Original Article

Recovery of metals by ion exchange process using chelating resin and sodium dithionite

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ABSTRACT

Chelating ion exchange resins can be used to recover metals from nickel laterite leach solution. The main problem is the high presence of iron. In pH above 2.00, iron precipitates and there is co-precipitation of copper and cobalt, which decreases recovery process efficiency. To solve this problem, a conversion of Fe(III) to Fe(II) can be the solution, where Fe(II) will precipitate just at pH 5.00. This reducing process can also increase metals recovery, where ferrous iron occupies less active sites on the resin than ferric iron. However, studies do not evaluate what happens to the resin under this situation. This work aimed to study the copper, nickel and cobalt recovery using chelating ion exchange resin Lewatit TP 207 and reducing process using sodium dithionite $1\,mol.L^{-1}$. Sodium dithionite was used to convert Fe(III) to Fe(II). The effect of reducing agent on the resin was studied. Three different solutions where prepared to simulate the real nickel laterite leach solution. Batch experiments were performed to study the effect of pH to recover metals and to compare the results with and without the reducing agent. Results showed that metals adsorption increased when the ferric iron was converted to ferrous iron by reducing process. Chelating resin adsorbed more copper and also was selective for this metal at pH 2.50. Nickel and cobalt adsorption were higher at pH 3.50, but the resin was not selective for these metals under this pH. The order of selectivity of chelating resin changed when pH increased.

1. Introduction

There are two mainly nickel resources: sulfides or laterites ores. Laterites represent 70% of nickel reserves, but only 40% of nickel production. It occurs due to the fact that laterites ores require more complex processing than sulfides [1–3]. Despite that, in 2022 nickel production might be 70% from laterite ores. These ores are divided into three different layers, where limonite layer occurs near of surface. There are different elements in its compositions, such as copper, cobalt and iron. These layer has the highest iron concentration among all laterite layers (40–50%) [4–6]. Among processes can be used to extract valuable metals from laterite ores, High Pressure Acid

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Leach (HPAL) and Atmospheric Acid Leach (AAL) using sulfuric acid can be cited as an example of hydrometallurgical process [1,4,7].

After leaching process, a separation and purification technique is necessary for metals recovery. Ion exchange resins can be used in this step. An ion exchange reaction with cationic resins may be defined as the reversible inter-change between cation in a solution phase and cation in the resin. Equation 1 details this reaction. Resins with short hydrocarbon bridges cross-linked insoluble *polyions* supplied as spherical beads represents the major class of exchange being commercially produced [8–10]. Each resin has a functional group or sites that provides specific features [10,11].

$$\overline{RA} + BC \Leftrightarrow \overline{RB} + AC \tag{1}$$

[8]

Chelating ion exchangers are a subgroup of ion exchange resins. These resins are coordination compounds that may establish selective covalent-like bonds between the central ion of the functional group of them and donor ions in solution, usually ions of transitional metals. The functional group are composed by atoms like nitrogen, sulfur and oxygen. These atoms are able to donate electron pairs [10]. There are different functional groups available for specific applications, as well as to recover metals from nickel laterite ores [11]. Iminodiacetate resins are chelating resins with functional groups that contains two carboxylic groups and one nitrogen as central atom [10,12].

Fig. 1 shows an example of iminodiacetate group forming a strong chelating complexes with a copper ion (Cu^{+2}). Chelating complexes are strongly associate with pH, that H^+ ions are deprotonated from functional group when pH increase [11,13]. In metals recovery by ion exchange resins, the process efficiency increases when the pH increases. It occurs, because H^+ competes with metallic ions for the functional group, and decreasing H^+ concentration (increasing the pH) decreases this competition [13,14].

The main problem to recover metals from nickel laterite leach solution is the presence in high concentration of iron (55% wt). Iron precipitates in pH above 2.00, with copper and cobalt (co-precipitation). Jimenez Correa et al. (2016) studied the iron removal from nickel laterite leach solution. Two different solutions where prepared, the first with ferric iron and the second with ferrous iron. Results showed that, for solution prepared with ferric iron, the co-precipitation of copper and cobalt starts at pH 2.00 with iron precipitation. All iron precipitates at pH 3.00, and 20% of copper and 60% of cobalt. Experiments performed using solution with ferrous iron showed that iron precipitation began at pH 4.50 (5%), and copper precipitation began at pH 4.00 (20%) [15]. Moreover, metals recovery by chelating resins with ferrous iron are higher than solution with ferric iron [16].

The aim of this work was to study the recovery of copper, nickel and cobalt from synthetic solution of nickel laterite leach by the chelating resin Lewatit TP 207. Sodium dithionite was used to convert ferric iron to ferrous iron. The effect of reducing agent on the resin was studied during the experiment. The chelating resin has iminodiacetate as functional group. The metals adsorption was studied using two different solutions: with and without the sodium dithionite. The effect of pH on metals adsorption was studied from 0.50 to 3.50. The effect of temperature was studied from 25 °C to 60 °C. Samples were analyzed using Energy-dispersive X-ray spectroscopy (EDX).

2.　Materials and methods

Solutions were prepared to simulate the real nickel laterite leach. Table 1 presents the metals concentration in the three solutions studies. Solutions were prepared dissolving sulfate salts of each metal. The pH was corrected to pH 0.50 using sulfuric acid concentrated, as the same as real solution. Solution 1 shows the concentration of solution after leaching step of nickel laterite, to study the copper recovery by the chelating resin; Solution 2 was prepared to study the nickel recovery; and Solution 3 was prepared to study the cobalt recovery. Chelating resin used in this study was the Lewatit TP 207. This resin is a cationic chelating resin with functional group iminodiacetate, microporous resin with matrix crosslinked polystyrene, pH range 0–14 and density of 1.17 $g.mL^{-1}$. The effect of pH was studied between 0.50 and 2.50. The effect of temperature was studied from 25 °C to 60 °C.

Batch experiments were performed using Erlenmeyer flasks 250 mL with 100 mL of solution and 1 mL of resin (1.17 g) in shaker orbital at 200 rpm and 25 °C during 180 min [17]. Sodium dithionite 1 $mol.L^{-1}$ was prepared to convert Fe(III) to Fe(II) reducing the potential [18–20]. The reducing process were performed before the contact with the resin. Sodium dithionite was added to the solution to reduce the redox potential. Then, the mix was placed in Erlenmeyer, where it was stirred at 200 rpm and 25 °C during 180 min. In pH 0.50–2.00, the redox potential was decreased until 590 mV (Standard Hydrogen Electrode - *SHE*). In pH 2.50–3.50, the redox potential was decreased until 240 mV (*SHE*) [19].

Equations below were used to quantify the metals adsorbed by the resin. Equation 2 was used for determination of metal quantity adsorbed, where q_t is capacity of resin at equilibrium in mass of metal ion per mass of resin ($mg.g^{-1}$), C_0 e C_t are ion concentration at time 0 and time t ($mg.L^{-1}$), v is volume of solution (L) and m is mass of resin (g) [13,16,21]. Equation 3 was used to quantify the percentage of ion adsorbed by the chelating resin. Equation 4 was used to quantify the distribution coefficient, a measure of the effectiveness of the ion exchange resins to remove particular metal ion from solution [8].

$$q_t = (C_0 - C_t) . \frac{v}{m} \tag{2}$$

$$\%S = \frac{(C_0 - C_t)}{C_0} . 100\% \tag{3}$$

$$Kd = \frac{q_t}{C_t} \tag{4}$$

The measure of pH was performed using electrode Ag/AgCl (Sensoglass) and potential was measured using electrode redox, adding 240 mV to compare with Standard Hydrogen
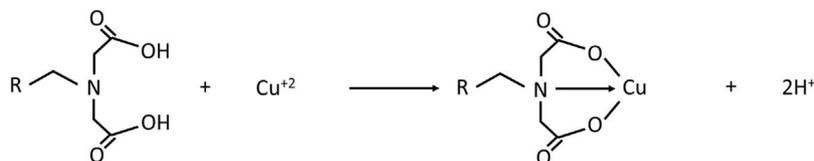
Fig. 1 – An example of iminodiacetate group which form a strong chelating complexes with a copper ion – Cu^{+2} [10].

Table 1 – Metals concentration in synthetic solutions of nickel laterite leach solution (mg.L^{-1}).

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

Electrode (*SHE*) [22,23]. The samples were analyzed using Energy-dispersive X-ray spectroscopy (EDX).

3. Results

The first part of the experiments was to study the copper recovery. Experiments were performed at 25 °C during 120 min and stirring speed 200 rpm. Fig. 2 shows the effect of percentage on copper recovery by the chelating resin with and without reducing process of Solution 1. Experiments in pH above 2.00 in solution without reducing process were not performed due to the iron precipitation and co-precipitation of copper. Copper recovery was higher in solution with sodium dithionite. The difference among these solutions is that, without sodium dithionite there are ferric iron in solution, while in solution with sodium dithionite ferric iron was converted to ferrous iron. The theoretical order of selectivity of Lewatit TP 207 is Fe(III) > Cu > Ni > Zn > Fe(II) > Mn > Mg, which indicate that the resin is more selective for copper than ferrous iron, but it is more selective for ferric iron than copper. Copper recovery increased also because ferrous iron occupies less active sites than ferric iron.

The effect of pH on capacity of resin in Solution 1 after reducing process are shown in Fig. 3. Between pH 0.50–2.50, the resin had more selective for copper than other metals. At
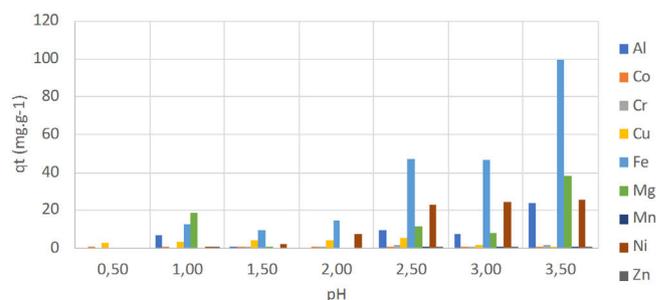

Fig. 3 – The effect of pH on capacity of resin at equilibrium by the resin Lewatit TP 207 at 25 °C.

pH 2.50, the chelating resin had the highest copper adsorption −71.18%. However, in pH above 2.50, the chelating resin had its selective changed and copper adsorption decreased. At pH 3.00, the resin was selective for copper, nickel and zinc where its recovery were 19.55%, 21.91% and 24.04%, respectively. At pH 3.50 the recovery of these metals were 8.95%, 25.20% and 21.25%, respectively. Copper recovery without sodium dithionite was higher at pH 2.00 (48.72%), as showed in Fig. 2.

In pH between 0.50 and 2.00, copper recovery was higher in solution with ferric iron converted to ferrous iron. At pH 2.50 all metals adsorption, including iron, increased in solution with sodium dithionite. These results indicated that, the
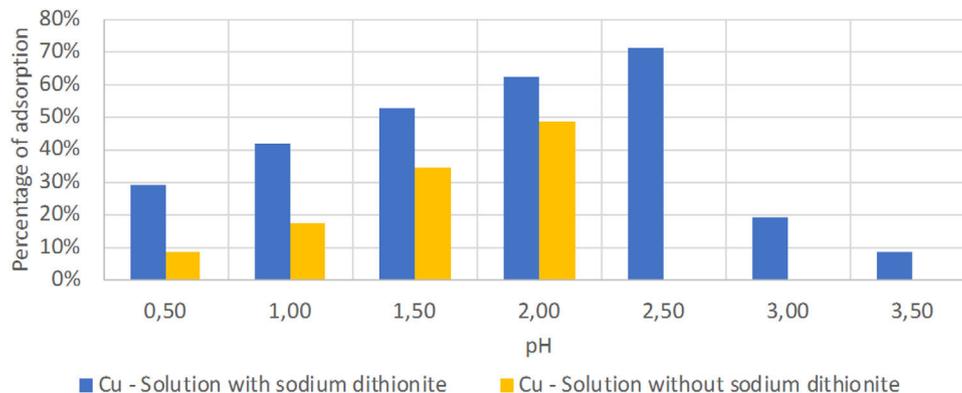

Fig. 2 – Effect of pH on copper recovery with and without reducing process by the resin Lewatit TP 207 at 25 °C during 180 min.
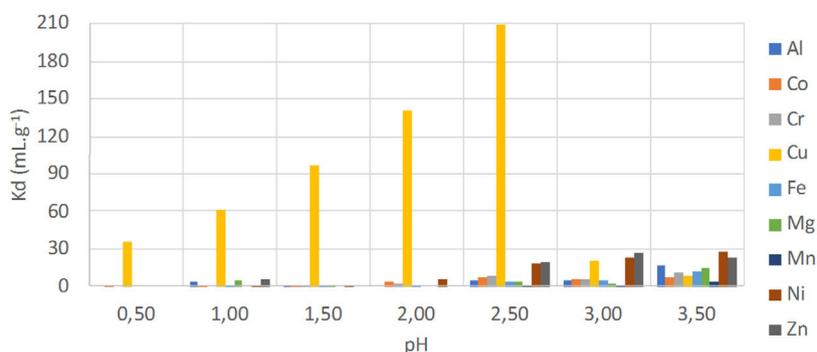
Fig. 4 – Distribution coefficient Kd of the metals by resin with iminodiacetate group Lewatit TP 207 at 25 °C.

selectivity of copper by the resin increased until pH 2.50. The use of reducing agent do not affect the chelating resin during the experiments.

Fig. 4 shows the distribution coefficient (Kd). At pH 2.50 copper had the highest Kd (210 mg.g^{-1}), which decreased substantially at pH 3.00 and 3.50 (20 mg.g^{-1} and 8 mg.g^{-1}, respectively). The decrease of distribution coefficient corroborates with results present in Fig. 3. Botelho Junior et al. (2018) studied the use of sodium sulfite as reducing agent to recover metals from sulfuric solution of nickel laterite. Results were similar, where the order of selectivity changed when the pH increased [24]. An explanation that can be given is that, when the pH increased the functional group of the chelating resin is deprotonated and the concentration of H$^+$ in solution decreased. Therefore, metals adsorption increase, but the order of selectivity is changed. There are few papers in the literature about it [24–26].

Copper recovery at pH 2.50 is possible only with reducing process using sodium dithionite, as discussed before [15]. The effect of temperature was studied between 25 and 60 °C. Results are present in Fig. 5 for cobalt, nickel, iron and copper recovery. Copper adsorption increased by the increase of temperature, from 62.39% at 25 °C to 68.70% at 60 °C. Iron adsorption slightly decrease by the effect of increasing the temperature. Cobalt adsorption increased from 25 °C to 35 °C, but decreased at 45 °C and 60 °C. Nickel adsorption was favored by the increase of temperature, from 6.37% at 25 °C to 13.06% at 60 °C. These results indicated that nickel and copper adsorp-

Fig. 6 – Effect of pH to recover nickel in Solution 2 by the resin Lewatit TP 207 at 25 °C during 180 min.

tion by Lewatit TP 207 are endothermic, while iron and cobalt are exothermic.

The study of nickel adsorption was performed using Solution 2 (Table 1). Fig. 6 shows the metals adsorption between pH 0.50 and 3.50 and using sodium dithionite to reduce the redox potential. At pH 2.00, Lewatit TP 207 was more selective for magnesium (8.42%), but it changed at pH 2.50, where the resin became more selective for nickel (13.65%). The selective changed again in pH 3.00 and pH 3.50.

At pH 3.50, nickel adsorption was higher (18.72%), while the chelating resin was more selectively for zinc (24.39%). However, in a continuum process and due to the low concentration of zinc in solution (36 mg.L^{-1}), it is expected that both metals will be recovered by the resin. Results obtained without sodium dithionite for Solution 2, at pH 2.00 the resin was more selective for zinc (7.69%), while the nickel recovery was 3.79%.

Fig. 7 shows the results of metals adsorption in Solution 3 with sodium dithionite by the resin. The effect of pH for cobalt recovery is present. At pH 2.00, cobalt adsorption was 4.95%. The chelating resin was more selective for cobalt at pH 3.00 (4.63%), but the order of selectivity changed. At pH 3.50, the chelating resin was more selective for chromium (17.36%) than cobalt (13.02%). For Solution 3 without sodium dithionite, cobalt recovery was maximum at pH 2.00–4.63%. Iron and manganese adsorption were 4.59% and 4.44%, respectively, at the same pH.
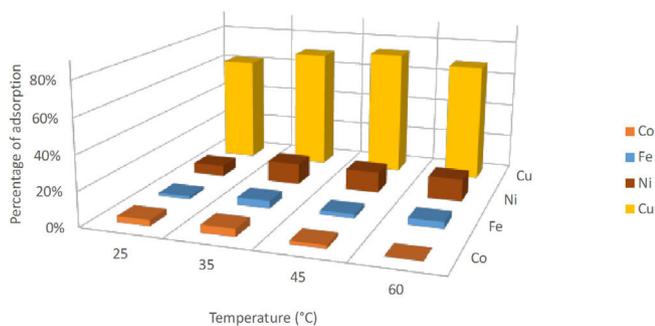

Fig. 5 – Effect of temperature for copper, nickel, cobalt and iron adsorption after reducing process in Solution 1 at pH 2.00 during 180 min and stirring speed 200 rpm.
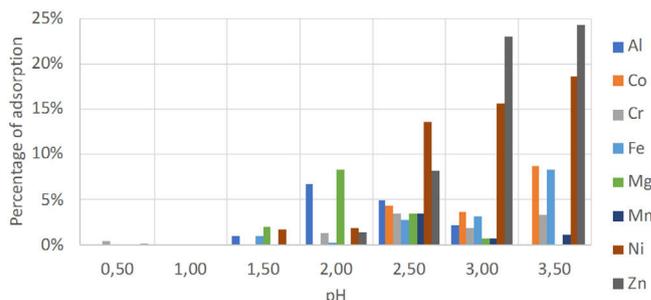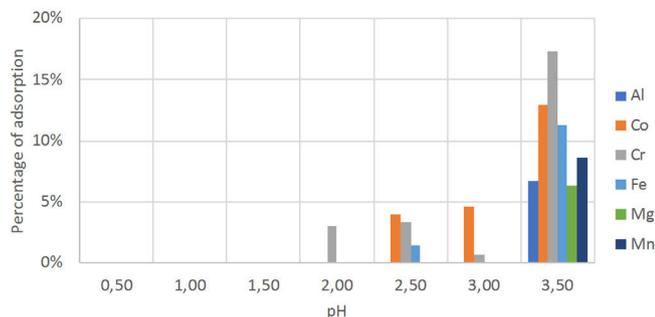
Fig. 7 – Effect of pH to recover cobalt in Solution 3 by the resin Lewatit TP 207 at 25 °C during 180 min.

4. Discussion

Results presented showed that the resin selectivity changed when the pH is changed. Chelating resin was more selective for copper in Solution 1 between pH 0.50 and 2.50 among all metals. At pH 3.00, the chelating resin was more selective for zinc, and at pH 3.50 it was more selective for nickel. Same changed on selective order was observed nickel (Solution 2) and cobalt (Solution 3) recovery experiments. These change in the order of selectivity is not discussed due to the fact that the solutions used on the experiments were multi-elementary. Studies comparing the adsorption of nine different metals at same time are rare [27–29]. The functional group of the chelating resin Lewatit TP 207 has been deprotonated when the pH increases. Chelating resins with iminodiacetate functional group, as well as Lewatit TP 207, until pH 2.21 the functional group is totally protonated. After that, the functional group is being deprotonated as the pH increases (Fig. 3). Thereby, metals adsorption increases and made the chelating resin less selective for a specific metal.

Results also showed that Lewatit TP 207 is a specific chelating resin for copper recovery. At pH 2.50 and reducing process, copper adsorption was 71.18%. Nickel (Solution 2) and cobalt (Solution 3) adsorption at pH 3.50 were 18.72% and 13.02%, respectively. Littlejohn and Vaughan (2012) studied metals recovery using chelating resins with iminodiacetate and bis-picolylamine. Iminodiacetate resins were suitable for copper recovery, and bis-picolylamine resins were suitable for nickel and cobalt recovery [30].

Botelho Junior et al. (2018) compared two different chelating resins for cobalt recovery: Lewatit TP 207 and Lewatit 220 (with bis-picolylamine functional group), and results showed that TP 220 was better for cobalt recovery (35% at pH 2.00) than TP 207 (5% at pH 2.00) [31]. Present results complement what is find in the literature. The sodium dithionite, during the experiments, just increase metals recovery, and do not affect the resin's structure.

5. Conclusions

The goal of this was to study the metals recovery using chelating resin Lewatit TP 207 and reducing process using sodium dithionite 1 mol.L^{-1}. The effect of reducing agent on the resin was studied. Three different solutions were studied, each one

suitable for copper, nickel and cobalt recovery. Results showed that maximum copper recovery was at pH 2.50, while nickel and cobalt recovery was at pH 3.50. Zinc and chromium can be recovered with nickel and cobalt, respectively. It is important to note that the resin presented different order of selectivity among pH values studied. In Solution 1 at pH 2.50 the resin was more selectively for copper, while at pH 3.00 resin was more selectively for zinc, nickel and cobalt, and at pH 3.50 for nickel. These results are rarely found on the literature. The reducing agent do not affect the ion exchange resin to adsorb metals.

Conflict of interest

The authors declare no conflicts of interest.

Acknowledgments

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