EFFECT OF pH TO RECOVER Cu(II), Ni(II) AND Co(II) FROM NICKEL LATERITE LEACH USING CHELATING RESINS

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Abstract

Copper, nickel and cobalt can be found in nickel laterite ores. After leaching process of nickel ore, it is necessary a purification step to recover these metals. Chelating ion exchange resins can be applied to purify the liquor generated. The aim of this work was study two different chelating resins to recover these metals by three different synthetic solutions to simulate real conditions. Batch experiments were performed, and effect of pH was studied. First solution was prepared with all metal, and resin Lewatit TP 207 with iminodiacetate functional group was used to recover selectively copper. The second solution, without copper, was prepared and resin Lewatit TP 220 with bis-picolylamine functional group to recover nickel. Then, the last solution was prepared without copper and nickel using Lewatit TP 220 to recovery cobalt selectively. Results shows that, at pH 2.00, it is possible recover selectively copper using TP 207, nickel had higher selectively than cobalt in Solution 2 experiments and cobalt was highly recovered in Solution 3 experiments. These results are important to design industrial process to recover these metals.
Keywords: Hydrometallurgy; Ion exchange; Nickel laterite.

EFEITO DO pH NA RECUPERAÇÃO DE Cu(II), Ni(II) E Co(II) DO LIXIVIADO DE NÍQUEL LATERÍTICO UTILIZANDO RESINAS QUELANTES

Resumo

Cobre, níquel e cobalto podem ser encontrados em minérios lateríticos de níquel. Após o processo de lixiviação do minério de níquel, é necessário uma etapa de purificação para recuperar estes metais. Resinas quelantes trocadoras de íons podem ser utilizadas para purificar o licor gerado. O objetivo deste trabalho foi estudar duas resinas quelantes diferentes para recuperar estes metais a partir de três soluções sintéticas para simular as condições reais. Ensaios em batelada foram realizados e o efeito do pH foi estudado. A primeira solução foi preparada com todos os metais, e a resina Lewatit TP 207 com grupo funcional iminodiacetato foi utilizada para recuperar o cobre seletivamente. A segunda solução, sem cobre, foi preparada e a resina Lewatit TP 220 com grupo funcional bis-picolilamina foi estudada para recuperar níquel. Então, a última solução foi preparada sem cobre e níquel utilizando Lewatit TP 220 para recuperar o cobre seletivamente. Resultados mostraram que, em pH 2,00, foi possível recuperar seletivamente cobre utilizando TP 207, níquel teve maior seletividade do que cobalto nos experimentos com a Solução 2 e cobalto teve alta recuperação em experimentos com a Solução 3. Estes resultados são importantes para projetar um processo industrial.
Palavras-chaves: Hidrometalurgia; Troca iônica; Níquel laterítico.

1 INTRODUCTION

Nickel resources can be found in two types of ores: laterites and sulfides. Laterites ores are found near of surface occurring in tropical climates and represents 70% of ore reserves, but only 40% of the nickel production [1,2]. This is because of processing of laterites ores is more expensive and difficult than sulfides. Despite of this, technologies have been developed to decrease laterite processing costs, once sulfides ores are decreasing [2-5].

Limonite layer is the first layer of nickel laterite, that may contain 0.8-1.5% of nickel, 0.1-0.2% of cobalt

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and 40-50% of iron, further other metals such as copper. Hydrometallurgical process is applied to recover metals from limonite ores. High Pressure Acid Leaching (HPAL) and Atmospheric Acid Leaching (AL) are two hydrometallurgical process that can be used. After leaching process, purification step has to be used [2,6,7]. Ion exchange process may be applied in other to separate *solid-liquid* metals from solution, where cation is adsorbed by functional group of resin [8-10].

Chelating resins is a subgroup of ion exchange resins that are more selective for a metal than others by coordinate bonds interaction, and each resin had its selectivity order due to functional group. These selectivity orders are theoretical, and it can change in solution with presence of different metals in different concentrations [9]. Zainol & Nicol [11] studied five different resins with iminodiacetate functional group to recover nickel and cobalt from laterite leach tailings, and each resin had different results, which may be caused by variations in the structure of the matrix, degree of crosslinking and proportion of iminodiacetate groups [11]. Jiménez Correa et al. [12] studied resin M4195 with bis-picolylamine functional group to recover metals synthetic solution of nickel laterite. The resin had more selective for copper, followed by nickel and iron [13].

The goal of this work was study the effect of pH for copper, nickel and cobalt recovery from nickel laterite leach of limonite layer using two different chelating resins: Lewatit TP 207, with iminodiacetate functional group, and Lewatit TP 220, with bis-picolylamine functional group. Three synthetic solutions were prepared. Solution 1 with all metals that compound nickel laterite leach and using TP 207 to study copper recovery, Solution 2 without copper and using TP 220 to study nickel recovery, and Solution 3 without copper and nickel and using also TP 220 to study cobalt recovery. Time reaction was also studied. Samples were analyzed using ICP-EOS.

2 MATERIALS AND METHODS

2.1 Materials

Composition of synthetics solutions is present in Table 1. The pH was adjusted to 0.50 using sulfuric acid concentrated P.A. to balance the sulfate concentration to simulate the leachate liquor. There were prepared three different solutions. Solution 1 was prepared with all metals that composes the liquor; Solution 2 was prepared without copper; and Solution 3 was prepared without copper and nickel. Therefore, it is possible study effect of other metals presented in leach solution for copper, nickel and cobalt adsorption in three steps.

Two different chelating resins were studied: Lewatit TP 207 and Lewatit TP 220. TP 207 is a cationic resin with iminodiacetate functional group, crosslinked polystyrene macroporous matrix, pH range 0.00 – 14.00 and density 1.17g.mL-1 [14]. The theoretical selectivity order for this resin is: $Fe(III) > Cu(II) > Ni(II) > Zn(II) > Fe(II) > Mn(II) > Mg(II)$ [15]. TP 220 is also a cationic resin, but with bis-picolylamine functional group, crosslinked polystyrene macroporous matrix, density 1.1g.mL^{-1}. The theoretical selectivity order for this resin is $Cu(II) >> Ni(II) > Fe(III) > Co(II) > Mn(II) > K(I) > Ca(II) > Na(I) > Mg(II) > Al(III)$ [16,17].

2.2 Method

The experiments were performed in batch using flasks of 100mL with 50mL of solution and 0.50mL of resin in 150rpm at 25°C. The following time reaction was studied: 0, 30, 60, 120, 240, 360 and 480min at pH 0.50. The effect of pH was studied between 0.50 and 2.00. At pH above 2 there are iron precipitation with copper and cobalt (co-precipitation) for solution with same composition [12], and for this reason high pH values was not studied. The pH was measured using electrode Ag/AgCl (Sensoglass) and samples were analyzed using ICP-OES (Varian 725ES Optical Emission Spectrometer).

Resins were washed using Hydrochloric Acid 6mol.L^{-1} and Sodium Hydroxide 1mol.L^{-1} for three times, and using water deionized between each step. Sulfuric acid 1mol.L^{-1} was used after wash finished. Sulfuric acid concentrated P.A. and Sodium hydroxide pellet was used to correct the pH [9].

In order to quantify cations adsorbed, Equation 1 was used, where q_t is the capacity of ion adsorbed in time *t* in mass of ion per mass of resin (mg.g^{-1}), C_0 e C_t are concentrations of ions in time = 0 and time = t (mg.L^{-1}), v is volume of solution (L) and m is the mass of resin (g) [15,18]. Equation 2 was used to quantify coefficient of distribution of ion, which one is measure of the effectiveness of ion adsorption from solution [9]. Equation 3 was used to quantify of ion was adsorbed, in percentage.

Table 1. Metal's concentrations in Solution 1, Solution 2 and Solution 3 in mg.L^{-1}

Conc. (mg.L^{-1})		Al	Co	Cu	Cr	Fe	Mg	Mn	Ni	Zn
		METALS								
	Sol. 1	4101	78	146	195	18713	7774	387	2434	36
	Sol. 2	4101	78		195	18713	7774	387	2434	36
	Sol. 3	4101	78		195	18713	7774	387		36

$$q_t = \left(C_0 - C_t\right) x \frac{v}{m} \qquad (1)$$

$$Kd = \frac{q_e}{C_t} x 1000 \qquad (2)$$

$$\%S = \frac{\left(C_0 - C_t\right)}{C_0} x 100\% \qquad (3)$$

3 RESULTS AND DISCUSSION

3.1 Reaction Time

Experiments to study reaction time were performed in Solution 1 and Solution 2 at pH 0.50 between 0 and 480min. Figure 1 presents results of Solution 1 using Lewatit TP 207 with iminodiacetate functional group. Iron was the metal highest adsorbed, in mg.g^{-1} of resin, and adsorption reach equilibrium after 120min., as well as other metals Chelating resins with iminodiacetate group has high selectivity for Fe(III), that justify high quantity of this metal adsorbed. Iron adsorption, in 120min, was 151mg.g^{-1}, representing 5.53%. Due to low pH, copper adsorption was low, 9,66%, the highest metal adsorbed in percentage; cobalt and aluminum adsorption was 6.56% and 3.78% after 120min, respectively.

Figure 2 presents results obtained in reaction time experiments in Solution 2, without copper, using resin Lewatit

TP 220. Iron was also in this case highest metal adsorbed in mg.g^{-1} of resin. In 120min, where reaction reach equilibrium, 85mg.g^{-1} of iron was adsorbed, less than study of reaction time in Solution 1 using Lewatit TP 207, which represents 2.84% of metal adsorbed by resin. Cobalt was the metal highest adsorbed, 17.91%, follow by nickel, 5.15%, after 120min. According with results obtained in reaction time experiments, in 120min adsorption reach equilibrium, and effect of pH was studied during 120min of reaction.

3.2 Effect of pH

An example of effect of pH in ion exchange reaction of iminodiacetate functional group can be seen in Figure 3. At pH 2.21 and below, there are high H+ concentration in solution that can repulse cations from surface of resin due to protonation of functional group. At pH 2.00 - 4.00, functional group H+ ions compete with metals in solution for the functional group. At pH 7.41, the carboxylic acids are deprotonated and at pH 12.36 the functional group is totally deprotonated, which can increase metal adsorption efficiency. However, at pH 5.00 metals in general starts precipitates [11,15,19]. For this reason, working pH is dependent of solution composition.

For solutions worked, the limit of work is pH 2.00 due to iron precipitation and co-precipitation of cobalt and copper 17. In Solution 1 (Figure 4) it is possible see that copper adsorption increase while pH also increases.
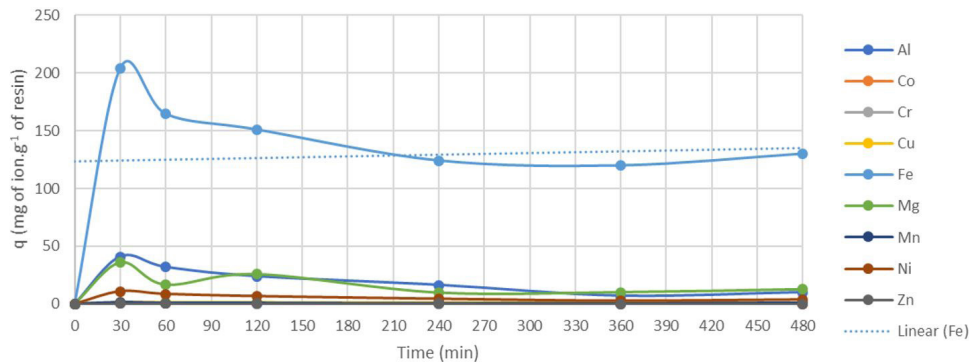

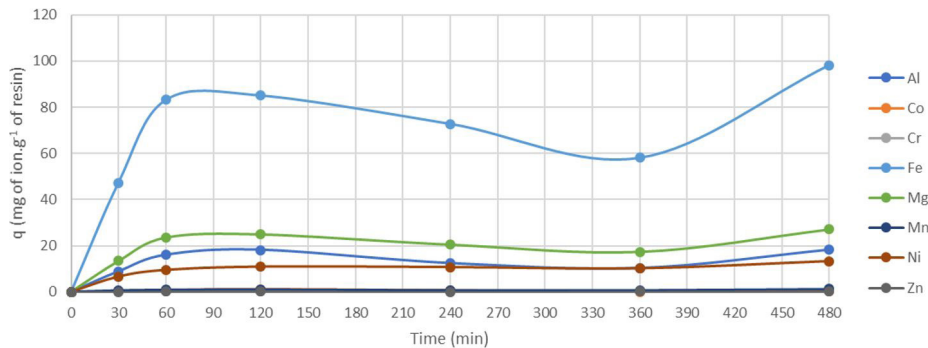**Figure 1.** Results of reaction time of Solution 1 using resin Lewatit TP 207.

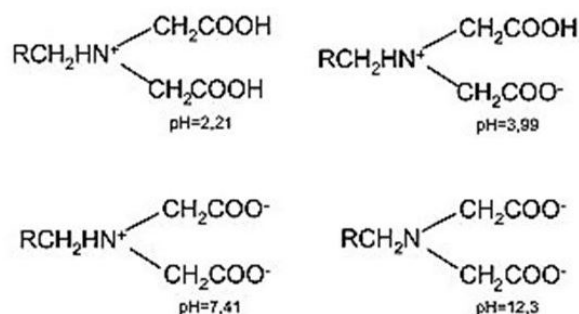**Figure 2.** Results of reaction time of Solution 2 using resin Lewatit TP 220.

Figure 3. Effect of pH in iminodiacetate functional group [19].
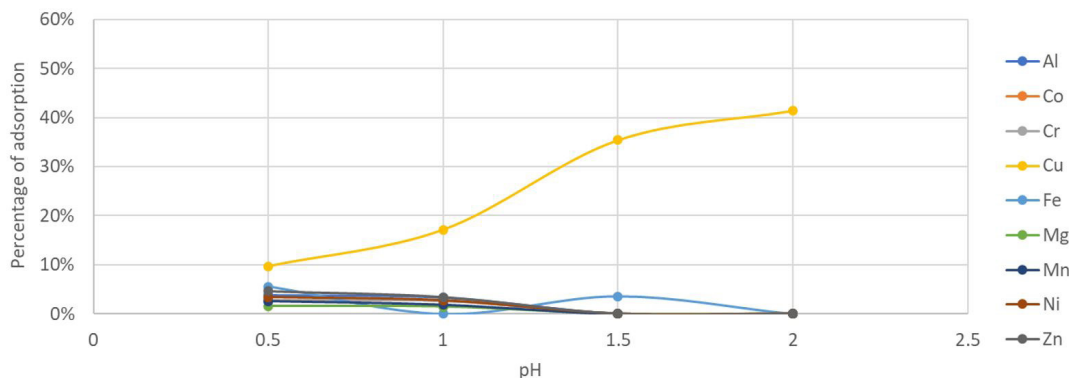

Figure 4. Effect of pH in Solution 1 by iminodiacetate resin.

At pH 0.50, copper adsorption was 9.66%, 17.12% at pH 1.00 and 35.42% at pH 1.50. At pH 2.00, copper adsorption was maximum (41.43%). In all pH values, the resin was more selectivity for copper than other metals.

In Solution 2, without copper, nickel adsorption increases also while pH increases (Figure 5). At pH 0.50, cobalt was highly adsorbed than other metals (17.81%). At pH 1.00, the resin with bis-picolylamine functional group was more selective for nickel (12.64%), 19.06% at pH 1.50 and 20.04% at pH 2.00. Cobalt was the second metal highly remove by resin, 5.88%, 12.50% and 16.44% at pH 1.00, 1.50 and 2.00, respectively. The selectivity order of resin Lewatit TP 220 is Ni(II) > Co(II), which may change depending on the pH value, how it was verified at pH 0.50 which the resin was more selective for cobalt than nickel. Littlejohn and Vaughan [20] studied difference between TP 207 and TP 220 for nickel laterite leach solution, and according to the authors resins with iminodiacetate group has more selective for iron, aluminum, manganese and magnesium than nickel and cobalt, while resins with bis-picolylamine functional group was more selective for nickel and cobalt than others metals [20]. According to Mendes and Martins [21], resin with bis-picolylamine functional group is the best choice for nickel and cobalt recovery [21]. Copper adsorption is higher using TP 207 [14].

The effect of pH for Solution 3 by bis-picolylamine resin is shows in Figure 6. At pH 1.00, 1.50 and 2.00 resin were highly selective for cobalt (10.45%, 31.94% and

35.21%, respectively). At pH 2.00, zinc was the second metal highest selectivity by resin (21.92%). Figure 7 shows the comparison of distribution coefficient (Kd) between copper, nickel and cobalt in each solution studied. Lewatit TP 207 with iminodiacetate functional group had high selective for copper, how shows in Figure 7 with copper distribution coefficient 120.00mL.g^{-1} at pH 2.00.

Hubicki et al. [22] studied metals adsorption using TP 207, and resin had high selectivity for copper followed by cobalt, nickel and zinc in all pH values studied [22], which it is not observed in these experiments, were at pH 1.50 and 2.00 nickel, cobalt and zinc weren't adsorbed, while at pH 0.50 and 1.00 metals adsorption were around 5.00%. Kuz'Min and Kuz'Min [23] studied resin Purolite S930 with iminodiacetate functional group for copper and nickel removal from leach pulps of low-grade sulfide ore, and resin was more selectivity for copper than nickel [23], that was observed in experiments performed using Solution 1. Littlejohn and Vaughan [16] worked with resin Lewatit TP 220 to recover nickel and cobalt from laterite leach tailings, and in every case studied nickel recovery was greater than 95% and cobalt was greater than 80% [12], that is possible by column experiments.

In Solution 2, due to nickel and cobalt were highly adsorbed by resin, how it is possible see in distribution coefficient (21.60mL.g^{-1} and 17.00mL.g^{-1}), nickel adsorption was lower than cobalt adsorption in Solution 3 (47.67mL.g^{-1}), besides of resin TP 220 selectively order.
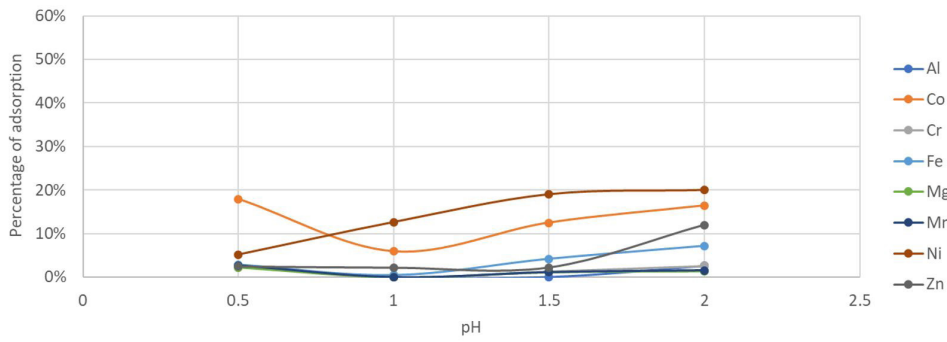
Figure 5. Effect of pH in Solution 2 by bis-picolylamine resin.
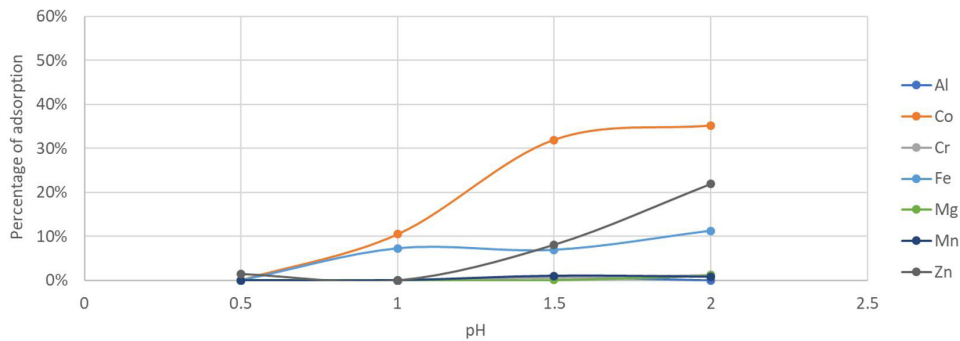

Figure 6. Effect of pH in Solution 3 by bis-picolylamine resin.
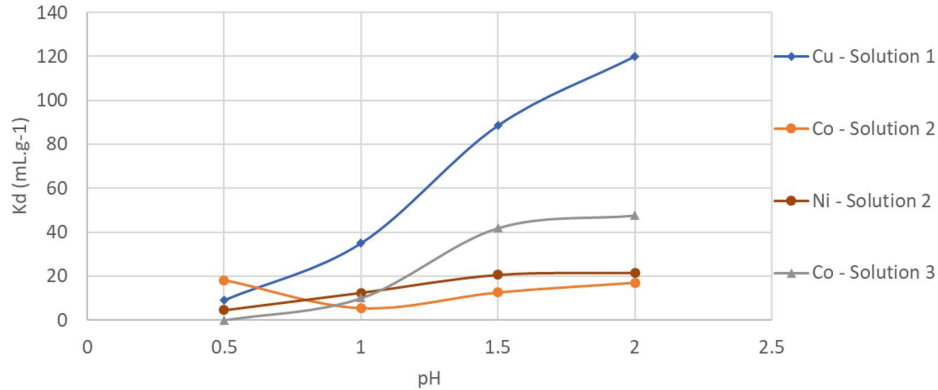

Figure 7. Distribution coefficient Kd in Solution 1 by iminodiacetate resin and Solution 2 and Solution 3 by bis-picolylamine resin.

4 CONCLUSION

The goal of this work was to study the effect of pH to recovery copper, nickel and cobalt using chelating resins Lewatit TP 207, selective for copper, and Lewatit TP 220, selective for nickel and cobalt. Results shows that TP 207 was high selective for copper in Solution 1, and TP 220 was high selective for nickel, followed by cobalt, in Solution 2 and high selective for cobalt in Solution 3. Experiments performed using Solution 2 indicated that selective order of TP 220 resin changed when pH value increased. At pH 0.50 the resin was more selective for cobalt, and at pH 1.00 the resin was more selective for nickel, indicating that pH has influence not only in percentage of metal recover, but also in chelating resin selective.

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