Recovery of copper and nickel from polymetallic sulphate leach solution of printed circuit boards using Dowex M 4195

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Abstract: Sulphuric acid leach solution of waste printed circuit boards (PCBs) contains predominantly copper and iron with later remain problematic during electrowinning of the formal. In this study, performance of Dowex M 4195 resin for recovery of copper and nickel from polymetallic sulphate leach solution of waste PCBs was investigated by batch experiments. It was observed that at pH 0.5, about 45.2 % Cu$^{2+}$ and 3.6 % Ni$^{2+}$ was selectively recovered respectively. Recovery efficiency of Ni$^{2+}$ increased with increase in pH from 0.5 - 5.0 while pH2 was optimum for the recovery of Cu$^{2+}$. Sharp increase in co-recovery of Fe$^{3+}$/Fe$^{2+}$ was observed at pH above 2 with that of Zn$^{2+}$ and Co$^{2+}$ became low due to hindrance from binding site by high concentration of Cu$^{2+}$. Adsorption data obtained for Cu$^{2+}$ and Ni$^{2+}$ were tested with adsorption isotherms as well as kinetics. It is shown that adsorption of Cu$^{2+}$ and Ni$^{2+}$ was well fitted to both Langmuir and Freundlich isotherm. Kinetics of Cu$^{2+}$ and Ni$^{2+}$ fitted into Pseudo-first and well fitted to second order. Reuse studies shows that the resin strong affinities for Cu$^{2+}$ and Ni$^{2+}$ remain unchanged.

Keywords: recovery, copper, nickel, Dowex M4195, kinetics, isotherms, reuse

1. Introduction

Demand for minerals and metals are increasing most especially in electronic products manufacturing with recycling offers great economic and environmentally benefits than primary ore sources. However, waste from these electronic products have been reported to contains precious metals including gold, silver, copper, platinum and palladium, but it also contains valuable bulky materials like iron, and aluminium, along with plastics that can be recycled (Balde et al., 2017). Recently, safe recycling of economic metals from these waste electrical electronic equipments (WEEE) has been sought after. The state of art in recovery of precious metals from WEEE highlights two major recycling techniques, such as pyrometallurgy and hydrometallurgy (Hoffmann, 1992; Sum, 1991; Lee et al., 2007). For safety and purity purposes attention has been shifted from pyrometallurgical to hydrometallurgical process for recovery of metals from electronic waste (Cui and Zhang, 2008; Quinet, et al., 2005). Acidic leach solution of PCBs contains largely copper and Iron with latter known to be problematic during electrowinning (Oishi et al., 2007; Das et al., 1996). Therefore, purification of the solution is required. Solvent extraction and precipitation are mostly used for metal separation and purification from leach liquor before electro winning, also reverse osmosis and membrane processes have been attempted (Joulie et al., 2014). As is known, conventional chemical precipitation processes have many limitations and it is difficult to meet the increasingly stringent environmental regulations by application of conventional precipitation processes This approach generate solids that are difficult to dispose because of heavy metals contained therein, also there is a significant cost associated with necessary pH control (Diniz et al., 2005).

In this research, our focus is on Ion-exchange resin since it provides more effective recovery/purification as compared to precipitation or solvent extraction, which are the most commonly

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method at present for these purpose (Leinonen et al., 1994; Kononova et al., 2000; Kholmogorov et al., 1997). In addition, uses of resins are beneficial to reagent loss, filtration and poor metals selectivity efficiency and other setback associated with solvent extraction process (Mendes and Martins, 2005). Of recent, many articles have considered recovery, selective sorption, and removal of metals from synthetic solutions using resins (Alyiiz et al., 2009; Edebali and Pehlivan, 2016; Rengaraj et al., 2003). However, information on recovery of metals by ion exchange resin from leach solutions contain many metals is scarce. To the best of our knowledge, uses of resin for recovery of metals from sulphate leach solution of (WPCBs) has not been reported and thus, was found suitable for this study. Therefore, in this paper Dowex M 4195 chelating resin was investigated for the recovery of copper, nickel, as well as co recovery of other metals impurities from sulphate leach solution of waste PCBs. The study also includes adsorption isotherms, kinetics, regeneration and reusability of the resin.

2. Material and methods

2.1. Material

Dowex M4195 chelating resin, sodium form was purchased from Supelco-Sigma Aldrich, USA. Bis(2-pyridylimethyl)amine (bpa) is an uncharged tridentate ligand having the ability to form charged complexes with most divalent metals (Hirayama and Umehara, 1996). Prior to uses, resin was preconditioned using 1.0 M H$_2$SO$_4$ and washed with de-ionized water to convert it to free base form. The waste PCBs was obtained from discarded laptop in the store of CSIR-Institute of minerals and Materials Technology, India. The composition of metals in the PCBs was presented in Table1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>8.81</td>
</tr>
<tr>
<td>Cu</td>
<td>21.04</td>
</tr>
<tr>
<td>Ni</td>
<td>1.98</td>
</tr>
<tr>
<td>Al</td>
<td>5.05</td>
</tr>
<tr>
<td>Zn</td>
<td>1.52</td>
</tr>
<tr>
<td>Pb</td>
<td>1.10</td>
</tr>
<tr>
<td>Sn</td>
<td>1.50</td>
</tr>
<tr>
<td>Ti</td>
<td>0.11</td>
</tr>
<tr>
<td>Balance</td>
<td>others</td>
</tr>
</tbody>
</table>

2.2. Methods

The leached solution in one of our previous studies where 1.0 M H$_2$SO$_4$ was used for the leaching of pulverized PCBs sample (30 g/L pulp density) in a 0.5 L glass reactor and the temperature was controlled using a thermostatic water bath (Julabo, Germany). The leaching conditions are: temperature-50°C, mixing-300 rpm, and time-1h. The metal contents of the leach solution were presented in Table 2. The metals sorption by the resin from the leach solution was carried out by batch equilibration. The pH of the solution was adjusted using 0.5 M NaOH and H$_2$SO$_4$ and measured by Oakton hand pH meter (pH Testr, 35634-20). The experiment was conducted by contacted an appropriate weight of resin with 30 ml of leach solution in 100 ml conical flask on orbital shaker with 200 rpm at 25°C except in the case of temperature studies. The metals content in the raffinate and eluate were analyzed by Perkin Elmer Atomic Absorption Spectrometer AAnalyst 200 (Germany). The quantity of metals adsorbed unto resin and percentage recovery were estimated using equation 1 and 2 respectively.

\[
q_t = (K_v-K_0) \times \frac{v}{m}
\]
\[ \% R = \left( \frac{K_o - K_t}{K_o} \right) \times 100/K_o \]  

\( q_t \) is quantity adsorbed at time (t) in mg·g\(^{-1}\), \( m \) is mass of resin in (g), \( v \) is volume (L), \( K_o \) and \( K_t \) is metal concentration at time 0 and t (mg·L\(^{-1}\)).

Table 2. Metal content of leached solution of waste PCBs

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
<th>Mn</th>
<th>Co</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg/L)</td>
<td>5975</td>
<td>1196</td>
<td>198.75</td>
<td>285.25</td>
<td>95.01</td>
<td>38.25</td>
<td>360.8</td>
</tr>
</tbody>
</table>

2.3.1. Regeneration and reusability

Preconditioned Dowex M4195 resin (0.3 g) was contacted with 50 mL of leach solution of pH 2 at 25 °C, 200 rpm for 180 minutes. After equilibration, the resin was carefully removed, rinsed and eluted with 2.0 M H\(_2\)SO\(_4\) for 30 minutes. The resin was washed with 100 mL of distilled water and reused. Complete flow sheet for this process was presented in Fig. 1.

3. Results and discussion

3.1. Effect of pH

The effect of pH on the recovery performance of Cu\(^{2+}\), Ni\(^{2+}\) and co-recovery of other metals by Dowex M 4195 was examined in the pH range of 0.5 to 5.0. In Fig. 2, it is shown that recovery efficiency of metals increased with increases in pH (0.5 - 5.0). Dowex M4195 still retain its affinity for metals even at very high acidic medium (Diniz et al., 2002) because all the nitrogen atoms of bis (2-pyridylmethyl) amine functional groups were protonated at low pH level and one or more nitrogen atoms were protonated at medium and high pH levels respectively (Grinstead et al., 1984). But it is imperative to evaluate the recovery efficiency since most of acidic leach solutions are always at this pH. At pH 0.5, selectivity of Cu/Ni ratio was observed to be more than 10 times. However, pH 2.0 was found to be optimum recovery for Cu\(^{2+}\) as further increase in pH to 5.0 has negligible effect on recovery efficiency. Also, the recovery efficiency of Ni increased as the pH of solution increases from 0.5 to 5.0 while at pH above 2.0, iron precipitation was noticed which lead to sharp increase in recovery efficiency. It was observed that recovery efficiencies of Co\(^{2+}\) and Zn\(^{2+}\) increased as pH increase from 1-4 whereas uptake
of Mn$^{2+}$ and Al$^{3+}$ were significantly low. The report by Ogden et al., (2017), shown that no extraction of Al$^{3+}$ was achieved by Dowex M4195 (Ogden et al., 2017). Therefore, apparent sequences of affinity were Cu > Ni > Zn > Fe > Co >>>>Mn=Al. Similar trend was reported in the literature using synthetic chloride medium and the recovery sequence was Cu >Ni>Pb>Fe>Co>Mn (Diniz et al., 2005) and Cu > Ni > Co >Pb> Fe>Mn (Diniz et al., 2002).

3.2. Effect of contact time

The effect of contact time on recovery of Cu$^{2+}$, Ni$^{2+}$ and co-recovery of other metals from sulphate leach solution by Dowex M 4195 chelating resin was studied at pH 2 to avoid precipitation of Fe$^{3+}$. As it is shown in Fig. 3, recovery efficiencies of Cu$^{2+}$ and Ni$^{2+}$ increased with contact time. About 23.8 and 12.4 % of Cu$^{2+}$ and Ni$^{2+}$ were recovered in 10 minutes, and when the time was increased to 180 minutes, 59.0 and 39.1 % of Cu$^{2+}$ and Ni$^{2+}$ recovered respectively. Whereas recovery efficiencies for Co$^{2+}$, Zn$^{2+}$ and Fe$^{3+}$/ Fe$^{2+}$ initially increased up to 30 minutes later decreased and reached a plateau at 120 to 180 minutes. However, subsequent increased in contact time to 240 minutes has negligible effects on the recovery efficiencies of all the metals. Also, the recovery efficiencies of Mn$^{2+}$ and Al$^{3+}$ were considerably low and negligible.

3.3. Effect of resin dosage

The effect of resin dose on the recovery efficiency of Cu$^{2+}$, Ni$^{2+}$ and co-recovery of other metals from leach sulphate solution was investigated. The results obtained in Fig. 4 shows that recovery efficiencies of Cu$^{2+}$ and Ni$^{2+}$ from leach solution by Dowex M 4195 increased proportionately with increases in the
quantity of resin. The recovery efficiencies of Cu$^{2+}$ at equilibrium time increased from 25.5 to 94.03% as dose increased from 0.1 to 0.5 g, whereas it increased from 7.2 to 53.4% for Ni$^{2+}$. Moreover, low recovery efficiencies of Co$^{2+}$ was due to its low concentrations and competition for binding site by strong affinity Cu$^{2+}$ and Ni$^{2+}$, despite that, Zn$^{2+}$, Fe$^{3+}$/Fe$^{2+}$, and Co$^{2+}$ recovery efficiencies were slightly increased as the resin dose increases. It is apparent that the amount of metal ions adsorbed per unit mass increased with increasing resin amount and the sorption density (Nguyen et al., 2009).

Fig. 4. Effect of resin dose on recovery of metals at pH 2 by Dowex M 4195 (Cu = 300 mg/L, Ni = 10.2 mg/L, Fe = 50.02 mg/L, Zn = 19.2 mg/L, Co = 2.21 mg/L, Mn = 5.29 mg/L, and Al = 19.11 mg/L)

3.4. Effect of temperature

There are few literatures on effect of temperature for the recovery of metals by resin. However, the temperature range of 25°C (298 K) to 50°C (333K) was selected based on the resin manufacturer manual. In Fig. 5, it is shown that temperature of the solution has influence on the recovery of Fe$^{3+}$/Fe$^{2+}$, Co$^{2+}$ and Zn$^{2+}$, while low effects were observed in the recovery of Cu$^{2+}$ and Ni$^{2+}$ with no traces of Mn$^{2+}$ and Al$^{3+}$ being recovered. In general, the optimum temperature was 40°C as further increase in the temperature to 50°C has insignificant effects. It was observed that recovery efficiencies for Cu$^{2+}$ and Ni$^{2+}$ increased from 50 and 30.1% at 25°C to 50.5 and 30.6% at 50°C respectively. Based on the report by Sirola et al., (2010a), reported Ni$^{2+}$ and Cu$^{2+}$ loadings increased from 0.5 to 0.8 mmol/L and 0.6 to 0.8 mmol/L respectively when the temperature was increased from 25°C to 90°C using 2-(aminomethyl) picolylamine (Sirola et al., 2010a).

Fig. 5. Effect of temperature on recovery of metals at pH 2 by Dowex M 4195 (equilibration time-3hrs, Cu = 298 mg/L, Ni = 10.42 mg/L, Fe = 52.05 mg/L, Zn = 18.01 mg/L, Co = 2.21 mg/L, Mn = 5.05 mg/L, and Al =17.31 mg/L)
3.5. Adsorption isotherms

Langmuir and Freundlich are mostly used to describe the adsorption equilibrium ion exchange relation between the solid and solution phases (Grimshaw and Harland, 1975). However, the data obtained for adsorptions of Cu\(^{2+}\) and Ni\(^{2+}\) were used since adsorptions recorded for Co\(^{2+}\), Fe\(^{3+}\)/Fe\(^{2+}\) and Zn\(^{2+}\) were low and at irregular manner.

Langmuir is used to study completely homogenous surface with negligible interaction between adsorbed molecules (Gode and Pehlivan, 2005). It assumes uniform adsorption energies onto the surface and maximum adsorption depends on saturation level of monolayer and represented in the following linear equation:

\[
\frac{C_e}{q_e} = \frac{1}{kV_m} + \frac{C_e}{V_m}
\]  

where \(q_e\) represents the mass of adsorbed metals per unit resin (mg/g), \(V_m\) is the monolayer capacity, \(k\) is the equilibrium constant and \(C_e\) is the equilibrium concentration of the solution (mg/L). \(k\) and \(V_m\) were determined from the slope, intercept of the plot (Fig. 6).

The Freundlich model is an empirical equation that shown to be consistent with exponential distribution of active centre, characteristic of heterogeneous surfaces (Ho, 2005; Veliev et al., 2006). The expression is represented in the following equation:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]  

where \(K_f\) and \(n\) are adsorption capacity and intensity respectively, \(K_f\) is an important constant used as relative measure for adsorption efficiency. From the results obtained in Table 2, it is shown that adsorption of Cu\(^{2+}\) and Ni\(^{2+}\) correlates with both Langmuir and Freundlich isotherms. High \(R^2\) value for Langmuir and Freundlich isotherms suggests a monolayer and multi-layer adsorption mechanism respectively (Nikoloski and Ang, 2014; Zainol and Nicol, 2009). However, adsorption of Cu\(^{2+}\) and Ni\(^{2+}\) follows monolayer and multi-layer mechanism.

Table 3. The parameters for isotherms

<table>
<thead>
<tr>
<th>Metals</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V_m)</td>
<td>(k)</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>-1460.41</td>
<td>555.62</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>-20.18</td>
<td>0.14</td>
</tr>
</tbody>
</table>

3.6. Kinetics of adsorption

Rate of adsorbate uptake, that determines optimum operating conditions for the full-scale batch process, is best described by adsorption kinetics (Gupta and Sharma, 2003). However, pseudo first and second order mechanisms were used.

For pseudo first order kinetic, the following simple linear expression is used (Sharma and Bhattacharyyya, 2004).

\[
\ln (q_e - q_t) = \ln q_e - k_1t
\]  

where \(k_1\) is the rate constant of the first-order adsorption, \(q_t\) is the amount of metals adsorbed at time \(t\) in mg/g and \(q_e\) is the amount of metals adsorbed at saturation of resin in mg/g. The plot of \(\ln (q_e - q_t)\) against \(t\) allows calculation of the \(q_e\) and \(k_1\) (Fig. 7).

Pseudo second order kinetic can be expressed thus (Ho and McKay, 1998).

\[
t/q_t = 1/k_2q_e + t/q_e
\]  

where \(k_2\) (g/mg min) is the pseudo-second order rate constant, \(q_e\) is the amount of metals adsorbed onto resin at equilibrium or saturation and \(q_t\) is the amount of metal also adsorbed onto resin at time \(t\). However, \(q_e\) and \(k_2\) values can also be determined from the intercept and slope of the plot of \(t/q_t\) versus \(t\) (Fig. 7). The calculated values of the kinetic parameters for adsorption of metals solutions are tabulated in Table 3.
It is shown that $R^2$ values for Cu$^{2+}$ and Ni$^{2+}$ were both fitted into Pseudo first and second order kinetics (Table 3). More so, it was observed that Pseudo-second order kinetic was well fitted for adsorption of Cu$^{2+}$ and Ni$^{2+}$ as the $R^2$ values were close to unity which indicates that the rate limiting step controlling the adsorption is chemisorptions (Fig. 7).

<table>
<thead>
<tr>
<th>Metals</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (g/mg min$^{-1}$)</td>
<td>$q_e$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>-0.0042</td>
<td>-1.968</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-0.0067</td>
<td>1.368</td>
</tr>
</tbody>
</table>

4. Regeneration and reuse studies

For economic implication, reusability efficiency of DOWEX M4195 chelating resin for recovery of Cu$^{2+}$, Ni$^{2+}$ and co-recovery of other metals from leach solution was studied. It was observed that the recovery efficiencies of Cu$^{2+}$ was almost the same while that of Ni$^{2+}$ was found to have decreased only after 1st cycle and remain constant for the rest of cycles (Fig. 8). Decrease in recovery efficiencies of Fe$^{3+}$/Fe$^{2+}$,
Zn$^{2+}$ and Co$^{2+}$ were also observed. The results showed that Dowex M4195 resin has strong affinity for Cu$^{2+}$ and Ni$^{2+}$ as efficiencies remains unchanged.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Cu</th>
<th>Ni</th>
<th>Fe</th>
<th>Zn</th>
<th>Mn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>74.4</td>
<td>5.9</td>
<td>1.6</td>
<td>0.2</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>1</td>
<td>71.9</td>
<td>5.5</td>
<td>0.9</td>
<td>0.1</td>
<td>0</td>
<td>-0.2</td>
</tr>
<tr>
<td>2</td>
<td>72.0</td>
<td>4.6</td>
<td>0.1</td>
<td>0.2</td>
<td>0</td>
<td>-0.6</td>
</tr>
<tr>
<td>3</td>
<td>70.2</td>
<td>5.2</td>
<td>0</td>
<td>0.1</td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>73.1</td>
<td>4.9</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>71.8</td>
<td>4.3</td>
<td>0.2</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>72.3</td>
<td>4.7</td>
<td>0.1</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>70.8</td>
<td>4.7</td>
<td>0.1</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>69.9</td>
<td>4.9</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>-0.2</td>
</tr>
<tr>
<td>9</td>
<td>70.9</td>
<td>4.1</td>
<td>0.3</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Cu-310 mg/L, Ni-8.50 mg/L, Fe-40.8 mg/L, Mn-2.5 mg/L, Zn-15.5 mg/L and Al-15.2 mg/L*

5. Conclusions

Batch experiment studied revealed that selective recovery of Cu$^{2+}$ and Ni$^{2+}$ from polymetallic sulphate leach solution of WPCBs by Dowex M 4195 chelating resin is possible. The overall results obtained showed that co-recovery of Co$^{2+}$, Zn$^{2+}$, Fe$^{3+}$/Fe$^{2+}$ at pH 2 were significantly low with negligible amount of Mn$^{2+}$ and Al$^{3+}$. Effect of temperature was more pronounced on the recovery of Fe$^{3+}$/Fe$^{2+}$ with 40 $^\circ$C observed to be optimum temperature as further increase to 50 $^\circ$C has insignificant effects on the recovery efficiency. Adsorption of Cu$^{2+}$ and Ni$^{2+}$ completely fit to isotherms and kinetics tested and the resin can be reused for many times as its affinities for Cu$^{2+}$ and Ni$^{2+}$ remains unchanged.

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