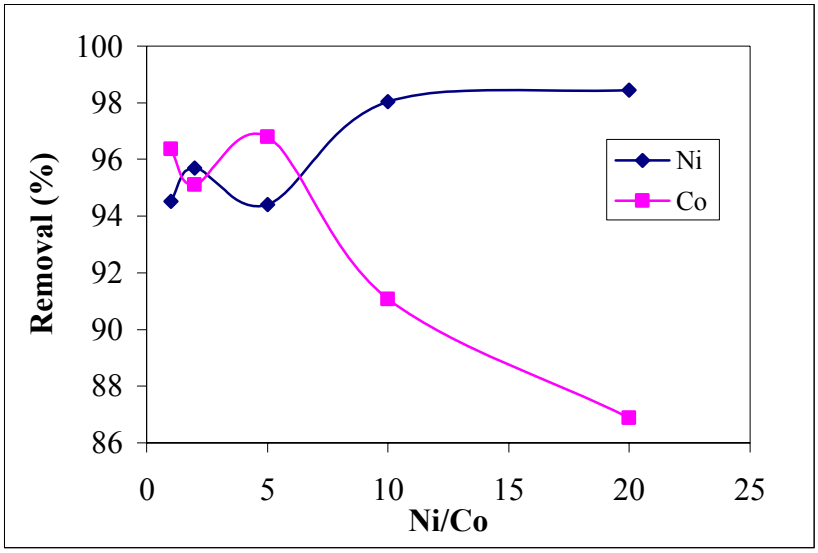

Figure 3.33 Ni/Co ratio effect on selective loading onto Purolite S-930

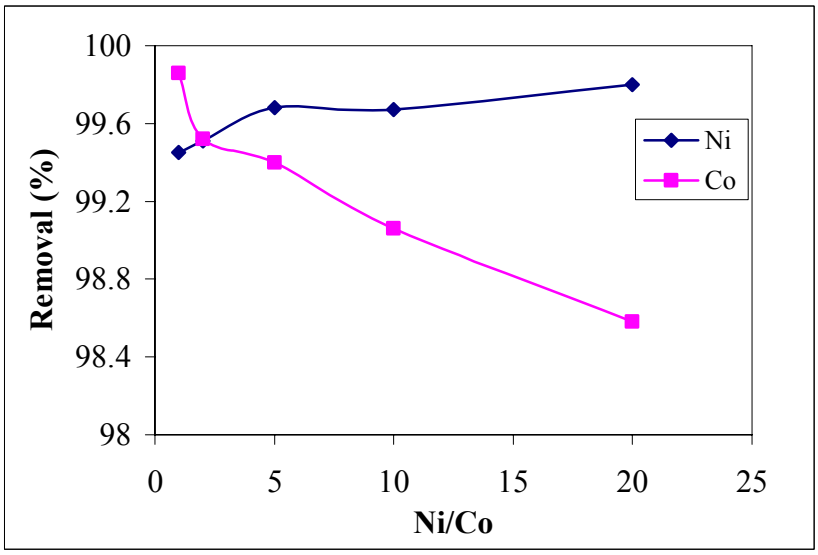

Figure 3.34 Ni/Co ratio effect on selective loading onto Purolite S-950

3.1.5 Selection of Optimum pH Range of Eluting Agent Tests

A series of batch elution tests of Ni(II) and Co(II) from Purolite S-930 and S-950 were performed by using H_2SO_4 at various concentrations (0.5, 1, 2, 4, 6 M). 0.5 g of resin was used at each batch elution test. The results have been summarized in Tables 3.14 and 3.15. As shown in Figures 3.35 and 3.36 Ni(II) and Co(II) ions were eluted with the 95% efficiency by 4 and 6 M H_2SO_4.

Table 3.14 Ni(II) and Co(II) stripping performance from Purolite S-930 at various pH

Concentration of eluting agent (M)		**0.5**	**1**	**2**	**4**	**6**
Ni	Ce (mg/L)	271	271	271	271	271
	mg sorbed	6.69	6.69	6.69	6.69	6.69
	mg eluted	0.13	5.13	5.6	6.2	6.33
	Elution Efficiency (%)	2.01	76.64	83.67	92.65	94.58
Co	Ce (mg/L)	302	302	302	302	302
	mg sorbed	7.53	7.53	7.53	7.54	7.54
	mg eluted	5.53	5.76	6.3	6.97	7.2
	Elution Efficiency (%)	73.36	76.4	83.56	92.45	95.49

Table 3.15 Ni(II) and Co(II) stripping performance from Purolite S-950 at various pH

Concentration of eluting agent (M)		**0.5**	**1**	**2**	**4**	**6**
Ni	Ce (mg/L)	271	271	271	271	271
	mg sorbed	6.78	6.78	6.77	6.77	6.78
	mg eluted	0.14	5.10	5.60	6.44	6.50
	Elution Efficiency (%)	2.07	75.28	82.66	95.06	95.94
Co	Ce (mg/L)	302	302	302	302	302
	mg sorbed	7.55	7.55	7.55	7.55	7.55
	mg eluted	5.53	5.76	6.30	6.97	7.55
	Elution Efficiency (%)	73.25	76.29	83.44	92.32	95.36

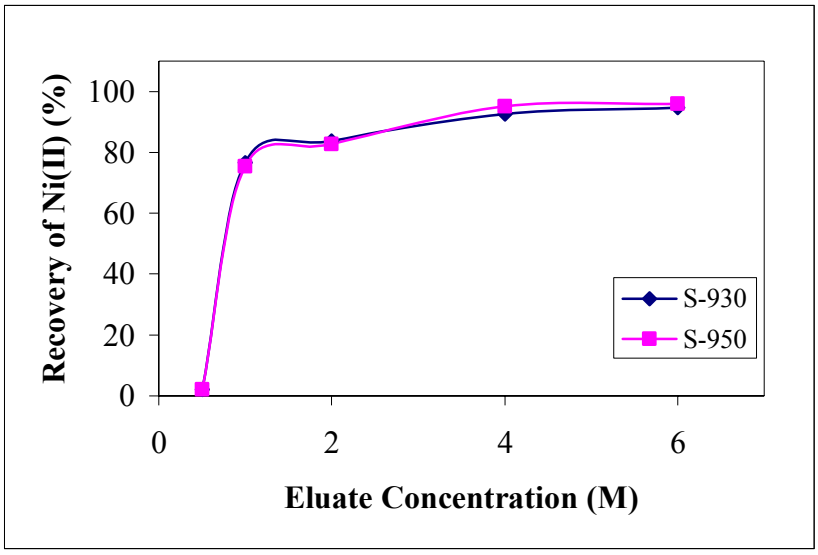

Figure 3.35 Effect of H_2SO_4 concentration on the stripping of Ni(II) from Purolite S-930 and S-950

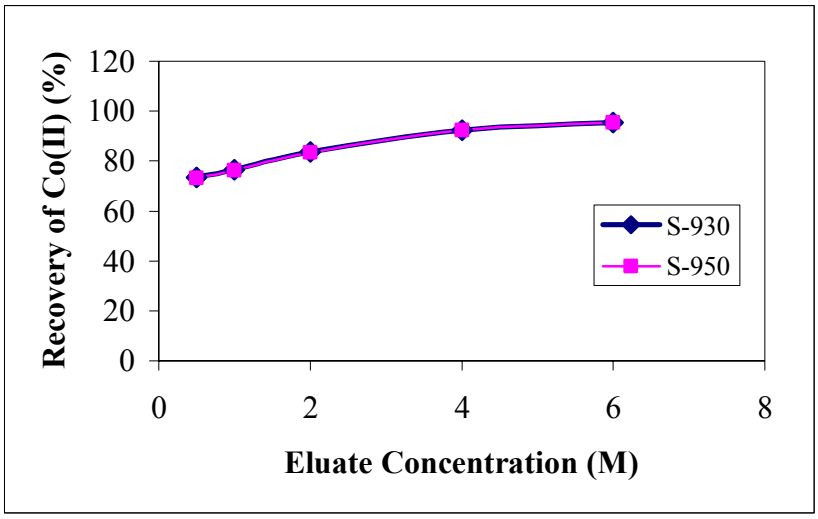

Figure 3.36 Effect of H_2SO_4 concentration on the stripping of Co(II) from Purolite S-930 and S-950

3.1.6 Fe Precipitation Tests

In these studies PLS (Pregnant Leach Solution) supplied from Bosphorus Nickel Madencilik was used. Tests were carried out different pH (3, 3.2, 3.6, 4, 4.2, 4.3, 4.35, 4.8) to obtain maximum removal of Fe. Fe(III) was precipitated as $Fe(OH)_3$ to optimize the removal of Ni(II) and Co(II) by cation exchange resins. pH of the solutions were adjusted by means of concentrated NaOH. Original PLS solution pH was 1. In Table 3.16 PLS and processed PLS (after Fe precipitation) chemical analysis can be seen. The results in Figures 3.37-3.40 show that in pH: 4.35 minimum Fe, maximum Ni and Co concentration were obtained.

Table 3.16 Chemical analysis of PLS and Processed PLS

	Ni (ppm)	**Fe (ppm)**	**Mn (ppm)**	**Co (ppm)**	**Al (ppm)**
Original PLS analysis	1310	6260	400	56.3	606

Processed PLS analysis

pH	**Ni (ppm)**	**Fe (ppm)**	**Mn (ppm)**	**Co (ppm)**	**Al (ppm)**
3.00	974	520	288	42	342
3.20	998	50	284	44	340
3.60	1060	62	312	48	301
4.00	1044	6,62	316	46	176
4.20	986	4,26	298	42	118
4.30	1104	5,31	308	50	172,2
4.35	1138	3,9	320	52	202,4
4.80	488	0,4	178	16	3,01

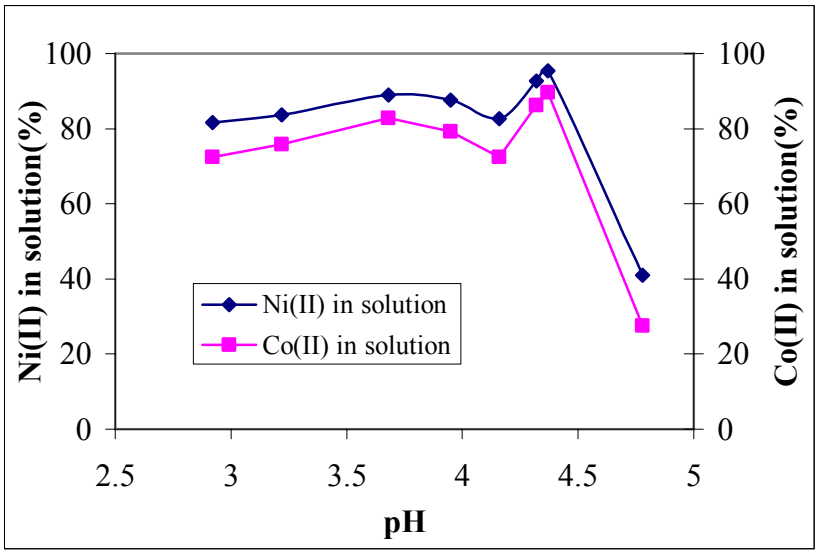

Figure 3.37 Ni(II) and Co(II) amount remaining in solution against pH

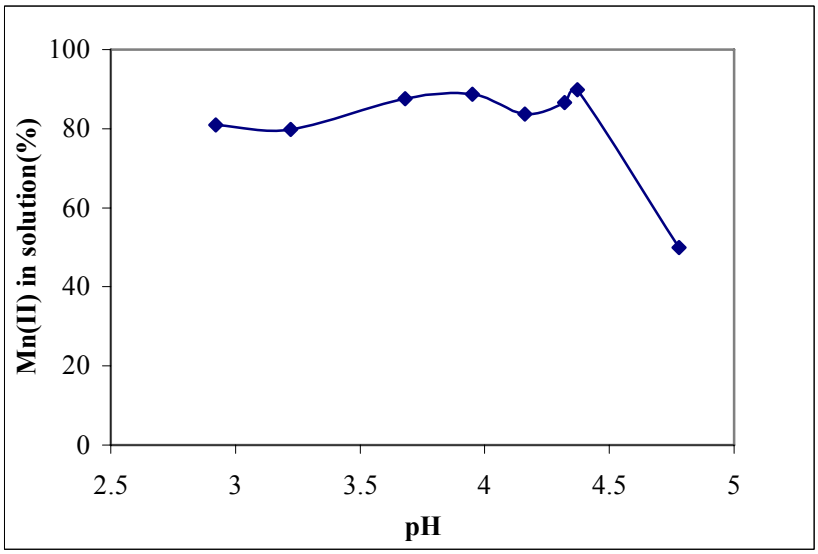

Figure 3.38 Mn(II) amount remaining in solution against pH

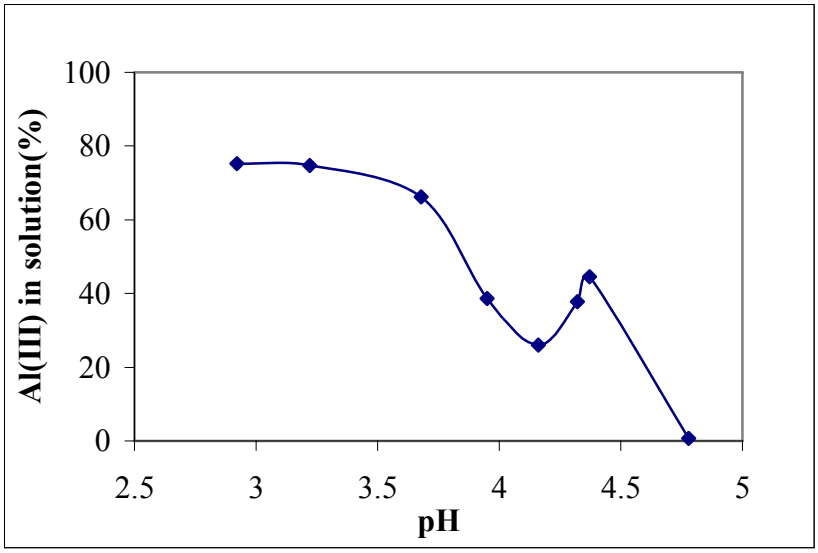

Figure 3.39 Al(III) amount remaining in solution against pH

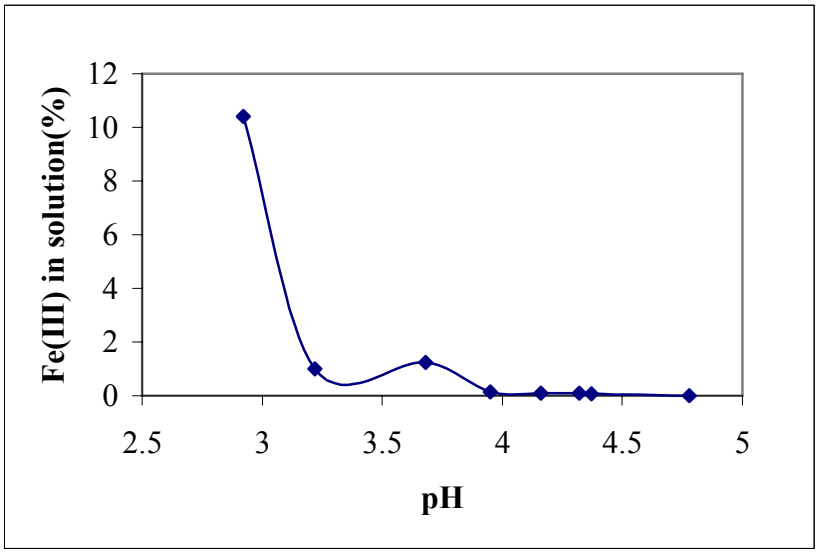

Figure 3.40 Fe(III) amount remaining in solution against pH

3.1.7 Kinetic Tests

The kinetic performances of Purolite S-930 and Purolite S-950 resins were investigated using 4.0 g dry resin. Figure 3.41 and 3.42 illustrates the relative concentration decrease of nickel and cobalt for each resin versus time. Equilibrium conditions were assumed to have been achieved once the metal concentration in solution attained a steady value. This is usually the value at the contact time of 24 hours.

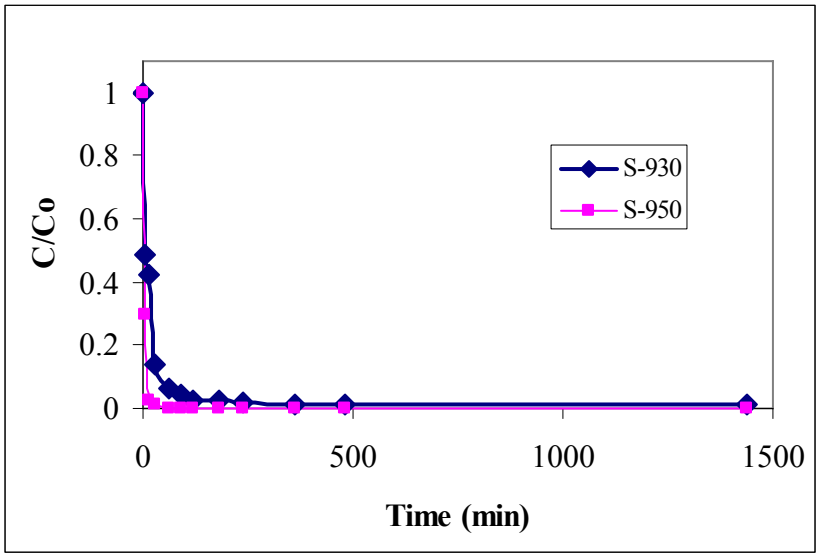

Figure 3.41 Comparison of kinetic performances of Purolite S-930 and S-950 for Ni(II) removal

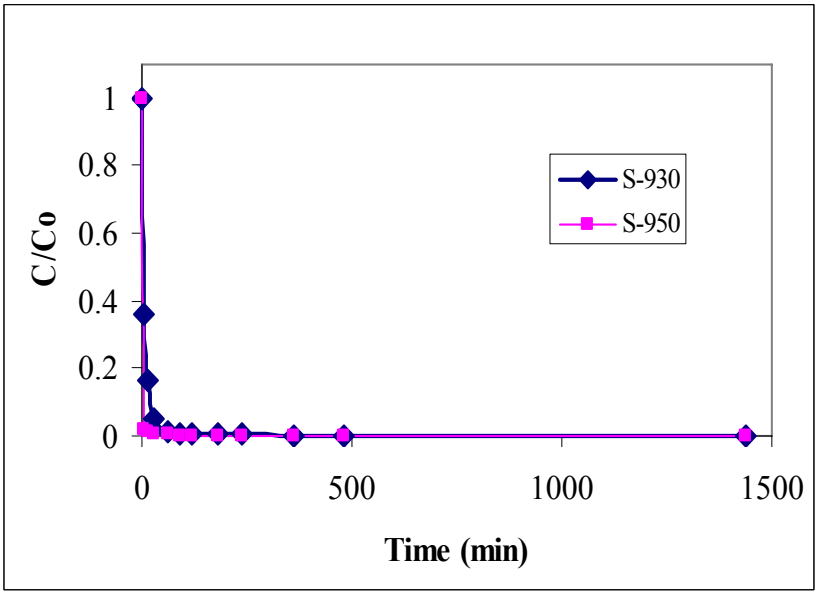

Figure 3.42 Comparison of kinetic performances of Purolite S-930 and S-950 for Co(II) removal

The equilibrium half-time for Ni(II) removal was 5 min both with Purolite S-930 and Purolite S-950. The corresponding values for Co(II) removal was 5 min both with Purolite S-930 and Purolite S-950.

The kinetic data were fitted to the following simplified lineer models using equations given in Section 1.4.6 to facilitate the data analysis.

3.1.7.1 Infinite Solution Volume Models (ISV)

3.1.7.1.1 Particle Diffusion. Manipulating Vermeulen's approximation given by Eqn. (1.14), a simple expression can be obtained:

$$-\ln(1-X^2) = 2kt \qquad \text{where } k = \frac{D_r \pi^2}{r_o^2} \tag{3.1}$$

If the particle diffusion is the rate controlling mechanism, a plot of $-\ln(1-X^2)$ versus time should result in a straight line. The value of diffusion coefficient can be found from the slope. (Descriptions of parameters can be found in Section 1.4.6)

3.1.7.1.2Film Diffusion. If the film diffusion is the rate controlling mechanism, derivation of Eqn. (1.23) results in;

$$\ln(1-X) = k_{li}t \qquad \text{where } k_{li} = \frac{3DC}{r_o \delta \overline{C}} \tag{3.2}$$

3.1.7.2 Unreacted Core Model (UCM)

3.1.7.2.1Film Diffusion. When the fluid is the rate controlling layer, Eqn. (1.27) can be modified to represent the fractional attainment of equilibrium as a function of time.

$$X = \frac{3C_{Ao}K_{MA}}{ar_oC_{so}}t \tag{3.3}$$

In the case of the film diffusion is in control of the ion exchange mechanism, the extent of the resin conversion X, plotted against t should produce a straight line and its slope is given by the expression 3 $C_{Ao}K_{MA}/ar_oC_{so}$.

3.1.7.2.2Reacted Layer Diffusion. If reacted layer diffusion controls the ion exchange process, Eqn. (1.28) can be used to find the mass transfer coefficient

$$\left[3-3(1-X)^{2/3}-2X\right]=\frac{6D_{e,r}C_{Ao}}{ar_o^2C_{so}}t \qquad \textbf{(3.4)}$$

A straight line should be obtained by plotting $\left[3-3(1-X)^{2/3}-2X\right]$ against time, t if reacted layer diffusion controls. The slope is given by the expression $6\overline{D_e}C_{Ao}/ar_o^2C_{so}$.

3.1.7.2.3 Chemical Reaction. By manipulating the Eqn. (1.29) the following equation can be obtained to represent the rate controlling mechanism, in the case of the slowest step is the chemical reaction,

$$\left[1-(1-X)^{1/3}\right]=\frac{k_sC_{Ao}}{r_o} \qquad \textbf{(3.5)}$$

Then, a plot of $\left[1-(1-X)^{1/3}\right]$ versus time should produce a straight line. The slope is given by $C_{Ao}k_s/r_o$.

The summary of the models fitted to experimental results to find the rate control mechanism is given in Table 3.17.

Table 3.17 Diffusional and reaction models (Samuelson, 1963)

Method	**Equation**	**Rate Controlling Step**
ISV	**-ln (1-X)**=kt, where k=Drл^2/r_o^2	Film Diffusion
	-ln (1-X^2) =k_{li}t, where k=3DC/r_oδCr	Particle Diffusion
UCM	**X**=($3C_{Ao}K_{MA}/ar_oC_{So}$)t	Liquid Film
	3-3(1-X)$^{2/3}$-2X = ($6D_{CR}C_{Ao}/ ar_o^2 C_{So}$)t	Reacted Layer
	1-(1-X)$^{1/3}$= (k_sC_{Ao}/ r_o)t	Chemical Reaction

The various functions plotted to determine the kinetic behavior of Purolite S-930 and S-950 are shown Figures 3.34 – 3.43.

Since Purolite S-930 reaches equilibrium after about 60 minutes, the data obtained at contact time later minutes were neglected for film diffusion model described by Unreacted Core Model. In the application of Infinite Solution Volume and Unreacted Core Models contact times after 60 min. were neglected.

Since Purolite S-950 reaches equilibrium after about 30 minutes, the data obtained at contact time later minutes were neglected for film diffusion. In the application of Infinite Solution Volume and Unreacted Core Model contact times after 30 min. were neglected.

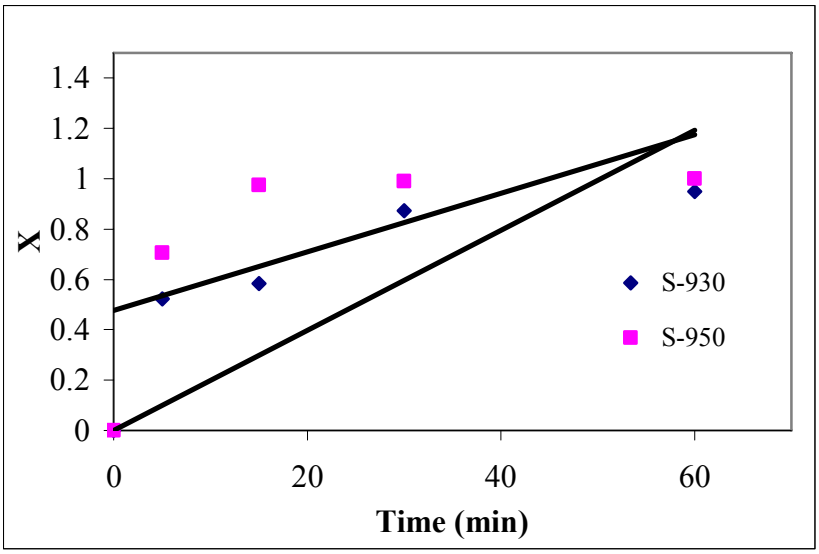

Figure 3.34 Fractional attainment of Ni(II) equilibrium for Purolite S-930 and S-950

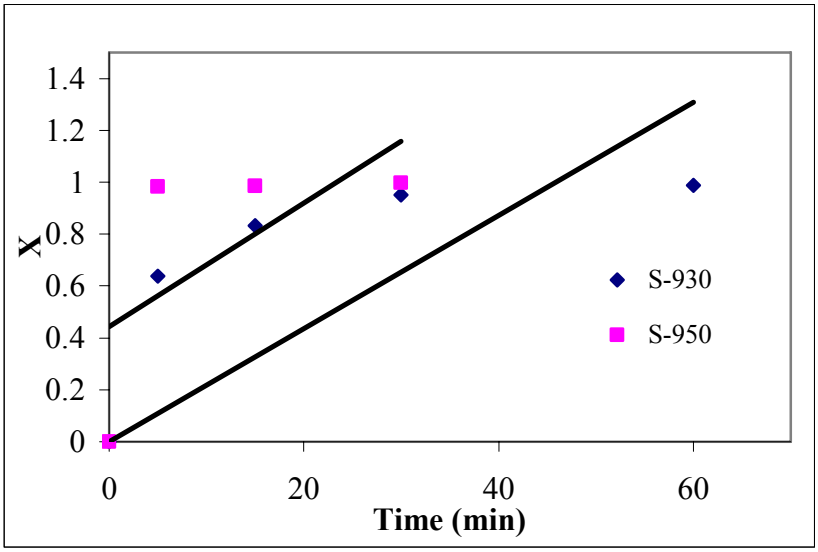

Figure 3.35 Fractional attainment of Co(II) equilibrium for Purolite S-930 and S-950

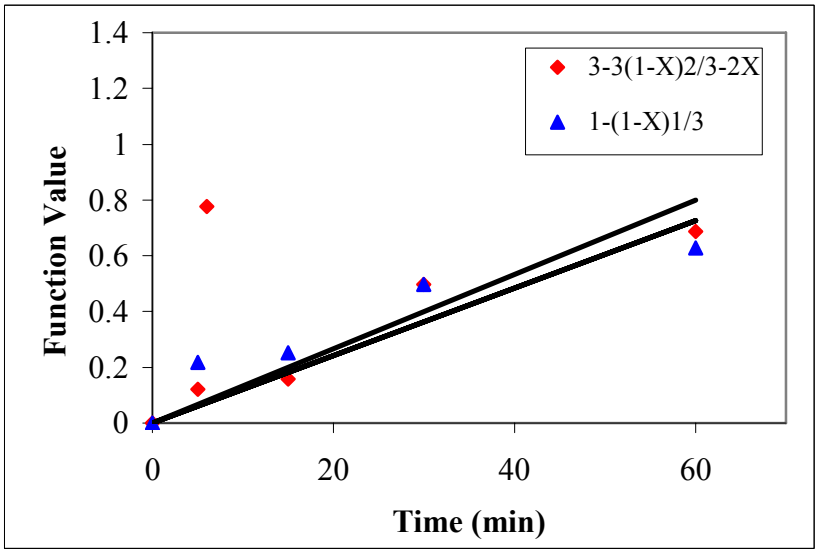

Figure 3.36 Kinetic behavior of Purolite S-930 for Ni(II) based on Infinite Solution Models

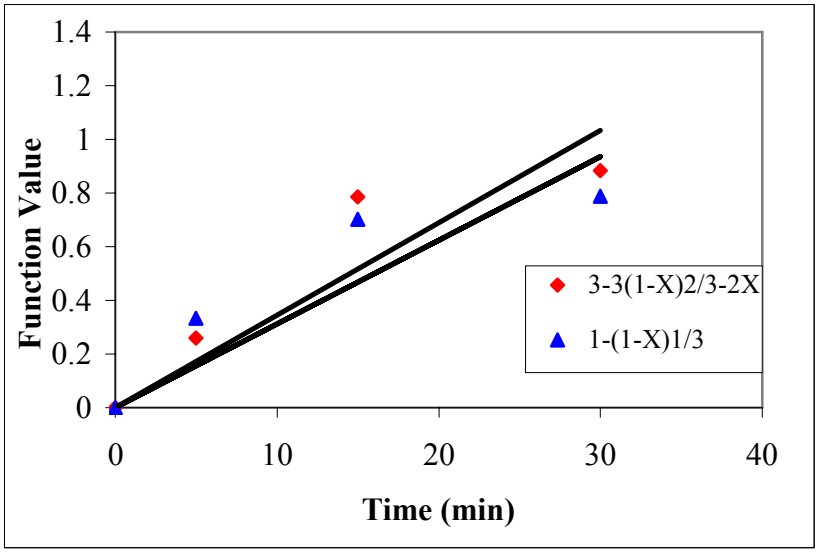

Figure 3.37 Kinetic behavior of Purolite S-950 for Ni(II) based on Infinite Solution Models

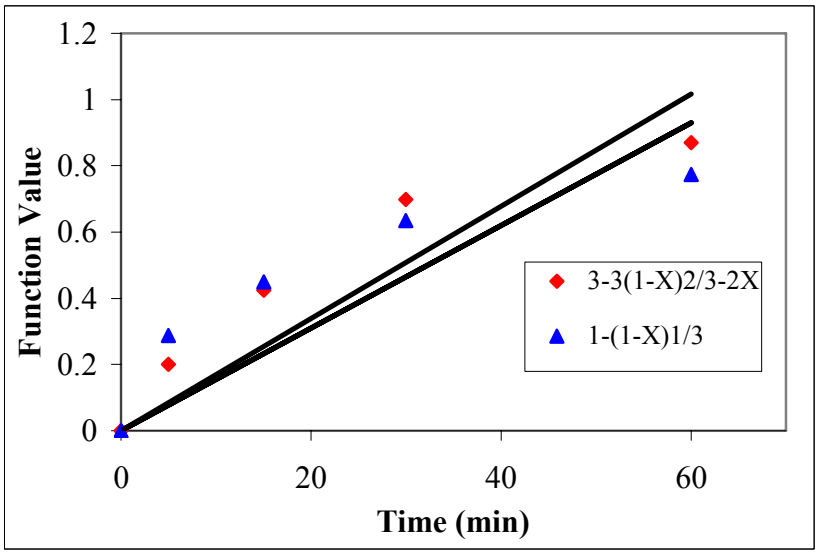

Figure 3.38 Kinetic behavior of Purolite S-930 for Co(II) based on Infinite Solution Models

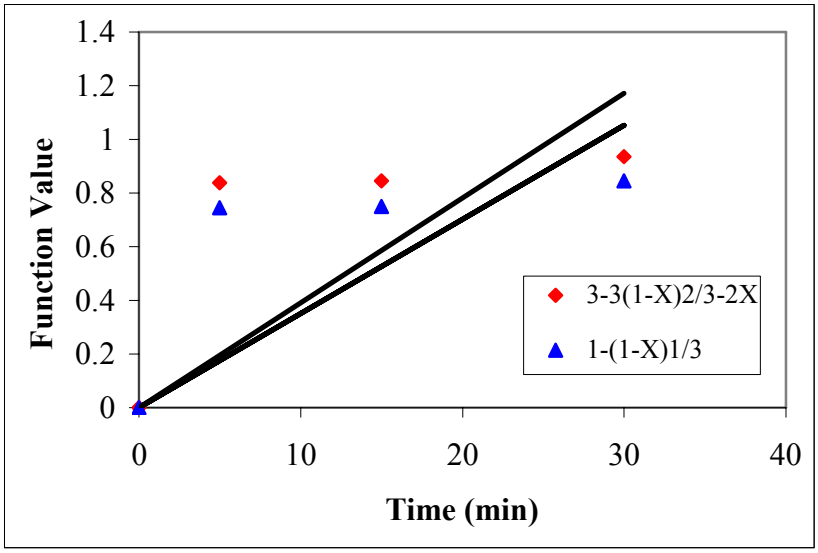

Figure 3.39 Kinetic behavior of Purolite S-950 for Co(II) based on Infinite Solution Models

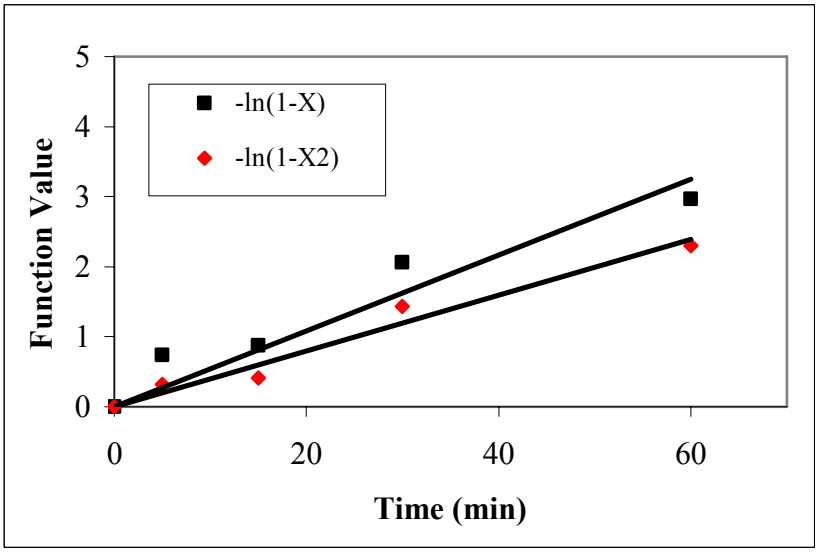

Figure 3.40 Kinetic behavior of Purolite S-930 for Ni(II) based on Unreacted Core Models

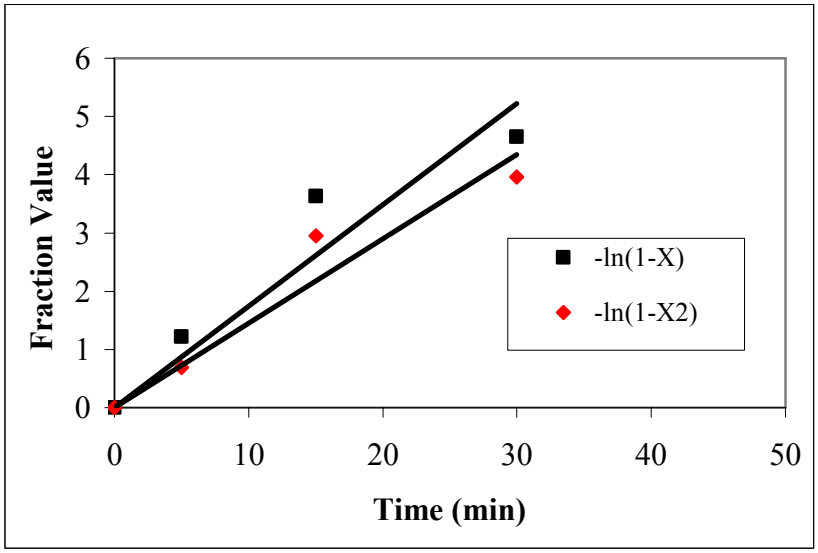

Figure 3.41 Kinetic behavior of Purolite S-950 for Ni(II) based on Unreacted Core Models

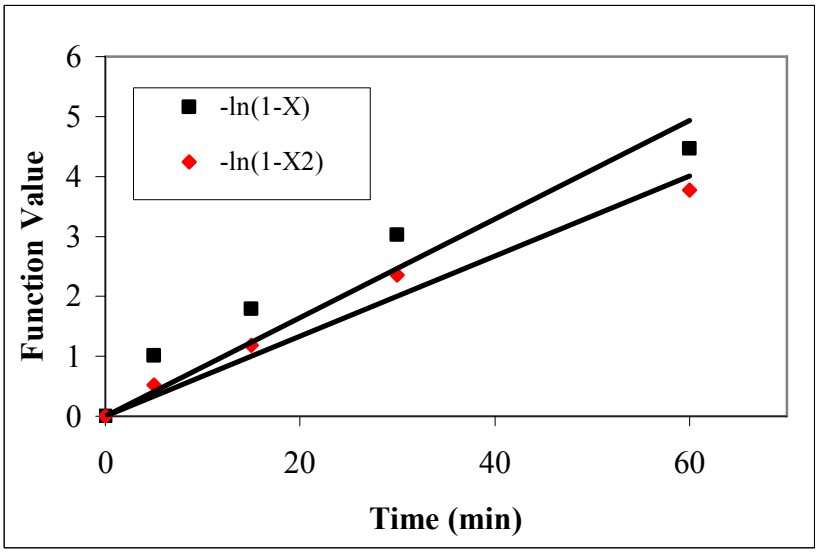

Figure 3.42 Kinetic behavior of Purolite S-930 for Co(II) based on Unreacted Core Models

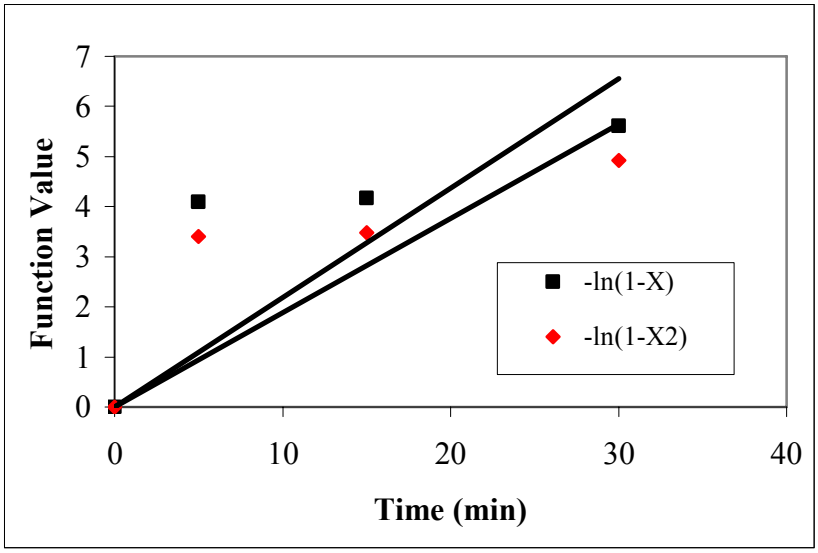

Figure 3.43 Kinetic behavior of Purolite S-950 for Co(II) based on Unreacted Core Models

Table 3.18 gives the slope values and the linear correlation coefficients. As seen in the Table 3.28, the correlation coefficients of the model function $-\ln (1 - X^2)$ for Purolite S-930 and Purolite S-950 show that the particle diffusion control is the rate determining step according to Infinite Solution Volume Model.

Table 3.18 Evaluation of kinetic models for Purolite S-930 and S-950

Model	S-930				S-950			
	Ni(II)		Co(II)		Ni(II)		Co(II)	
	slope	r^2	*slope*	r^2	*slope*	r^2	*slope*	r^2
-ln (1-X)	0.0541	0.9108	0.0822	0.8994	0.1547	0.9164	0.1483	0.6602
-ln (1-X^2)	0.0398	**0.9687**	0.0668	**0.9727**	0.1362	**0.9337**	0.1318	**0.6978**
X*	0.0199	0.2938	0.0218	0.1079	0.0116	0.4304	0.0239	0.4079
3-3(1-X)$^{2/3}$-2X	0.0344	0.8074	0.0169	0.8007	0.0121	0.7635	0.0391	0.0732
1-(1-X)$^{1/3}$	0.0312	0.7235	0.0155	0.6046	0.0133	0.0257	0.0351	0.0997

* The results obtained by using the contact time until 60 min. for Purolite S-930, 30 min. For Purolite S-950.

3.2 Column-mode Ni(II) and Co(II) Sorption Tests

In order to get some information about column performances of chelating resins on removal of nickel and cobalt from aqueous solutions, commercially available chelating resins Purolite S-930 and S-950 were used. In the studies, same

particle size as in batch studies (0.355-0.710 mm) was used with a feed flow rate (SV) of 15 h^{-1} in a glass column (ID: 0.7 cm).

The column studies were done with processed PLS solution at pH 2. Processed PLS contains 4x 10^{-3} M Ni(II) and 2x10^{-4} M Co(II). Loaded resins were eluted with 4 M H_2SO_4 solution at SV 5 h^{-1}. Breakthrough and elution curves of resins are given in Figures 3.44 and 3.45, respectively.

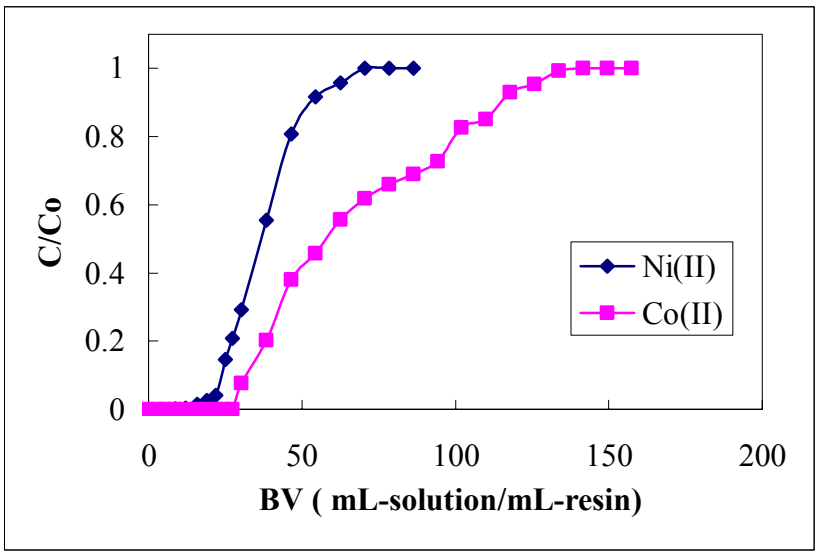

Figure 3.44 Breakthrough curves of Ni(II) and Co(II) obtained by Purolite S-950

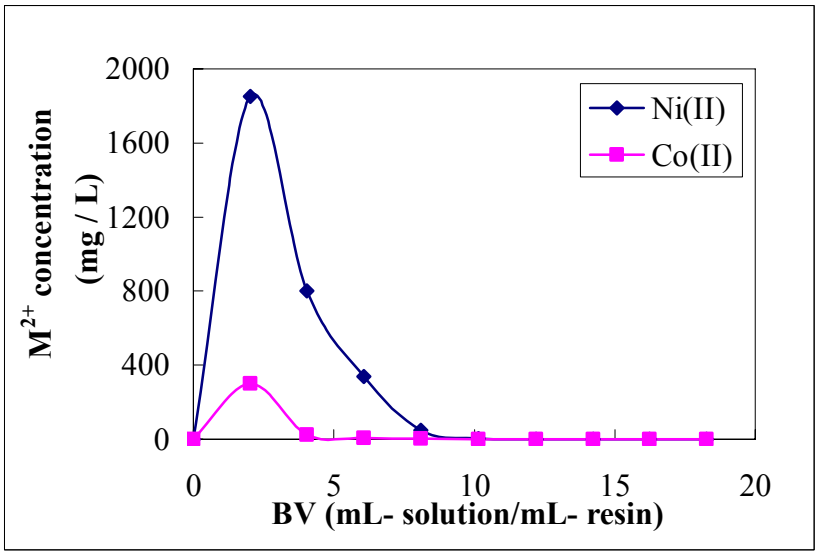

Figure 3.45 Elution curves of Ni(II) and Co(II) obtained for Purolite S-950

In the column-mode sorption studies, breakthrough capacity, total capacity, degree of column utilization of resins were calculated. Breakthrough capacity was

calculated by accepting the breakthrough point as a concentration which is just before than 1 mg Ni (II)/L and 1 mg Co (II)/L. The data obtained for Purolite S-950 are given in Table 3.20. As shown in Table 3.20, Purolite S-950 has a larger breakthrough capacity through Ni(II) than Co(II). Breakthrough capacities of Purolite S-950 are 4.21 mg Ni(II) /g-resin and 0.37 mg Co(II)/g-resin, respectively.

Table 3.20 Column-mode sorption-elution performances of Purolite S-950

	Ni(II)	***Co(II)***
Break. Point (mL)	12.13	38.43
Breakthrough Capacity (mg M^{2+} /mL-resin)	4.21	0.36
Total BV (mL)	86.27	157.40
Total Capacity (mg M^{2+} /mL-resin)	10.53	1.01
Elution Efficiency (%)	84.90	98.01

As seen in Figure 3.44 while Purolite S-950 showed almost ideal breakthrough profile for Ni(II) removal. The plateau concentration of Purolite S-950 remained below the equilibrium concentration. This can be possibly due to the different binding mechanism of Ni(II) and Co(II) to the chelating resin.

CHAPTER FOUR
CONCLUSION

In this study, removal of nickel and cobalt from aqueous solutions was investigated by using commercial chelating resins.

The sorption performances of chelating resins *Purolite S-930* was compared with *Purolite S-950* for Ni(II) and Co(II) removal from aqueous solutions. Both Purolite S-930 and Purolite S-950 were found to be effective for Ni(II) and Co(II) removal from aqueous solutions.

The studies were done to investigate optimum pH range. The optimum pH range was found between 1-2 but in all studies pH:2 was used. Also optimum resin amount was found as 0.5 g-dry resin for both Purolite S-930 and Purolite S-950.

Better Langmuir fits are obtained for the equilibrium data than Freundlich fits for Purolite S-930 and Purolite S-950.

The kinetic studies were performed by both Purolite S-930 and Purolite S-950. More than 50 % of Ni(II) and Co(II) removal was obtained within the first 5 min for Purolite S-930 and Purolite S-950.

The data obtained from kinetic studies were applied to the kinetic models of Infinite Solution Volume and Unreacted Core Models. As a result of this, the rate controlling step was found as particle diffusion for Purolite S-30 and Purolite S-950.

In the studies, original leach solution (PLS) supplied from Bosphorous Madencilik was used. Therefore Fe(III) ions in the solution effected the Ni(II) removal, Fe(III) ions were precipitated by NaOH at pH:4.3. In this pH, maximum Fe(III) and minimum Ni(II) removal were obtained.

The column performance for Purolite S-950 for Ni(II) removal was larger than Co(II) removal from processed PLS.

The selectivity studies were done in the presence of Co(II), Mn(II), Al(III) and Fe(III) ions to investigate the effect of competing ion on column performance. The decrease in removal of Ni(II) for Purolite S-930 was 3.98% and for Purolite S-950 was 0.35% in the presence of competing ions.

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