FeCl₃ coagulant production from waste pickle liquor using electrolysis

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Abstract. Pickling is a typical method used in a cold milling plant to remove impurities from hot rolled coil by immersing the coil in strong acidic solution. The spent acidic solution or waste pickle liquor (WPL) requires certain waste treatment before it can be disposed to environment because of its metallic ion and acid content. WPL contains a number of metallic ions that can be utilized as ferric chloride coagulant. The purpose of this paper is to evaluate the kinetics of Fe²⁺ oxidation into FeCl₃ and the performance of the ferric chloride coagulant using the proposed electrolysis configuration. The electrolysis process was conducted in ambient condition with voltage 3 & 6 V, electrolysis time of 120 minutes, and addition of excess NaCl or HCl. The result shows that metal impurities in WPL and excess chlorine do not significantly affect the Fe²⁺ conversion. It can also be concluded that the optimum condition for electrolysis is using 6V of voltage, 90 minutes of electrolysis time, and excess chlorine at 0% stoichiometry which gave 60% conversion of Fe²⁺ in WPL. Due to the equilibrium between the Fe³⁺ dan Fe⁴⁺ which is formed during electrolysis process, the full conversion of Fe²⁺ is not possible yet, and the maximum conversion of Fe²⁺ is 60%. The presence of impurities in WPL is proven not affecting the Fe²⁺ conversion during the electrolysis process.

1. Introduction
The finishing stage of the steel industry consists of pickling, galvanizing and plating process, which aims to remove impurities in the form of dust, scale, and rust on the steel [4]. Pickling process is a process in which the steel is immersed in concentrated acid to remove rust from the steel surface [1]. The pickling process will produce liquid waste in the form of waste pickle liquor (WPL) in large quantities. WPL contains metallic ion and acid content that classified it as hazardous waste for the environment[6]. In this research, the WPL feed contains 120 g/L of Fe²⁺ and 40 g/L of HCl. To prevent environmental pollution, direct processing by steel industries or third parties is required before WPL can be disposed into the environment [11].

Commonly WPL treatment carried out by the steel industries aims to recover the acids and the dissolved metallic ions [8]. The recovery of the acids and metallic ions in WPL can be done through various methods. The treatment methods for WPL are pyrometallurgy, crystallization, separation using membrane, and liquid extraction [13].

Another alternative for WPL treatment is to use an oxidation method, specifically the oxidation of FeCl₂ in WPL that is produced from steel pickling process with HCl solution. To oxidize FeCl₂ in WPL,
oxidizer that can be used also diverse, but the most economical is to use Cl₂ gas. Oxidation of FeCl₂ to FeCl₃ by using Cl₂ gas is more economical compared to other oxidizing agents because WPL contains Cl compound which can be oxidized to Cl₂ gas to minimize treatment costs. Moreover, other oxidizer such as H₂O₂ is expensive and Cl₂ gas is quite difficult in handling process if used. Previous study from Pradana had proven the feasibility for electrolyzing WPL, but the dosage from the produced FeCl₃ are 155 and 300 ppm [11]. The aim of this paper is to determine the effect of metal impurities with Fe²⁺ conversion in WPL, determine the optimum equipment set up and condition for WPL electrolysis, and producing FeCl₃ coagulant with higher performance.

2. Methodology
This research consists of 5 stages, the first stage is making a feed solution to be electrolyzed, the second stage is electrolyzing feed solution, and the third stage is concentrating the sample through distillation. The fourth stage is determining the concentration of ferro (Fe²⁺) and ferric (Fe³⁺) ions from each sample, and the last stage is jar test to determine the quality of the FeCl₃ coagulant produced.

The materials required for the experiment are NaCl salt, H₂SO₄, H₃PO₄, HCl, SnCl₂, HgCl₂, K₂Cr₂O₇, Na₂S₂O₃ 0,1 N, and KI from Merck, mixed acid which was created from mix of H₂SO₄ and H₃PO₄ each at 5% with ratio of 1:1, and demineralized water.

Feed solution is made by mixing WPL with NaCl or HCl. NaCl and HCl are used to increase the content of chlorine compounds in the feed (excess). Therefore, the oxidation rate will not be affected by the concentration of chlorine compounds, and the oxidation rate can be assumed to be influenced only by Fe²⁺ concentration. In order to create the electrolysis feed, WPL is mixed with HCl or NaCl in a beaker and stirred for 15-20 minutes. The finished feed is then electrolyzed using the configuration in figure 1. The electrolysis process is done in 120 minutes with 10 minutes interval time for sampling.

![Figure 1. The electrolysis configuration](image)

Notes:
1. DC electrical source
2. Platinum electrodes
3. Electrolysis reactor
4. Liquid gas contactor with raschig ring
5. Hose
6. Gas collector
7. Sample collector

The gas collector is used to dissolve the excess Cl₂ in water. The electrolysis samples are then distilled. The purpose of the distillation is to increase the FeCl₃ concentration in the sample to meet the commercial criteria for FeCl₃ coagulant. The distillation process is carried out using a simple distillation flask where the sample is heated in a boiling flask and the evaporated water is cooled with a condenser. The distillation process will reduce the volume up to 60% sample’s volume. To analyze the content of Fe²⁺ and Fe³⁺ ions in the sample, an analysis of redox titration is performed using potassium dichromate for FeCl₂ and sodium thiosulfate for FeCl₃. The last stage is to perform jar test in order to determine the quality of FeCl₃ coagulant.
3. Result and Discussion

3.1. Electrolysis configuration

The proposed electrolysis configuration had been tested on various models. The process variables that had been studied were the amount of oxidation process needed, the use of contactor column, electrodes type, the source of excess chlorine, and whether or not the electrolyzed product is distilled.

3.1.1. Oxidation process. The oxidation process of Fe\(^{2+}\) compounds in WPL can be done through one or two stages of oxidation. The oxidant used in the one-stage-oxidation is Cl\(_2\) gas produced by electrolysis of Cl\(^-\) ions in WPL (with excess chlorine). In two-stage oxidation, after oxidation with chlorine gas, the remaining Fe\(^{2+}\) is further oxidized by adding NaOCl to the electrolysis product. The coagulant performance from both methods can be seen in Table 2.

### Table 1. One and two stages coagulant performance

| Sample         | Dose (ppm) | pH  | TDS (µS/cm) | Turbidity (NTU) |
|----------------|------------|-----|-------------|-----------------|
| One-stage      | 60         | 5.4 | 123.1       | 0.86            |
| Two-Stage      | 110        | 5.81| 169.6       | 1.6             |

From Table 1, FeCl\(_3\) coagulant produce by a single-stage oxidation process not only able to reduce TDS and turbidity from the treated water in jar test lower than the two-stages, but also has lower dose than the two-stage.

3.1.2. Contactor column. The function of the contactor column is to prolong the contact time between Cl\(_2\) gas produced from the electrolysis process with FeCl\(_2\) in order to increase Fe\(^{2+}\) conversion. The result of FeCl\(_3\) coagulant which is produced with and without contactor column can be seen in Table 2 and Table 3. The coagulant produced using contactor column (filled by raschig ring) results in higher conversion and coagulant performance because of the packing increase both reaction time and the contact between chlorine gas with WPL.

### Table 2. Effect of contactor column

| Sample         | Fe\(^{2+}\) (g/L) | Fe\(^{3+}\) (g/L) | Conversion (%) |
|----------------|------------------|------------------|---------------|
| Without column | 51.00            | 72.02            | 58.54         |
| With column    | 44.28            | 67.53            | 60.4          |

### Table 3. Effect of packing

| Sample         | Dose (ppm) | pH  | TDS (µS/cm) | Turbidity (NTU) |
|----------------|------------|-----|-------------|-----------------|
| Without packing| 250        | 5.62| 206         | 1.4             |
| With packing   | 200        | 5.4 | 166         | 1.5             |

3.1.3. Electrodes type. The type of electrodes in an electrolysis reaction needs to be considered since some electrodes are inert. The ability of certain electrodes in conducting electrons also affects the conversion of Fe\(^{2+}\) during electrolysis. Table 4 shows the performance of coagulants produced using iron and platinum electrodes after being electrolyzed for 10 minutes.
Table 4. Effect of electrode

| Sample       | Fe^{2+} (g/L) | Fe^{3+} (g/L) | Conversion (%) |
|--------------|---------------|---------------|---------------|
| Iron electrode | 80.36         | 24.42         | 23.30         |
| Platinum electrode | 68.90         | 43.60         | 38.76         |

Based on Table 4, the conversion from platinum electrode is higher than iron electrode. In the electrolysis process using iron electrode, there is a side reaction of oxidation Fe into Fe^{2+}. This reaction has higher selectivity than the oxidation of Cl\textsuperscript{-}, so the amount of Fe^{2+} will accumulate in the electrolysis reactor overtime. Though it seems like the amount of FeCl\textsubscript{3} produced will increase, but on the contrary, the number of electrons which is needed to oxidize Cl\textsuperscript{-} is decreasing and lower the Cl\textsubscript{2} gas production. In platinum electrode, this phenomenon does not occur because of its inert nature. Based on those reasons, platinum electrodes are selected as electrodes to be used in the electrolysis process.

3.1.4. Chlorine sources. Table 5 and 6 below show the effect of excess chlorine from HCl and NaCl.

Table 5. Effect of chlorine sources and feed solution pH

| No | Sample       | Fe^{2+} (g/L) | Fe^{3+} (g/L) | Conversion (%) |
|----|--------------|---------------|---------------|---------------|
| -  | WPL + NaOH   | 80.26         | 31.27         | 28.04         |
| -  | WPL + HCl 100 ml | 62.03         | 43.42         | 41.18         |
| 1  | WPL + HCl 320 ml | 39.47         | 40.32         | 50.53         |
| 2  | WPL +NaCl excess 10% | 73.31         | 51.32         | 41.18         |
| -  | WPL +NaCl excess 75% | 69.36         | 40.32         | 36.76         |

Table 6. Coagulant performance from excess HCl and NaCl

| Sample Number | Dose (ppm) | pH | TDS (µS/cm) | Turbidity (NTU) |
|---------------|------------|----|-------------|-----------------|
| WPL only      | 350        | 3.14 | 590         | 2.05            |
| 1             | 300        | 3.20 | 482         | 2.9             |
| 2             | 250        | 3.61 | 257         | 2.8             |

Based on Table 5, the addition of 100-320 ml HCl has a positive effect on Fe^{3+} conversion, while the addition of NaCl above 10% excess decreases the Fe^{2+} conversion. The addition of base (NaOH) to WPL reduced the conversion of Fe^{2+}. The conversion reduces because according to the Pourbaix diagram, in order to form Fe^{3+} the feed solution must be in acidic condition \[2\], and the base addition will make it harder for FeCl\textsubscript{3} to be formed. As shown in Table 6, both TDS and turbidity increases from the jar test result. This indicates that the addition of excessive chlorine sources will leave residual in the coagulant product. The phenomenon should be avoided to prevent the coagulant performance from decreasing due to the impurity which is carried. The effect of excessive addition of HCl is that the coagulant product will be too acidic, while excessive NaCl increases the TDS on the treated water.

3.1.5. Product concentration. Table 7 shows the difference on performance from electrolyzed samples with and without product distillation. The distillation process is able to increase the concentration of FeCl\textsubscript{3} in the product, hence it requires a lower dose than the non-distilled samples in the jar test.
Table 7. Effect of product concentration

| Sample          | Dose (ppm) | pH  | TDS (µS/cm) | Turbidity (NTU) |
|-----------------|------------|-----|-------------|-----------------|
| Feed 1          | 250        | 5.62| 206         | 1.4             |
| Feed 2          | 200        | 5.40| 166         | 1.5             |
| Distilled feed 1| 80         | 5.65| 147.4       | 1.2             |
| Distilled feed 2| 60         | 5.40| 123.1       | 0.86            |

3.2. Kinetic study

3.2.1. Kinetic profile of Fe^{2+} oxidation. Figure 2 shows the kinetic profile from the oxidation process of Fe^{2+} into Fe^{3+}.

![Figure 2](image.png)

**Figure 2.** The kinetic profile from Fe^{2+} oxidation

As shown in Figure 2, the kinetic profile of Fe^{2+} oxidation represents a 1st order reaction. The concentrations of Fe^{2+} and Fe^{3+} do not change after the electrolysis process is carried out for more than 90 minutes. This can be seen from the non-intersecting Fe^{2+} and Fe^{3+} concentration curves, in addition for samples which are electrolyzed for more than two hours, the conversion is similar with the result from the two-hour electrolyzed samples. It means that the oxidation process will reach an equilibrium at certain Fe^{2+} and Fe^{3+} concentrations, so the 100% conversion of FeCl_{2} into FeCl_{3} cannot be achieved. In addition, experiments to electrolyze WPL in more than 2 hours with higher voltage had been carried out, however, the highest conversion of FeCl_{3} that can be achieved was only around 60%. Figure 3 below shows the relation between voltage and Fe^{2+} conversion.
Higher voltage during electrolyzing process gives higher conversion since more electron are transferred and more Cl$_2$ created. However, higher voltage also means more thermal loss due to thermal dissipation whether from the DC generator, or the electrodes.

### 3.2.2. Excess chlorine effect

The data from the main experiments in this research is shown in Table 8.

#### Table 8. Effect of product concentration

| Voltage | Excess Variation | Conversion |
|---------|------------------|------------|
| 3 V     | 0% NaCl          | 18.2%      |
|         | 25% NaCl         | 20.0%      |
|         | 50% NaCl         | 21.8%      |
|         | 0% HCl           | 25.5%      |
|         | 25% HCl          | 20.9%      |
|         | 50% HCl          | 25.0%      |
|         | Synthetic WPL 0% NaCl | 51.8%  |
|         | 0% NaCl          | 50.9%      |
|         | 25% NaCl         | 49.1%      |
| 6 V     | 50% NaCl         | 55.9%      |
|         | 0% HCl           | 52.7%      |
|         | 25% HCl          | 59.1%      |
|         | 50% HCl          | 60.0%      |

As shown in Table 8, the excess variation of 0%, 25%, and 50% HCl for 3 and 6V voltage have relatively similar conversion. This shows that the conversion of FeCl$_2$ during the electrolysis process is not significantly affected by the excess chlorine condition. The optimum excess chlorine more likely in saturated chlorine condition (0% excess) rather than 25 or 50% excess stoichiometry. The amount of chlorine needed to saturate a WPL solution is influenced by temperature and the HCl content in WPL [10].

### 3.2.3. Effect of metal impurities in WPL

Alongside with Fe ions, there are other ions such as Sn, Ni, Cu, and others. The impurities in WPL do not affect the Fe$^{2+}$ conversion, as shown by results in Table 9.
Table 9. Effect of impurities

| Voltage | Excess Variation | Conversion |
|---------|------------------|------------|
| Synthetic WPL 0% NaCl | 51.8% | |
| 6 V | 0% NaCl | 50.9% |
| | 0% HCl | 52.7% |

The synthetic WPL was made from pure FeCl$_2$ which is dissolved in demineralized water. HCl was then added to duplicate the concentration from the Fe$^{2+}$ ions and the acidic concentration. The result proves that the presence of impurities in WPL does not affect the Fe$^{2+}$ conversion. If the impurities in WPL inhibit the oxidation reaction, the conversion of the synthetic WPL should be lower than the saturated WPL.

3.3. Coagulant performance

Samples chosen to be tested in jar test were the excess 25% HCl, 50% HCl, 50% NaCl, and the synthetic WPL. The concentration of FeCl$_3$ coagulant in each sample is shown in Table 10.

Table 10. FeCl$_3$ concentration in samples

| Variation       | [Fe$^{3+}$] before distillation (g/L) | [Fe$^{3+}$] after distillation (g/L) |
|-----------------|--------------------------------------|-------------------------------------|
| 50% HCl         | 72.86                                | 121.85                              |
| 25% HCl         | 73.91                                | 112.31                              |
| 50% NaCl        | 63.86                                | 60.78                               |
| Synthetic WPL   | 45.37                                | 75.58                               |

The coagulant concentration in samples increases due to the distillation except for 50% NaCl sample. When the distilled sample was cooled, the NaCl solubility decreased and the dissolved NaCl in the sample crystallized. Because of the crystalized NaCl, the separation process was difficult for the distilled sample even after using a vacuum filter. To aid the separation process, demineralized water is used. Therefore, there was a decrease in the concentration of the Fe$^{3+}$ coagulant in the 50% NaCl sample. The result from the jar testing on those samples is shown in Table 11.

Table 11. Results of jar test

| Sample        | Dose (ppm) | pH   | TDS (µS/cm) | Turbidity (NTU) |
|---------------|------------|------|-------------|-----------------|
| Target        | -          | 7.8  | <250        | <3              |
| Dirty water   | -          | 7.52 | 304         | 43              |
| 50% HCl       | 125        | 2.61 | 2.10        | 27              |
| 25% HCl       | 125        | 2.55 | 2.32        | 30              |
| 50% NaCl      | 100        | 2.50 | 2.33        | 10              |
| Synthetic WPL | 25         | 5.70 | 3.01        | <1              |

From the jar test analysis, the FeCl$_3$ coagulant samples had been able to reduce TDS in dirty water in accordance with the required target of a commercial coagulant. However, as shown in Table 11 there is no sample from original WPL which able to meet the turbidity standard. The turbidity standards can only be met by coagulant sample produced from synthetic WPL. In addition, the treated waters pH was
around 3 except for synthetic WPL samples. The low pH from the treated water was caused by HCl residuals which were present in the distilled FeCl₃ coagulant. To overcome this problem further separation is needed to separate the HCl residuals from the FeCl₃ coagulant.

4. Conclusion

The optimum configuration to electrolyze WPL is one-stage oxidation using platinum electrodes and contactor column which packed by rasching ring. The electrolysis process parameters are 6V voltage, electrolysis time is 90 minutes, and excess chlorine at 0% using NaCl as the chlorine source. In order to increase the coagulant performance and lower the usage dose of the coagulant, distillation need to be done to the electrolyzed product.

Due to the equilibrium between the Fe²⁺ dan Fe³⁺ which is formed during electrolysis process, the full conversion of Fe²⁺ is not possible yet, and the maximum conversion of Fe²⁺ is 60%. Though the excess of chlorine does not affect the conversion significantly, the source of chlorine must be considered because it will affect the coagulant performance. The presence of impurities in WPL was not affecting the Fe²⁺ conversion during the electrolysis process and though produced FeCl₃ has lower the dosage, further study is required to enhance the FeCl₃ coagulant because the pH and turbidity have not been met.

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