3. RESULTS AND DISCUSSION

3.1. Electrolysis

3.1.1 Qualitative observations

With stainless steel electrodes:

After a few minutes (about 5 minutes) of electrolysis at current densities 5 mA/cm² and above at ambient temperature, the solution turned greenish and then slowly to orange-brown. A thin layer of green precipitate/deposit was also formed on the electrode (cathode) surface. This colour change was due to the dissolution reaction of the steel metal anode used.

When these metal-ions migrated to the cathode, the ions were either discharged and deposited out as metal or they were precipitated out by hydroxyl ions (which also raised the near cathode surface pH) as a green gel-like sludge (metal hydroxide) near the cathode surface. The ferrous ions were also oxidized by dissolved oxygen or by anodic reaction to formed ferric ions which give rise to the orange colour of the solution. After prolonged electrolysis, the solution pH increased and suspended solids appeared.

The iron species present in the solution were probably aquo-complexes such as Fe(H₂O)₆³⁺. When their concentration was less than the solubility of their metal hydroxide, soluble monomeric, dimeric and perhaps even polymeric hydroxo-metal complexes were formed.²,⁴,₂,⁹₆-⁹⁹

\[
\text{Fe(OH)}^{2+} + \text{H}_2\text{O} = \text{Fe(OH)}_2^{+} + \text{H}_3\text{O}^+ \quad (31)
\]
\[
2\text{Fe}^{3+} + 4\text{H}_2\text{O} = \text{Fe(OH)}_2^{4+} + 2\text{H}_3\text{O}^+ \quad (33)
\]
When the solubility activity product of the metal hydroxide was exceeded, formation of colloidal metal hydroxide (or hydroxo-metal polymers) occurred.\textsuperscript{42,97} Hydroxo-metal complexes were adsorbed at the interfaces,\textsuperscript{97,100} while aquo-metal ions were not adsorbed. This adsorption neutralized the electrical charge of the colloidal particles and the colloids were consequently destabilized.

The form of precipitate varied, depending on the manner of agitation and the type of heavy metals in the simulated effluent. The various forms were green ferrous hydroxide, orange-brown ferric hydroxide and black magnetic ferrite. Magnetic ferrite was formed when chromium (found after 60 minutes electrolysis) or copper (found after solution electrolysed for 240 minutes) solutions were electrolyzed, with magnetic stirring. The precipitate settled (magnetic ferrite settled faster than ferrous or ferric hydroxide) after the electrolysis process was stopped and filtration yielded a clear/colorless solution for initial effluents which contained sodium chloride (0.03 mol/L and above).

Figures 6-9 are photographs of samples of Cu and Cr solutions before and after specified periods of electrolysis.

With aluminium electrodes:

The solution turned cloudy after a few minutes of electrolysis at current densities above 5 mA/cm\textsuperscript{2} and at ambient temperature. A white gelatinous colloidal precipitate was formed. The colloidal precipitate remained suspended in the solution but most of it
Figure 6: A photograph showing the original 100 ppm Cu + 0.03 mol/L NaCl solution before the treatment process (air bubbling). Electrodes: Stainless steel.

Figure 7: A photograph showing the 100 ppm Cu + 0.03 mol/L NaCl solution after 46 minutes electrolysis at current density 15mA/cm² (air bubbling). Electrodes: Stainless steel.
Figure 8: A photograph showing the original 100 ppm Cr + 0.03 mol/L NaCl solution before the electrolysis process (magnetic stirring). Electrodes: Stainless steel.

Figure 9: A photograph showing the 100 ppm Cr + 0.03 mol/L NaCl solution (A) after 30 minutes electrolysis at current density 15 mA/cm² (magnetic stirring). (B) was the solution showed in Fig. 3 during settling process after 60 minutes electrolysis. Electrodes: Stainless steel.
was floated up to the solution surface by the air bubbles when air agitation was used. With prolonged treatment, the heavy metal ions co-deposited with the aluminium hydroxide as was seen by the change in colour of the precipitate formed (brownish red for copper, green/orange for chromium, and green for nickel).

The following monomeric and dimeric hydroxo-metal complexes could have been formed prior to precipitation of solids.\(^2,42,96-99\)

\[
\text{Al}^{3+} + 8\text{H}_2\text{O} = \text{Al(OH)}_4^- + 4\text{H}_3\text{O}^+ \quad (34)
\]

\[
\text{Al(H}_2\text{O)}_6^{3+} + \text{H}_2\text{O} = \text{Al(H}_2\text{O)}_5\text{(OH)}^{2+} + \text{H}_3\text{O}^+ \quad (35)
\]

3.1.2. Effect of aeration

When air-bubbling was used to agitate the solution during the electrolysis, generally, the solution changed colour (from green to orange-brown) faster than when a magnetic stirrer was used. This was because the air accelerated the oxidation of ferrous ions to ferric ions.

Agitation enhanced the precipitation process and it was also found that floc was formed in a shorter period than when there was no agitation. This could be because of increase in inter-particle contact which caused aggregation of these colloidal particles.

It was apparent that the effects of aeration and agitation used in the electrolysis process were important as it would affect precipitate aggregation and final treatment efficiency for the different types of heavy metal ions contained in the solutions treated.

For solutions containing copper and nickel ions, air agitation was preferable in the electrolysis process because it increased the rate of oxidation of ferrous ions to ferric ions.
and precipitation occurred faster, since ferric hydroxide could precipitate at lower pH. Ferrous hydroxide settles much slower than ferric hydroxide.\textsuperscript{42} 

On the other hand, for effluents containing chromium ions, the stirring method was preferred. The Fe\textsuperscript{2+} ion was a well known agent for the reduction of chromium(VI) to chromium(III), even in the chemical precipitation process for chromium treatment.

\begin{align*}
\text{CrO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{CrO}_4 \tag{36} \\
2\text{CrO}_4^{2-} + 2\text{H}_2\text{O}^+ & = \text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{O} \tag{37} \\
\text{CrO}_4^{2-} + 3\text{Fe}^{2+} + 8\text{H}_3\text{O}^+ & \rightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+} + 12\text{H}_2\text{O} \tag{38} \\
\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}_3\text{O}^+ & \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 21\text{H}_2\text{O} \tag{39}
\end{align*}

If magnetic stirring was used, there was less air oxidation of Fe\textsuperscript{2+} so that most of the ferrous ions generated could be used for reactions (38) & (39). As a result of reactions (37) - (39), solution pH increased as a result of the consumption of the hydrogen ions, and the ferric ions would start to precipitate once the solution pH is above 3\textsuperscript{39}.

When aluminium was used as anode, air agitation caused flotation of the light aluminium hydroxide formed and reduced interactions with other particles or absorbed/occluded heavy metal ions in solution.

Fig. 10 compares treatment efficiency by plotting percentage of heavy metal remaining versus treatment time for the different agitation processes.
Figure 10: Plots of heavy metal concentration versus treatment time for copper, nickel and chromium under air agitation or magnetic stirring. Added electrolyte: 0.03 mol/L NaCl. Current density: 15 mA/cm². Electrodes: stainless steel. Temperature: Ambient.
3.1.3. Voltage changes

Results of measurements of potential (voltage) difference between anodes and cathodes during electrolysis are tabulated in Appendix 8.

In the absence of NaCl, the voltage across the cell increased with electrolysis time, especially for solutions containing low concentrations of heavy metal (100 ppm and below). For solutions with metal concentrations 100 ppm and below, current densities of 10 mA/cm² and above could not be obtained because the solution resistance was too high and the voltage was too high for the instrument used in the study. The presence of NaCl increased electrolytic conductivity of the solution and decreased the voltage across the cell.

In the presence of NaCl (0.01mol/L to 0.10mol/L), the voltage across the electrolysis cell remained steady to within ±0.2 V at the current densities used. Increase in NaCl concentration lowered the voltage across the cell.

A lower voltage was obtained when aluminium electrodes were used in the electrolysis as shown in Appendix 9.
3.2. Quantitative data

3.2.1 Solution containing 500 ppm of copper

As shown in Figs. 11 & 12, with a current density of 5 mA/cm², the treatment process could remove almost 90% (10.8 ppm Cu remained in solution after 240 min.) of copper in an hour (solution contained dissolved Fe³⁺ ion, orange in colour) in the absence of sodium chloride, but the treatment was not successful when small amounts of sodium chloride were added (solution clear).

At a higher current density (15 mA/cm²), the treatment was improved, as shown in Figs 13 & 14. The addition of sodium chloride in the range 0.01-0.1 mol/L did not lead to significant differences in the results obtained in the treatment process at both current densities.

With high copper ion concentration, much Cu was deposited out on the cathode surface and this caused a drastic drop in copper ions concentration for the solution. The deposited copper on the steel cathodes decreased the rate of generation of OH⁻ ions due to the higher cathodic overpotential for hydrogen evolution at the Cu-coated electrodes. There was little increase in solution pH and less ferric hydroxide was formed. The sample obtained after one, four and seven hours of electrolysis still contained a substantial amount of ferric ions and the solution was orange in colour. (Appendix 10) However, the copper concentration was still above the allowed discharge limit.

When sodium hydroxide was used to bring the solution pH to 9-10, ferric hydroxide was precipitated and the final copper concentration fell below 1 ppm.
Figure 11: Plots of copper concentration versus treatment time at different NaCl concentrations. Electrodes: stainless steel. Current density: 5 mA/cm². Temperature: Ambient.

Figure 12: Plots showing the effect of NaCl concentrations on the treatment of copper-containing effluents at current density 5 mA/cm². Electrodes: stainless steel. Temperature: Ambient.
Figure 13: Plots showing the effect of NaCl concentrations on the treatment of copper-containing effluents at current density 15 mA/cm². Electrodes: stainless steel. Temperature: Ambient.

Figure 14: Plots showing the effect of NaCl concentrations on the treatment of copper-containing effluents at current density 5 mA/cm². Electrodes: stainless steel. Temperature: Ambient.
This finding differed from the observation of Veeraraghavan & Dambal\textsuperscript{73} who mentioned that clear solutions could be obtained without any further pH adjustment.

The small amount of ferric hydroxide that settled on the bottom was found to have converted to a form of magnetic oxide after prolonged electrolysis with stirring.

A rise in the solution temperature (up to 40\degree C) was observed. This was caused by IR heating due to the rising cell resistance. During electrolysis, the cathode was slowly covered by a semi-porous copper or iron hydroxide and affected the conductivity of the electrode. At the same time, the concentration of the heavy metal in solution was depleted as some were deposited. This also reduced the solution conductivity. High overpotential and rise in temperature in the absence of sufficient oxygen will favor the formation of magnetic oxide.\textsuperscript{81}

Addition of sodium chloride as supporting electrolyte to increase solution conductivity led to results which were less desirable.

In the presence of NaCl, less copper was being deposited, and more ferric hydroxide was formed. The solution pH increased during the electrolysis to about 5-6. The treatment sample obtained after filtration was clear and no further ferric ions precipitated when hydroxide was added to the sample.

It was seen that the treatment efficiency for higher concentration of copper (500 ppm) dropped when sodium chloride was added as supporting electrolyte.
3.2.2. Solutions containing 100 ppm of copper

For a simulated effluent containing 100 ppm copper, addition of NaCl to solution gave no significant improvement in heavy metal removal at current density 5 or 10 mA/cm².

At current density 10 mA/cm² and in the presence of 0.1 mol/L NaCl, the treatment process required about 90 minutes to remove Cu to below the discharge limit.

With the use of a higher current density (15 mA/cm²), the treatment process could remove copper in solution to below the discharge limit if the added sodium chloride concentration was above 0.02M. The final copper content after 90 minutes was 0.2 ppm. In the presence of 0.01 mol/L sodium chloride, heavy metal removal was slow initially. This could be because the hydrogen evolution overpotential was still high and a longer time was needed to generate sufficient hydroxide ions to react with the ferric ions. Above 90 minutes of the treatment time, the copper removal was the same as that obtained with higher concentrations of NaCl.

Figs. 15 to 17 summarise these observations.

At a current density of 15 mA/cm² in the presence of 0.03 mol/L sodium chloride, the treatment using steel (iron) anodes performed better than when aluminium anodes were used during the first 60 minutes. But when the electrolysis was extended to 90 minutes, the end result was the same. This could be because aluminium hydrous oxide precipitation occurred at higher pH. This observation is summarised in Fig 18.
Figure 15: Plots of copper concentration versus treatment time for different NaCl concentrations. Current density: 5mA/cm². Electrodes: Stainless steel. Initial [Cu²⁺] = 100 (± 5 %) ppm. Temperature: Ambient.

Figure 16: Plots of copper concentration versus treatment time for different NaCl concentrations. Current density: 10mA/cm². Electrodes: Stainless Steel. Initial [Cu²⁺] = 100 (± 5 %) ppm. Temperature: Ambient.
Figure 17: Plots of copper concentration versus treatment time for different NaCl concentrations. Current density: 15mA/cm². Electrodes: Stainless Steel. Initial [Cu²⁺] = 100 (± 5 %) ppm. Temperature: Ambient.

Figure 18: Comparison of treatment performance between steel and aluminium anodes. Current density: 15mA/cm². Added electrolyte: 0.03mol/L NaCl. Temperature: Ambient.
3.2.3. Effluent containing 50 ppm of copper

It can be seen from Figs. 19 & 20 that NaCl concentration had little effect on the trend of heavy metal removal when the current density was 2 or 5 mA/cm².

For current densities 10 and 15 mA/cm² (Figs. 21 & 22) and above a NaCl concentration of 0.03 mol/L, treatment (removal of Cu) was satisfactory within one hour of electrolysis.

3.2.4. Treatment reproducibility

Certain tests were duplicated to check on the reproducibility of the treatment process for the Cu effluents and some results are presented in Figs. 23-25. There was reasonably good reproducibility (+/- 5 %) in most cases.

3.2.5. Effect of sodium chloride

Fig 26 showed that the trend of copper removal for different copper concentrations were the same in the absence of sodium chloride at a current density 5 mA/cm². Increase in current density did not lead to significant improvement in treatment.

In the presence of sodium chloride (0.01 - 0.10 mol/L), the treatment process was more dependent on the current density used and the concentration of heavy metal, as shown in Figs 27-29. It was not effective for high (500 ppm copper) copper concentrations although higher current density slightly increased the efficiency of metal removal.
Figure 19: Plots showing the effect of NaCl concentration on treatment trend for a Cu solution initially at 50 (± 5%) ppm concentration. Electrodes: Stainless steel. Temperature: Ambient. Current density: 15 mA/cm².

Figure 20: Plots showing the effect of NaCl concentration on treatment trend for a Cu solution initially at 50(± 5%) ppm concentration. Electrodes: Stainless steel. Temperature: Ambient. Current density: 5 mA/cm².
**Cu Conc. Vs. Treatment Time**

Figure 21: Plots showing the effect of NaCl concentration on treatment trend for a Cu solution initially at 50 (± 5%) ppm concentration. Electrodes: Stainless steel. Temperature: Ambient. Current density: 10 mA/cm².

**Cu Conc. Vs. Treatment Time**

Figure 22: Plots showing the effect of added NaCl concentration on Cu removal at current density 2 mA/cm² using stainless steel anodes.
Figure 23: Plots of $[\text{Cu}^{2+}]$ versus time, over a period of 60mins, for duplicate test at current density 15 mA/cm$^2$ in solutions containing 0.03 mol/L NaCl + 250 (± 5%) ppm Cu. Temperature: Ambient. Electrodes: Stainless steel.

Figure 24: Plots of $[\text{Cu}^{2+}]$ versus time, over a period of 120mins, for duplicate test at current density 5 mA/cm$^2$. Solutions: 100 (± 5%) ppm Cu in 0.03 mol/L NaCl. Temperature: Ambient. Electrodes: Stainless steel.
Figure 25: Plots of $\left[\text{Cu}^{2+}\right]$ versus time, over a period of 60mins, for duplicate test at current density 15 mA/cm$^2$ in solutions containing 0.03 mol/L NaCl $\pm$45 ($\pm$ 5 %) ppm Cu. Temperature: Ambient. Electrodes: Stainless steel.

Figure 26: Plots of percentage of copper remaining versus treatment time for solutions containing different initial Cu concentrations at current density 5 mA/cm$^2$ in the absence of NaCl. Temperature: Ambient. Anodes: stainless Steel.
Figure 27: Plots of $[\text{Cu}^{2+}]$ versus time for different applied current densities, with addition of 0.01 mol/L NaCl. Temperature: Ambient. Electrodes: Stainless Steel. Initial $[\text{Cu}^{2+}] = 500 \pm 5\%$ ppm

Figure 28: Plots of $[\text{Cu}^{2+}]$ versus time for different applied current densities, with addition of 0.03 mol/L NaCl. Temperature: Ambient. Electrodes: Stainless Steel. Initial $[\text{Cu}^{2+}] = 500 \pm 5\%$ ppm
Cu Conc. Vs. Treatment Time

500 ppm Cu, 0.05 M NaCl

Figure 29: Plots of [Cu$^{2+}$] versus time for different applied current densities, with addition of 0.05 mol/L NaCl. Temperature: Ambient. Electrodes: Stainless Steel.
Initial [Cu$^{3+}$] = 500 (± 5%) ppm
Increase in sodium chloride concentration did not significantly increase treatment efficiency for high [Cu$^{2+}$] concentrations.

When a current density of 5 mA/cm$^2$ was used, the treatment process was not that effective, and even a 50 ppm Cu solution required more than an hour to remove the metal ions below the discharge limits. The treatment trend at this low current density was similar for the 100 ppm and 50 ppm Cu solution in the presence of 0.03 M or above of NaCl. Treatment efficiency at this current density improved when sodium chloride concentration was increased. The results are summarised in Figs. 30-32.

At a current density of 10 mA/cm$^2$ and in the presence of 0.01 M NaCl, the treatment process could only remove about 75% of copper after an hour for initial copper concentrations of 100 and 50 ppm. When the NaCl concentration was increased to 0.03 M, there was an improvement (from 75 % increased to 98 % Cu removal for 60 minutes electrolysis) in copper removal for 50 ppm Cu solution. Further increase in NaCl concentration only increased the treatment efficiency slightly. The results are shown in Figs. 33-36. Addition of sodium chloride at current density 10 mA/cm$^2$ only helped the treatment of the solution containing 50 ppm to below the discharge limit within 90 minutes of electrolysis.

Figures 37-40 show the rate of decrease of copper concentration with electrolysis time for a fixed current density of 15 mA/cm$^2$ for the different initial Cu concentrations in the presence of different low NaCl concentrations. There appeared to be significant improvement in treatment efficiency with increase in NaCl concentration, especially for the 50 ppm Cu solutions. At this current density, the addition of sodium chloride will
Figure 30: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.01 mol/L NaCl solution. Current density: 5 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.

Figure 31: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.03 mol/L NaCl solution. Current density: 5 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.
Figure 32: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.05 mol/L NaCl solution. Current density: 5 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.

Figure 33: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.01 mol/L NaCl solution. Current density: 10 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.
Figure 34: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.03 mol/L NaCl solution. Current density: 10 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.

Figure 35: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.05 mol/L NaCl solution. Current density: 10 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.
Figure 36: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.10 mol/L NaCl solution. Current density: 10 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.

Figure 37: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.01 mol/L NaCl solution. Current density: 15 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.
Figure 38: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.03 mol/L NaCl solution. Current density: 15 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.

Figure 39: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.05 mol/L NaCl solution. Current density: 15 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.
increase solution conductivity. Copper deposition has a lower overpotential compared to hydrogen evolution, but when the copper concentration was low, it has a high deposit overpotential and eventually the condition favor the hydrogen evolution. The hydrogen evolution occurring at the cathodes led to formation of hydroxyl ions which reacted with the copper ions in solution and the ferric-/ ferrous ions dissolving out from the stainless steel anode.

During the formation of ferric hydroxide, copper ions were coprecipitated by absorption (surface complexation and electrostatic attraction) onto the surface of the iron hydroxide particles and / or by occlusion (mechanical entrapment of foreign ions within a precipitate particle by physical encapsulation within the particle walls and by chemical bonding within the particle structure to form a continuous three dimensional network.) within the interior of ferric hydroxide. Copper hydroxide has a higher solubility product than ferric hydroxide and required a higher pH to precipitate out by itself.

The colloidal stability of hydrous oxide may be affected by electrolytes in ways that are different from those affecting hydrophobic colloids. Specific adsorption of cations and anions on hydrous oxide surfaces may be interpreted as surface coordination reactions. As indicated in Fig 41, hydrous oxides exhibit amphoteric behavior and can be compared with amphoteric polyelectrolytes. (Me = metal )

\[ \equiv \text{MeOH}_2^+ = \equiv \text{MeOH} + \text{H}^+; \quad K_{a1}^e \quad (40) \]

\[ \equiv \text{MeOH} = \equiv \text{MeO}^- + \text{H}^+; \quad K_{a2}^e \quad (41) \]
Figure 40: Plots of percentage of copper remaining versus treatment time for solutions containing different initial concentrations of copper in 0.10 mol/L NaCl solution.

Current density: 15 mA/cm². Temperature: Ambient. Anodes: Stainless Steel.
Fig. 41. Interactions of hydrous oxides with cations and anions interpreted in terms of surface complex formation and ligand exchange equilibria.\textsuperscript{101}

\[
\begin{align*}
\text{MeOH}_2^+ & \rightleftharpoons \text{MeOH}^+ + \text{OH}^- & K_{o_1}^s \\
\text{MeOH} & \rightleftharpoons \text{MeO}^- + \text{OH} & K_{o_2}^s \\
\end{align*}
\]

\[
\begin{align*}
\text{MeOH}_2^+ + \text{C}^+ & \rightleftharpoons \text{MeOC}^+ & (Z-1)^+ \\
\text{C}^- + \text{MeO}_{2}^- & \rightleftharpoons \text{MeA}^- & (Z-1)^- \\
\end{align*}
\]

\text{cation complexation}

\text{anion complexation}

\text{C = cation}
\text{A = anion}
\text{Me = Metal}

Operationally, there is a similarity between $\text{H}^+$, metal ions and other Lewis acids.

The OH groups on a hydrous oxide surface have a complex-forming O-donor group like OH\textsuperscript{−} or OH groups attached to other elements(silicate, phosphate, polysilicate). Proton
and metal ions compete with each other for the available coordinating sites on the surface:

\[
\equiv \text{MeOH} + \text{M}^{x+} = \equiv \text{MeOM}^{(x-1)+} + \text{H}^+; \quad \text{K}_1^x \tag{42}
\]

\[
2(\equiv \text{MeOH}) + \text{M}^{x+} = (\equiv \text{MeO})_2 \text{M}^{(x-2)+} + 2\text{H}^+; \quad \text{K}_2^x \tag{43}
\]

Similarly, ligand exchange with coordinating anions leads to release of OH\(^-\) from the surface

\[
\equiv \text{Me-OH} + \text{A}^{x-} = \equiv \text{Me-A}^{(x-1)-} + \text{OH}^-; \quad \text{K}_1^x \tag{44}
\]

\[
2(\equiv \text{Me-OH}) + \text{A}^{x-} = (\equiv \text{Me})_2 \text{A}^{(x-2)-} + 2\text{OH}^-; \quad \text{K}_2^x \tag{45}
\]

As mentioned early, adsorption has been identified as a viable removal mechanism. Surface complexation and electrostatic attraction are the two most commonly used adsorption terms.\(^{97,101}\) Heavy metal contaminants can exist as either cations or anions. After forming all possible surface complexes, it is possible to remove contaminants by simple electrostatic attractions. Hydrous ferric oxide in combination with various surface complexes contains areas of apparent positive and negative charges. Opposite charges attract and are strong enough to remove some dissolved species from the aqueous phase.

With reference to the above mechanism, with the addition of NaCl, the increase in anions concentration will cause solution pH to increase faster according to reaction (45). When aluminium was used as anode material, the rate of copper removal was slower than when steel anodes were used, at current density 15 mA/cm\(^2\) in the presence of 0.03 or 0.05 mol/L NaCl, (initial Cu concentration = 500 (± 5 %)) (Fig. 42). In the
presence of 0.10 mol/L NaCl, more than 95% copper could be removed in one hour. (cf. Fig. 43). This could be because the solubility product of aluminium hydroxide was higher than that for ferric hydroxide, therefore a higher pH was required to cause precipitation. Thus, a high sodium chloride concentration was an advantage (more anions) when Al anodes were used.

3.2.6. Effect of current Density

In the absence of NaCl and with the used of steel electrodes, the applied (from 5 mA/cm² to 15 mA/cm²) current density has little effect on the heavy metal removal efficiency, though small differences were observed at the beginning of the treatment process (Fig. 44). In the presence of NaCl, increase in current density improved the treatment efficiency for high copper concentration (500 ppm) (Figs. 28 & 29). For lower copper concentration (100ppm and below), the effect of current density varied, depending on the amount of NaCl present. For both the 50 and 100 ppm copper solutions containing 0.01 mol/L NaCl, the first 60 minutes of electrolysis at all the current densities applied did not give good treatment results, cf. Figs. 45 & 46.

At 0.03M and above of sodium chloride concentration (Figs. 47-51), increase in current density from 5 to 10 mA/cm² led to significant improvement in copper removal for initial Cu concentrations of 100 (± 5%) ppm or below. Rate of Cu removal increased more rapidly at current densities above 10 mA/cm². Solutions containing lower Cu contents (50 ppm) could be treated to below the discharge limit with a lower current
Figure 42: Plots showing the treatment trend for the copper solutions when different types of anodes were used at current density 15 mA/cm² and with the addition of 0.03 mol/L or 0.05 mol/L NaCl. Temperature: Ambient.

Figure 43: Plots of copper concentration versus treatment time at 15 mA/cm² at different NaCl concentrations. Anodes: Aluminium. Temperature: Ambient.
Figure 44:  
Plots indicating the trend of copper removal at different current densities in the absence of NaCl.  
Electrodes: Stainless steel.  
Temperature: Ambient

Figure 45:  
Plots showing the effect of current density on the treatment trend of 0.01 mol/L NaCl solutions, containing 100 ppm Cu.  
Electrodes: Stainless steel.  
Temperature: Ambient
Figure 46: Plots showing the effect of current density on the treatment trend of 0.01 mol/L NaCl solutions, containing 50 ppm Cu. Electrodes: Stainless steel. Temperature: Ambient

Figure 47: Plots showing the effect of current density on the treatment trend of 0.03 mol/L NaCl solutions, containing 100 ppm Cu. Electrodes: Stainless steel. Temperature: Ambient
Figure 48: Plots showing the effect of current density on the treatment trend of 0.03 mol/L NaCl solutions, containing 50 ppm Cu. Electrodes: Stainless steel. Temperature: Ambient

Figure 49: Plots showing the effect of current density on the treatment trend of 0.05 mol/L NaCl solutions, containing 100 ppm Cu. Electrodes: Stainless steel. Temperature: Ambient
Figure 50: Plots showing the effect of current density on the treatment trend of 0.05 mol/L NaCl solutions, containing 50 ppm Cu. Electrodes: Stainless steel. Temperature: Ambient

Figure 51: Plots showing the effect of current density on the treatment trend of 0.10 mol/L NaCl solutions, containing 100 ppm Cu. Electrodes: Stainless steel. Temperature: Ambient
density (10 mA/cm$^2$), but higher current densities (such as 15mA/cm$^2$ or above) were required for optimal treatment of solutions containing 100 ppm and above of copper.

3.2.7. pH changes, (cause and effect)

Since pH was an important factor in the precipitation or co-precipitation processes,$^{42}$ the pH of each sample collected during the treatment process was determined, the aim being to determine whether there was any correlation between pH and removal of heavy metal.

From the pH-time curves shown in Figs. 52-54, with the used of steel electrodes, it is seen that generally a rapid drop in pH occur during the first 15 minutes, followed by more gradual decreases in pH for both Cu and Ni solutions in the absence of sodium chloride. In the presence of sodium chloride, the pH at the end of the process (after 90 minutes) was only slightly higher than the initial pH.

The decreases in pH could be due to ferrous ions discharged from the anode forming polymeric complexes and releasing $H^+$ according to reactions (32) & (33). In addition, formation of ferrous hydrous oxide, oxidation of ferrous ions to ferric ions, heavy metal hydroxide formation, hydrolysis of ferrous/ferric hydrous oxide and co-precipitation (adsorption) of heavy metal (copper) in ferrous/ferric hydrous oxide lattice could occur and all these processes would either take up hydroxyl ions or generate hydrogen ions which lead to pH changes.

95
Figure 52: pH changes with time during the treatment process for the 100 ppm nickel solutions in the present and absence of NaCl at different current densities. Electrodes: Stainless steel. Temperature: Ambient

Figure 53: pH changes with time during the treatment process for the 100 ppm copper solutions in the present and absence of NaCl at different current densities. Electrodes: Stainless steel. Temperature: Ambient
Figure 54: pH changes with time during the treatment process for the 50 ppm copper solutions in the present and absence of NaCl at different current densities. Electrodes: Stainless steel. Temperature: Ambient
The addition of sodium chloride would prevent solution pH from decreasing further and this could be because of increase in rate of hydrogen evolution reaction and adsorption of chloride ions onto the metal hydrous oxide surface which promoted release of hydroxyl ions.
3.3.1. Treatment of solutions containing chromium, Cr (VI) ions

The treatment of chromium (VI) using the electrolysis method was efficient and a 2.5 L solution of Cr concentration up to 500 ppm could be treated in 90 minutes with a current density of 15 mA/cm² and above, but was dependent on amount of sodium chloride added (cf. Figs. 55 & 56). Chromium (VI) was first reduced to chromium (III) by the ferrous ions generated, and this was indicated by a colour change from orange to green in the solution (Eqs. (36) to (39) and (46) to (48)).

\[
\text{Cr}^{3+} + 3\text{OH}^- \rightarrow \text{Cr(OH)}_3 \quad (46)
\]

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \quad (47)
\]

After that, the solution colour changed back to orange-brown with the formation of ferric hydroxide, and finally to black ferrite hydroxide. The bubbling with oxygen into the solution inhibited the above mentioned reaction (Eqs. (38) & (39)).

When magnetic stirring was used in the electrolysis, formation of black magnetic (ferrite) oxide occurred. This magnetic oxide could settled faster and could be separated from the solution by magnets (cf. Figs. 57 & 58).\textsuperscript{110,111}

The results obtained from the microscopy and image analysis showed the ferrite precipitates were more clustered than the non-magnetic ferric hydroxide.(cf. Figs 59 & 60) Particles sizes were in the range of 1-2 μm. as shown in Appendix 11.
Figure 55: Plots showing Cr concentration versus time for a Cr solution at current density 20 mA/cm² in the presence of 0.03 mol/L NaCl. Electrodes: Stainless steel Initial [Cr] = 500 (± 5 %) ppm. Temperature: Ambient.

Figure 56: Cr concentration versus time for Cr solutions at different current densities in the presence of 0.03 mol/L NaCl. Electrodes: Stainless steel Initial [Cr] = 500 (± 5 %) ppm. Temperature: Ambient
Figure 57: A photograph showing bar magnets and the two different types of iron hydrous oxide produced. (A) non-magnetic, (B) magnetic hydrous oxide.

Figure 58: A photograph showing bar magnets and the two different types of iron hydrous oxide after settling. (A) non-magnetic, (B) magnetic hydrous oxide.
Figure 59: A computer printout of magnetic iron hydrous oxide image obtained by using Leica Q500MC image processing and analysis system.

Figure 60: A computer printout of non-magnetic iron hydrous oxide image obtained by using Leica Q500MC image processing and analysis system.
3.3.2. Effluent containing 500 ppm of chromium (VI)

With reference to Figs 55 & 56, it appears that the chromium removal process was slow at the beginning (first 15 minutes) when the main reaction was the reduction of this chromium (VI) to chromium (III) by Fe$^{2+}$ ion (Eqs (36) & (37)) or at the cathode.

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- = 3\text{Cr}^{3+} + 21\text{H}_2\text{O} \quad E^0 = 1.33 \text{ V} \quad (48)$$

Once the Cr reduction reaction neared completion, increase in hydroxide precipitation and co-precipitation occurred.

Figure 61 indicated that increase in sodium chloride concentration and current density led to improvement in the treatment process.

In the absence of sodium chloride, using aluminium anodes worked better than using steel anodes; the use of the former removed 95% of chromium in a 500 ppm solution at current density of 15 mA/cm$^2$ (cf. Fig. 62).

3.3.3. Solutions containing 100 or 50 ppm of chromium (VI)

As shown in Fig. 63, treatment of 100 ppm chromium was completed within 60 minutes for 5, 10, 15 mA/cm$^2$ current densities used in the presence of 0.03 M sodium chloride. But with increase of current density from 5 to 10 mA/cm$^2$ or above, there was a significant improvement in the removal of chromium for the first 30 min.

The results given in Figs. 64 and 65 showed that in the absence of sodium chloride the treatment process for Cr was not successful. In fact there was some increase in chromium content. The additional chromium probably came from the anodic corrosion of the steel anode.
Figure 61: Plots of chromium concentration versus treatment time at different NaCl concentrations. Electrodes: stainless steel. Temperature: Ambient. Current density: 15 mA/cm$^2$.

Figure 62: Plots showing Cr concentration versus time for a Cr solution at current density 15 mA/cm$^2$ in the absence of NaCl. Anodes: Aluminium. Initial [Cr] = 500 (± 5 %) ppm. Temperature: Ambient.
**Figure 63:** Cr concentration versus time for Cr solutions at different current densities in the presence of 0.03 mol/L NaCl. Electrodes: Stainless steel
Initial [Cr] = 100 (± 5 %) ppm. Temperature: Ambient

**Figure 64:** Plots showing the trend of Cr removal in the absence and in the presence of 0.03 mol/L NaCl at current density 15 mA/cm². Electrodes: Stainless steel
Initial [Cr] = 100 (± 5 %) ppm. Temperature: Ambient
Figure 65: Plots showing the trend of Cr removal in the absence and in the presence of 0.03 mol/L NaCl at current density 5 mA/cm². Electrodes: Stainless steel
Initial [Cr] = 100 (± 5 %) ppm. Temperature: Ambient
Under the same treatment conditions, the more dilute solutions could be treated in a shorter time, cf. Fig. 66.

As in the case of copper effluents, using steel anodes gave better treatment performance than using aluminium anodes if sodium chloride was present (cf. Fig. 67).

3.3.4. pH changes (Cr solutions):

From the pH-time curves shown in Figs. 68 & 69, the trend was slightly different from those obtained during the copper treatment. There were no significant changes in solution pH in the absence of sodium chloride, but the solution pH increased from 3.4 to 6.5 as the electrolysis was prolonged if the solution contained sodium chloride (0.03M and above). This increase in solution pH was also observed with aluminium anodes in the electrolysis process. (cf. Fig. 70)
Figure 66: Plots showing the treatment trend of different initial concentrations of chromium in 0.03 mol/L NaCl at 5 mA. Electrodes: Stainless steel. Temperature: Ambient.

Figure 67: Plots comparing the effectiveness of steel and Al anodes for treating chromium-containing solutions in the presence of 0.03 mol/L NaCl. Cathodes: Stainless steel. Temperature: Ambient.
Figure 68: pH changes with time during the treatment process for the 50 ppm Cr solutions in the present and absence of NaCl at different current densities. Electrodes: Stainless steel. Temperature: Ambient

Figure 69: pH changes with time during the treatment process for the 100 ppm Cr solutions in the present and absence of NaCl at different current densities. Electrodes: Stainless steel. Temperature: Ambient
Plots showing pH change versus treatment time for different heavy metal solutions at different current densities. Anodes: Aluminium. Temperature: Ambient NaCl added: 0.03 mol/L Mx = solution containing mixed of 100 ppm (each) Cu, Cr, Ni
3.4.1. Solutions containing nickel (II) ions

The treatment of solutions containing nickel (II) was less efficient than for treatment of Cu and Cr using the electrochemical co-precipitation method. Tests showed that even after 90 minutes of electrolysis of a 50 ppm nickel solution under similar conditions the Ni concentration could not be brought down to below 1 ppm.

3.4.2. Solutions containing 100 or 50 ppm nickel (II)

At a current density of 5 mA/cm², 70 % removal of Ni was obtained after 90 mins., as shown in Fig. 71. The addition of 0.03 M NaCl or 0.05 M NaCl did not lead to significant improvement.

In the absence of NaCl, the treatment at current density 10 mA/cm² led to a 50 % decrease in nickel concentration after 90 minutes. The presence of NaCl significantly improved ([Ni²⁺] = 7.2 ppm ± 5% after 90 minutes) removal although it showed slower removal in the first 15 mins. (cf. Fig. 72)

Increase in current density will improve the treatment efficiency as shown in Figs. 73 & 74. The lowest nickel concentration achieved at the end of the electrolysis treatment process (90 minutes) was 4.46 ppm ±5% for an initial 100 ppm Ni solution, and 1.18ppm ±5% for an initial 50 ppm Ni solution at current density 15 mA/cm² in the presence of 0.03 mol/L NaCl.

The amounts of nickel removed in the first 15 min. from the solutions containing 100ppm and 50ppm of Ni were similar at current densities 10 mA/cm² (about 20 ppm of Ni removed) and 15 mA/cm² (about 35 ppm of Ni removed), cf. Figs. 73 & 74.
Figure 71: A plots showing the treatment trend for Ni solutions in the presence of 0.03 mol/L and 0.05 mol/L NaCl.
Electrodes: Stainless steel. Temperature: Ambient
Current density: 5 mA/cm² Initial [Ni] = 100 (± 5 %) ppm.

Figure 72: Plots showing the effect of NaCl addition in the treatment trend of nickel-containing solutions at current density 10 mA/cm².
Electrodes: Stainless steel. Temperature: Ambient
Figure 73: Plots showing the effect of current density on the treatment trend of the nickel-containing solutions in the presence of 0.03 mol/L NaCl. Electrodes: Stainless steel. Temperature: Ambient. Initial [Ni] = 100 (± 5%) ppm.

Figure 74: Plots showing the effect of current density on the treatment trend of the nickel-containing solutions in the presence of 0.03 mol/L NaCl. Electrodes: Stainless steel. Temperature: Ambient. Initial [Ni] = 50 (± 5%) ppm.
3.4.3. pH changes in the Ni solutions during electrolysis.

From the pH-time curves shown in Fig 75, generally a rapid drop in pH for the first 15 minutes was observed, followed by a more gradual decrease in pH as the electrolysis was prolonged for solutions containing no sodium chloride. In the presence of sodium chloride, the solution pH remained relatively constant during the treatment process, cf. Figure 75.
Solution pH Vs. Treatment Time

100 ppm Ni, steel anode

Figure 75: pH changes with time during the treatment process for the 100 ppm Ni solutions in the present and absence of NaCl at different current densities. Electrodes: Stainless steel. Temperature: Ambient
3.5.1. Artificial effluent containing a mixture of (100 ± 5) ppm each of copper (II), chromium (VI) and nickel (II)

A similar treatment trend was obtained at current densities 10 mA/cm² to 20 mA/cm² (Figs 76-78) for a solution mixture of (100 ± 5) ppm each of copper, nickel, and chromium in the presence of 0.03 M sodium chloride. However, the treatment trend was different from those for the single metal ion solutions in the electrolysis treatment process.

As shown in Figs. 76-78, chromium ions were the first heavy metal removed from the mixed effluent, followed by copper ions. The nickel ions were more difficult to remove and there was a slight increase at the beginning when nickel from the steel anode dissolved into the solution. Increase in current density enhanced the rate of heavy metal removal.

With aluminium anodes (cf. Fig. 79), the treatment process showed a similar removal trend for the three different heavy metals. There was better removal rate for nickel at the beginning but efficiency decrease with time of electrolysis. The percentage of removal after 90 minutes was close to that obtained when steel anodes were used. Using steel anodes also resulted in higher Cr removal.

When the results for the mixture and those for single metal ion solutions were compared, there was little change in chromium removal efficiency, but different trends for copper and nickel removal were apparent. This could suggest that adsorption of chromium ions on iron hydrous oxides was not affected by the presence of the other test ions and that the iron oxide/hydroxide surfaces had a higher affinity for Cr³⁺ than Cu²⁺.

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Figure 76: Plots showing the treatment trends of different heavy metals with addition of 0.03 mol/L NaCl and at current density 10 mA/cm². Electrodes: Stainless steel. Temperature: Ambient

Figure 77: Plots showing the treatment trends of different heavy metals with addition of 0.03 mol/L NaCl and at current density 20 mA/cm². Electrodes: Stainless steel. Temperature: Ambient
Figure 78: Plots showing the treatment trends of different heavy metals with addition of 0.03 mol/L NaCl and at current density 15 mA/cm². Electrodes: Stainless steel. Temperature: Ambient

Figure 79: Plots showing the treatment trends of different heavy metals with addition of 0.03 mol/L NaCl and at current density 20 mA/cm² for steel and Al anodes. Temperature: Ambient
and Ni\textsuperscript{2+}.\textsuperscript{112-115} Copper was more readily precipitated/co-precipitated than Ni, (solubility of copper hydroxide is lower than nickel). At the beginning, only chromium and copper were removed from the solution, the rates of chromium and copper removal being similar to those for the solutions containing the respective single metals. Nickel appeared to be removed only after the Cr and Cu concentrations became sufficiently low. The more highly charged Cr ions probably adsorbed more readily than Cu and Ni (solubility of chromium oxide/ hydroxide is vary low compared to hydroxides/ oxides of Cu and Ni).

3.5.2. **Solution pH changes during electrolysis.**

From the pH-time curves shown in Fig 80, in the presence of NaCl, solution pH increased rapidly for the first 15 minutes, followed by a more gradual increase in pH as the electrolysis was prolonged with the use of aluminium anodes. When steel electrodes were used in the electrolysis, the pH initially increased and then fell after 45 or 60 minutes of electrolysis.
Figure 80: pH changes versus treatment time for solution containing 100 ppm (each) Cu, Ni and Cr ions (Mx) when different types of anodes were used at current density 20 mA/cm² and with the addition of 0.03 mol/L NaCl. Temperature: Ambient
3.6.1. Real effluent from a chrome-plating facility in a local electroplating factory

The electrolysis treatment process was carried out at a current density of 15 mA/cm² in the presence of 0.03 M NaCl by using steel anodes. As shown in Fig. 81, after 90 minutes, the chromium concentration in 2.5 liter solution, initially containing 139 ppm of chromium ions was reduced to below 1 ppm ( <0.02 ppm) and the solution pH increased to 6.5 from 3.8. This indicated that the process can be used for treating this type of effluent.
Figure 81: [Cr] versus time plot for the electrolytic treatment of a sample of real effluent from a chrome-plating facility in a local electroplating factory. 0.03 mol/L NaCl was added. Current density: 15 mA/cm². Electrodes: Stainless steel. Temperature: Ambient
3.7. Chemical Co-precipitation Method

Chemical co-precipitation using ferric ions as precipitant (carrier) was tested and the results are given in Table 17. This method could decrease the copper concentration to below the discharge limit too, provided the solution pH was high enough. Compared to the electrolysis method, the chemical method required shorter reaction times, but required addition of alkali (sodium hydroxide) to raise solution pH to the desired value for precipitation.

For chromium (VI) solutions, ferrous ions are required to convert Cr(VI) to Cr(III) first, before co-precipitation for successful treatment.\textsuperscript{15,42} But when ferric ions were directly applied into the chemical treatment process, the co-precipitation process was not successful and the final solution still contained high concentrations of chromium ions.

Chemical treatment of nickel solutions was less effective than for Cu removal when solution pH dropped below pH 8 and the amount of ferric iron required was more compared to copper. Below pH 8, precipitation of nickel hydroxide could not occur and nickel removal would depend solely on the co-precipitation process.

From the results obtained for Cr and Ni treatments, the chemical co-precipitation process was less successful than the electrolysis method.
Table 17: Results of treatment using the chemical co-precipitation method.

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<th>Original heavy metal in solution / ppm (±5%)</th>
<th>Ferric chloride used / ppm (±5%)</th>
<th>Solution pH after added ferric chloride</th>
<th>Final solution pH</th>
<th>Final heavy metal concentration / ppm (±5%)</th>
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3.8 Results of Potentiodynamic Study of Stainless Steel 304 and Aluminium 91100

Electrodes Behaviour

Fig. 82 shows a potential-log (current) curve for type 304 stainless steel in 0.1 M H$_2$SO$_4$ solution. Sweep rate was 2 mVs$^{-1}$. This test was carried out to check whether the material used reproduced known behaviour$^{116-118}$.

All the potentiodynamic plots recorded were steady-state plots obtained after several sweeps, cf. Figs. 83 & 84. Reproducible plots were obtained for the different scan rates (2mVs$^{-1}$, 10mVs$^{-1}$ and 20mVs$^{-1}$) used under similar conditions (Figs. 85-87).
Figure 82: Polarization plot for stainless steel 304 electrode in 1.0 mol/L H₂SO₄ solution at scan rate 2 mVs⁻¹, from -400 mV to +1000mV (reference to SCE).

Figure 83: Multiple polarization sweeps for stainless steel 304 electrode in 500 ppm copper solutions with addition of 0.03 mol/L NaCl. Scan rate: 10 mVs⁻¹, from -2000 to +2000mV (reference to SCE.).
Figure 84: Multiple polarization sweeps for stainless steel 304 electrode in 500 ppm copper solutions with addition of 0.03 mol/L NaCl. Scan rate: 20 mVs\(^{-1}\), from -2000 to +2000mV\(^{-1}\) (reference to SCE.).

Figure 85: Polarization plots for aluminium A91100 electrode in 500 ppm copper solutions at different scan rate: (a) 20 mVs\(^{-1}\), (b) 10 mVs\(^{-1}\), (c) 2 mVs\(^{-1}\), from -2000 to +2000mV (reference to SCE.).
Figure 86. Polarization plots for stainless steel 304 electrode in 100 ppm nickel solutions at different scan rate: (a) 20 mVs$^{-1}$, (b) 10 mVs$^{-1}$, (c) 2 mVs$^{-1}$, from -2000 to +2000mV (reference to SCE.).

Figure 87. Polarization plots for stainless steel 304 electrode in 100 ppm chromium solutions at different scan rate: (a) 20 mVs$^{-1}$, (b) 10 mVs$^{-1}$, (c) 2 mVs$^{-1}$, from -2000 to +2000mV (reference to SCE.).
3.8.1. Copper solution

Figs. 88 & 89, show polarization plots for type 304 stainless steel and Al electrodes, respectively, in solutions containing Cu in the absence of sodium chloride. From the plots, it can be seen that increase in concentration lowered the overpotential for copper deposition. In the cathodic region between -600mV and -1200 mV, the dominant reaction was probably copper deposition, diffusion limiting currents were observed. Mixed hydrogen evolution and copper deposition were observed at higher cathodic potentials (> -1200mV). It is well known that h.e.r. has a higher overpotential on Cu than on steel (iron). Therefore, deposited Cu increased h.e.r. (hydrogen evolution reaction) overpotential and slowed down the rate of h.e.r. and thus OH− generation.

The presence of copper ions seemed to have negligible effect on the potentiodynamic behaviours of Al and steel electrodes in solutions containing sodium chloride as shown in Figs. 90-92.

From Fig. 90, it can be deduced that increase in sodium chloride concentration from 0.03 M to 0.05 M did not affect electrode behaviour to a large extent. This explains the observation that increase in sodium chloride concentration from 0.03 M to 0.05 M led to only a slight improvement in the electrolysis treatment process. The degree of improvement depended on the current density used in the treatment.

For a given anodic current, the dissolution of aluminium required a lower overpotential than steel (iron) and the passivation potential region of the former is also narrower. This observation can be used to explain why the total voltages across the electrolysis cell were higher when stainless steel anodes were used compared to when
Figure 88.  Polarization plots for stainless steel 304 electrode in: (a) 500 ppm, (b) 100 ppm, (c) 50 ppm copper solutions.
Scan rate: 10 mVs\(^{-1}\), from -2000 to +2000mV (reference to SCE.).

Figure 89.  Polarization plots for aluminium A91100 electrode in:
(a) 500 ppm, (b) 100 ppm, (c) 50 ppm copper solutions.
Scan rate: 10 mVs\(^{-1}\), from -2000 to +2000mV (reference to SCE.).
Figure 90: Polarization plots for stainless steel 304 and aluminium electrodes in sodium chloride solution.  
(a) 0.05 mol/L NaCl, (b) 0.03 mol/L NaCl. Working electrode: aluminium  
(c) 0.05 mol/L NaCl, (d) 0.03 mol/L NaCl. Working electrode: stainless steel 304  
Scan rate: 10 mVs⁻¹, from -2000 to +2000mV (reference to SCE.).

Figure 91: Polarization plots for stainless steel 304 electrode in copper solutions with addition of 0.03 mol/l NaCl. (a) 500 ppm, (b) 100 ppm, (c) 50 ppm copper solutions.  
Scan rate: 10 mVs⁻¹, from -2000 to +2000mV (reference to SCE.).
Figure 92: Polarization plots for aluminium A91100 electrode in copper solutions with addition of 0.03 mol/l NaCl. (a) 500 ppm, (b) 100 ppm, (c) 50 ppm copper solutions. Scan rate: 10 mV/s, from -2000 to +2000 mV (reference to SCE).
aluminium anodes were used, in both cases, the cathode being stainless steel. (Appendix 9)

From Fig. 91 and 92, the plots showed similar electrode behaviour for three different copper concentrations, and no evidence of copper deposition in the cathodic region was observed. With stainless steel anodes, there were regions of passivation observed, and anodic dissolution mainly occurred above +1000mV (SCE) after the oxide film breakdown potential had been exceeded.

Figs 93 & 94 show plots for Al and steel electrodes used, with and without sodium chloride added for 500 ppm and 50 ppm copper ions solution. The addition of sodium chloride led to faster hydrogen evolution with negligible copper deposition. The treatment process for 50 ppm Cu solutions in the absence of NaCl required a higher over-voltage for a given current compared to that in which NaCl was added.

In the presence of Cl⁻ ions (from NaCl), the formation of copper chloride complexes, such as \( ([\text{CuCl}_2])^{119} \) etc., could have lowered (more cathodic) the deposition potential of copper, thus causing less or no deposition of copper during electrolysis. The adsorption of these complex anions on iron hydrous oxide surface will increase the solution pH according to reaction (44) and (45).
Figure 93: Polarization plots for stainless steel 304 and aluminium electrodes in 500 ppm copper solutions.
(a) absence of NaCl, (b) 0.03 mol/L NaCl. Working electrode: stainless steel 304.
(c) absence of NaCl, (d) 0.03 mol/L NaCl. Working electrode: aluminium A91100.
(e) absence of NaCl, (f) 0.03 mol/L NaCl. Electrodes: stainless steel 304.
Scan rate: 10 mVs⁻¹, from -2000 to +2000mV (reference to SCE.).

Figure 94: Polarization plots for stainless steel 304 and aluminium electrodes in 50 ppm copper solutions.
(a) absence of NaCl, (b) 0.03 mol/L NaCl. Working electrode: stainless steel 304.
(c) absence of NaCl, (d) 0.03 mol/L NaCl. Working electrode: aluminium A91100.
(e) absence of NaCl, (f) 0.03 mol/L NaCl. Electrodes: stainless steel 304.
Scan rate: 10 mVs⁻¹, from -2000 to +2000mV (reference to SCE.).
3.8.2 Nickel solutions

Figs. 95 & 96, show potentiodynamic plots for steel and aluminium working electrodes, respectively, in [Ni^{2+}] solutions in the absence of sodium chloride. Cathodic deposition of Ni was not observable.

Similar potentiodynamic plots were obtained for various nickel concentrations in the presence of NaCl as shown in Fig. 97 (stainless steel working electrode) and Fig. 98 (Al working electrode), except for the case when the Ni concentration was 500 ppm and the working electrode was aluminium where slight cathodic nickel deposition was observed prior to h.e.r. These results suggest that Ni ion removal in the treatment process relied mainly on the efficiency of the co-precipitation process.

Fig. 99 showed potentiodynamic plots for steel and Al electrodes in 100 ppm nickel solutions in the presence and absence of NaCl. Adding sodium chloride increased hydrogen evolution reaction rates and also lower the metal dissolution potentials.
Figure 95:  Polarization plots for stainless steel 304 working electrode in:
(a) 500 ppm, (b) 100 ppm, (c) 50 ppm nickel solutions.
Scan rate: 10 mVs⁻¹, from -2000 to +2000mV (reference to SCE.).

Figure 96:  Polarization plots for aluminium A91100 working electrode in:
(a) 500 ppm, (b) 100 ppm, (c) 50 ppm nickel solutions.
Scan rate: 10 mVs⁻¹, from -2000 to +2000mV (reference to SCE.).
Figure 97: Polarization plots for stainless steel 304 working electrode in nickel solutions with addition of 0.03 mol/l NaCl.
(a) 500 ppm, (b) 100 ppm, (c) 50 ppm nickel solutions.
Scan rate: 10 mV/s⁻¹, from -2000 to +2000 mV (reference to SCE.).

Figure 98: Polarization plots for aluminium A91100 working electrode in nickel solutions with addition of 0.03 mol/l NaCl.
(a) 500 ppm, (b) 100 ppm, (c) 50 ppm copper solutions.
Scan rate: 10 mV/s⁻¹, from -2000 to +2000 mV (reference to SCE.).
Figure 99: Polarization plots for stainless steel 304 and aluminium electrodes in 100 ppm nickel solutions.
(a) absence of NaCl, (b) 0.03 mol/L NaCl. Working electrode: stainless steel 304.
(c) absence of NaCl, (d) 0.03 mol/L NaCl. Working electrode: aluminium A91100.
(e) absence of NaCl. Electrodes: stainless steel 304.
Scan rate: 10 mVs⁻¹, from -2000 to +2000mV (reference to SCE.).
3.8.3 Chromium solutions

Figs 100 & 101, show potentiodynamic plots for steel and aluminium working electrodes in chromium solutions in the absence of sodium chloride. An extended anodic passivation region was observed in every one of these plots. Chromium reduction limiting current were observed in the cathodic region. The chromium ion in solution could inhibit anode dissolution of both iron and Al by forming an insoluble, chromium oxide layer on the working electrode surface. However, this passivation region was reduced in the presence of the sodium chloride as shown in Figs. 102 & 103. This may be because chloride ions are corrosive and lower the potentials for the breakdown of passivation films.

With reference to Fig 102, in the presence of sodium chloride, the potentiodynamic plots for stainless steel electrodes showed similar behaviour in 100 and 50 ppm chromium solutions with no clear evidence of cathodic reduction of the dichromate ion but this was observed for the 500 ppm Cr solution, before h.e.r.

Comparing the potentiodynamic plots for steel and aluminium in the absence and presence of sodium chloride in Fig. 103, it can be interpreted that addition of optimum quantities of sodium chloride will improve the treatment process (electrolysis) in terms of metal dissolution efficiency and hydrogen (thus OH⁻) generation.
**Figure 100:** Polarization plots for stainless steel 304 working electrode in:
(a) 500 ppm, (b) 100 ppm, (c) 50 ppm chromium solutions.
Scan rate: $10 \text{ mVs}^{-1}$, from $-2000$ to $+2000 \text{mV}$ (reference to SCE.).

**Figure 101:** Polarization plots for aluminium A91100 working electrode in:
(a) 500 ppm, (b) 100 ppm, (c) 50 ppm chromium solutions.
Scan rate: $10 \text{ mVs}^{-1}$, from $-2000$ to $+2000 \text{mV}$ (reference to SCE.).
Figure 102: Polarization plots for stainless steel 304 working electrode in chromium solutions with addition of 0.03 mol/L NaCl.
(a) 500 ppm, (b) 100 ppm, (c) 50 ppm chromium solutions.
Scan rate: 10 mV/s, from -2000 to +2000 mV (reference to SCE.).

Figure 103: Polarization plots for stainless steel 304 and aluminium electrodes in 100 ppm chromium solutions
(a) absence of NaCl, (b) 0.03 mol/L NaCl. Working electrode: stainless steel 304.
(c) absence of NaCl, (d) 0.03 mol/L NaCl. Working electrode: aluminium A91100.
Scan rate: 10 mV/s, from -2000 to +2000 mV (reference to SCE.).
3.8.4. Electrode behaviour in pure and mixed solutions of the heavy metals.

The potentiodynamic plots for steel electrodes show different behaviours in solutions containing the different kinds of heavy metals in Fig. 104. For the solution mixture of the three heavy metal ions, a higher cathodic currents were obtained at a given cathodic potential compared to the unmixed solution. This was caused by the increase in total heavy metals concentration. With steel anodes, there was more passivation in chromium or nickel solutions than in copper or the mixture of these three heavy metal ions. The small passivation range for copper containing solutions could also be caused by the auto-catalytic reaction of copper with iron in the steel electrode:

\[ \text{Cu}^{2+} + \text{Fe} \rightarrow \text{Fe}^{2+} + \text{Cu} \quad E^\circ = +0.7492 \text{V} \quad (49) \]

The adhered copper may then corrode at the anodic potentials applied.

In the presence of NaCl, the potentiodynamic plots were similar for all the different heavy metal solutions tested. Mixtures of the three heavy metal ions led to a higher current density (caused by the higher total heavy metals concentration) at a given anodic potential than the unmixed solutions as shown in Fig. 105.

For experiments with aluminium electrodes in solutions with absence of NaCl, the potentiodynamic plots showed a copper reduction at the cathodic potential region and the chromium solution showed a big passivation region cf. Figure 106. In the presence of sodium chloride, such features were not evident in the potentiodynamic plots, cf. Figs 107 and 108.
Figure 104: Polarization plots for stainless steel 304 electrodes in:
(a) 100 ppm chromium, (b) 100 ppm copper, (c) 100 ppm nickel solutions
(d) 100 ppm chromium, nickel and copper each
Scan rate: 10 mVs$^{-1}$, from -2000 to 2000 mV (reference to SCE.).

Figure 105: Polarization plots for stainless steel 304 electrodes in:
(a) 100 ppm chromium, (b) 100 ppm copper, (c) 100 ppm nickel solutions
(d) 100 ppm (each) chromium, nickel and copper solution, with addition of 0.03 mol/L NaCl
Scan rate: 10 mVs$^{-1}$, from -2000 to 2000 mV (reference to SCE.).
Figure 106: Polarization plots for aluminium A91100 working electrode in:
(a) 100 ppm Cr, (b) 100 ppm Cu, (c) 100 ppm Ni, (d) mixed of 100 ppm (each) Cu, Ni, Cr solutions.
Scan rate: 10 mVs$^{-1}$, from -2000 to +2000mV (reference to SCE.).

Figure 107: Polarization plots for aluminium A91100 working electrode in:
(a) 100 ppm Cr, (b) 100 ppm Cu, (c) mixed of 100 ppm (each) of Cu, Ni, Cr solutions with addition of 0.03 mol/l NaCl.
Scan rate: 10 mVs$^{-1}$, from -2000 to +2000mV (reference to SCE.).
Figure 108: Polarization plots for aluminium A91100 working electrode in:
(a) 50 ppm Cr, (b) 50 ppm Cu, (c) 50 ppm Ni, solutions with addition of 0.03 mol/l NaCl.
Scan rate: 10 mVs⁻¹, from -2000 to +2000mV (reference to SCE.)