Lauryl Amine as heavy metal collector of boiler ash from pulp and paper mill waste

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Abstract. The increasing demand of pulp and paper products, will following with the growing pulp and paper industry and generate significant mill waste. The total waste reached 1/3 of the amount raw materials used and ash boiler is the waste with the largest percentage of 52%. For that it takes effort to manage the existing waste. The boiler ash contained the chemical elements, it can be utilized such as fertilizer, because it also contains transition metals in form of heavy metal such as Cadmium (Cd), Cobalt (Co), Chrome (Cr), Cupprum (Cu), Ferrum (Fe), Nickel (Ni), and Zinc (Zn), the use of boiler ash must follow the threshold specified by the Government. Several studies have been undertaken to reduce and extract heavy metals from ash and sand of the boiler by using carbon dioxide as its ligand. Electrochemical method was used to remove and recovery of heavy metals from the incenerator. This study focused on removal of heavy metals using Lauryl Amine as collector and three solvents namely Dichloromethane, Ethanol and n-Hexane. The treatments was able to extract the heavy metal and generally reduce the heavy metal content of ash boiler pulp and paper mill waste. The combination treatment used to reduce the heavy metal content of 5 gram Lauryl Amine collector in Dichloromethane solvent for 4 hours process time.

1. Introduction
The pulp and paper industry generate significant mill waste such as boiler ash and lime by-products (lime mud, grit, and dregs) daily. As example, a pulp and paper company namely PT. Riau Andalan Pulp and Paper (RAPP) in 2012 produce 225,410 ton/adt of boiler ash, 83,380 ton/adt of dregs and grits, 66,138 ton/adt of lime mud, 24,529 ton/adt of screen reject[1]. Most of these products are placed in landfills. RAPP is examining the feasibility of these solid waste in road making, brick production and explore their use to be including in the construction and concrete manufacture. Land application of these solid waste especially boiler ash, for its potential as soil liming materials may also be conducted further as long as it meet Indonesia’s regulatory requirement. The research on the applications of waste is necessary.

Several studies shown that the nutrient content of these boiler and lime ash is generally low, especially for N, P and K, they have high pH and the ability to increase soil alkalinity [2]. Application of boilers and other wood ash to soil can improve the growth or yields[3-5]. Evaluation on boiler ash as soil amelioration on pulp wood plantation *Acacia crassicarpa* grown in peat areas have been also
conducted and in addition it increase the plant growth and yield, boiler ash application at 10 kg/tree do not change the peat properties[6]. However, considering its heavy metal content such as Cd, Co, Cr, Cu, Ni, Fe, and Zn that may potentially toxic to the plant when its concentration exceed the threshold that plant can tolerate and protecting environment by preventing soil contaminaton, the effort to explore the possibility to reduce or remove heavy metal content of boiler ash to meet the Indonesia’s regulatory requirement is important [7–9].

Some studies have been undertaken to reduce and extract heavy metals from ash and sand of the boiler using carbon dioxide as its ligand[10], absorption of Cs +, Co 2+, Eu 3+ on zirconium silikat [11], extraction [12,13], biosorption [14], pythoremediation[15] and separationkromatography sodium, cobalt and europium [16]. This study focused on removal of heavy metals that can be treated by converting the heavy metal into complex compounds with organonitrogen or amine compounds. In this study Lauryl Amine used as a collector to reduce the heavy metals.

The removal of heavy metals found in boiler ash can be done by converting the metal transition into complex compounds with organonitrogen or amine compounds. The formation of complex compounds with heavy metals by two phases (solid-solution) is determined by various factors such as collector type, collector concentration, particle size, stirring rate, reaction temperature, and contact time of the ligand solution with waste. Amines have distinctive properties that allow them to be absorbed in solids and form cationic films. In this research, the Lauryl Amine was used as collector with three different solvents including Dichlorometane, Ethanol and n-Hexane.

2. Material and method

This research was conducted in Organic Chemical Laboratory, Faculty of Matematic and Natural Science, University of Sumatera Utara, Medan and in Soil Laboratory of PT. Riau Andalan Pulp And Paper Pangkalan (RAPP) Kerinci, Pelalawan, Riau. The samples are obtained from the combustion boiler ash pulp and paper mill of PT. RAPP.

The boiler ash sample was smoothed to 400 mesh sizes, and then the sample was placed in an oven with 100°C for 30 minutes. A 5 g ash is prepared and separated then used as a control. 5 g ash was added to 250 ml Erlenmeyer which is filled with 5 g of lauryl amine collector, 30 ml of Dichloromethane solvent. This mixture was stirred for 4 hours, then it is left until the upper and lower layers are formed, the two layers were separated using a separation funnel. The bottom layer as slurry was dried using oven. Once the dried sample is obtained, the sample then analyzed using Inductively Couple Plasma (ICP) to determine the content of heavy metal. The same procedure was applied to Lauryl Amines with extraction time 8 hours. The same procedure was applied for Lauryl Amine 15 gram in Dichloromethane solvent with extraction time of 4 hours and 8 hours.

For ethanol, the same procedures also conducted for 30 ml ethanol with the following procedure. The 5 g ash was added to 250 ml Erlenmeyer which was filled with 5 g of Lauryl Amine collector, 30 ml ethanol. This mixture was stirred for 4 hours, then it is left until the upper and lower layers are formed, the two layers were separated using a separation funnel. The bottom layer as slurry was dried using oven. Once the dried sample is obtained, then the sample was analyzed using Inductively Couple Plasma (ICP) to determine the heavy metal content. The same procedure was applied to Lauryl Amine with extraction time 8 hours and also for Lauryl Amine 15 gram in Ethanol solvent with extraction time of 4 hours and 8 hours. For n-hexane the same procedure was also applied.

3. Results and discussion

3.1. Cadmium

All Lauryl Amine collector treatments combination with three solvents able to reduce Cadmium content compared than control (Figure 1 and Table 1). In term of dosage, 15 gram treatment combination is slightly better than 5 gram, the length of process time 4 hours is better than 8 hours except for n-Hexane with 5 gr Lauryl Amine. The highest Cadmium reduction at 42.5% shown by treatments with Dichloromethane both for 4 hours and 8 hours. The 5 gram Lauryl Amine in
Dichloromethane solvent for 4 hours process time is the best treatment that effectively and efficiently reduce Cadmium content from boiler ash.

![Figure 1](image)

**Figure 1.** Cadmium content on Lauryl Amine collector and three different solvents at 4 and 8 hours process length.

| Lauryl Amine Dose (gr) | Solvent       | Concentration (mg/kg) | Reduction to control (%) |
|------------------------|---------------|-----------------------|--------------------------|
|                        |               | 4 hours    | 8 hours | 4 hours | 8 hours |
| 5                      | Dichloromethane | 2.1        | 2.1     | 42.5     | 42.5    |
|                        | Ethanol       | 2.5        | 2.7     | 33.6     | 27.4    |
|                        | n-Hexane      | 2.7        | 2.7     | 26.8     | 27.1    |
| 15                     | Dichloromethane | 2.2        | 2.2     | 41.5     | 39.8    |
|                        | Ethanol       | 2.1        | 2.3     | 42.0     | 36.6    |
|                        | n-Hexane      | 2.2        | 2.6     | 40.1     | 28.7    |
| Control                |               | 3.69       |         |          |         |

### 3.2. Cobalt
Similar to Cadmium, Lauryl Amine collector and all three solvents treatments shown the reduction on Cobalt content compare than Control (Figure 2 and Table 2). Dosage of 15 gram show higher reduction compare than 5 gram, except in Dichloromethane solvent. Lauryl Amine collector at 15 gram with Dichloromethane solvent in 8 hours process time show the highest Cobalt reduction at 41% followed by ethanol solvent in 4 hours process time at 35.7%.

### 3.3. Chromium
Lauryl Amine collector and all three solvents treatments show reduction on Chromium content compare than Control (Figure 3), with range of 19.5–34.3% and 13.3 – 34.9% for length of process time 4 hours and 8 hours respectively (Table 3). Lauryl Amine collector at 15 gram dosage is better than 5 gram, while 4 hours process time better than 8 hours, except for Dichloromethane solvent. The highest Chromium reduction is shown by 15 gram Lauryl Amine in Dichloromethane solvent for 8
hours process time at 34.9% it is not so much different with 5 gram for 4 hours process time at 32.2%. Considering less Lauryl Amine and time used, treatment with 5 gram Lauryl Amine collector in Dichloromethane solvent for 4 hours process time is the best option.

![Figure 2. Cobalt content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length](image)

**Table 2.** Cobalt content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length; and it reduction to control.

| Lauryl Amine Dose (gr) | Solvent            | Concentration (mg/kg) | Reduction to control (%) |
|------------------------|--------------------|-----------------------|--------------------------|
|                        |                    | 4 hours  | 8 hours  | 4 hours  | 8 hours  |
| 5                      | Dichloromethane    | 4.03     | 4.18     | 32.7     | 30.2     |
|                        | Ethanol            | 4.44     | 4.99     | 25.9     | 16.7     |
|                        | n-Hexane           | 4.55     | 5.05     | 24.0     | 15.7     |
| 15                     | Dichloromethane    | 4.11     | 3.54     | 31.4     | 40.9     |
|                        | Ethanol            | 3.85     | 4.29     | 35.7     | 28.4     |
|                        | n-Hexane           | 3.96     | 4.88     | 33.9     | 18.5     |
| Control                |                    | 5.99     |          |          |          |

3.4. **Cuprum (copper)**
Reduction of Cuprum content occurs in all treatments combination Lauryl Amine collector and all three solvents (Figure 4 and Table 4). The highest Cuprum reduction is on Lauryl Amine collector at 15 gram with Dichloromethane solvent in 8 hours process time at 39.2%. The 15 gram dosage produce higher reduction in all solvent combination compare than 5 gram dosage. 4 hours processing time produce higher reduction compare to 8 hours, except for Dichloromethane solvent. It is more efficient to use 5 gram Lauryl Amine in Dichloromethane solvent for 4 hours process time.

3.5. **Ferrum**
Ferrum content of boiler ash is reduce after treated with Lauryl Amine collector with all three solvents (Figure 5). Overall the Lauryl Amine at 15 gram dosage produce higher reduction compared than 5 gram in both 4 hours and 8 hours process time, except in Dichloromethane solvent (Table 3). Process time of 4 hours will be reducing the heavy metal higher than 8 hours, except in Dichloromethane solvent.
solvent. The highest Ferrum reduction at 41.5% it shown that 15 gram Lauryl Amine in Dichloromethane solvent with 8 hours process time.

![Chromium Content Graph]

**Figure 3.** Chromium content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length.

**Table 3.** Chromium content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length; and it reduction to control

| Lauryl Amine Dose (gr) | Solvent          | Concentration (mg/kg) | Reduction to control (%) |
|------------------------|------------------|-----------------------|--------------------------|
|                        |                  | 4 hours | 8 hours | 4 hours | 8 hours     |
| 5                      | Dichloromethane  | 8.9     | 9.37    | 32.3    | 28.7        |
|                        | Ethanol          | 10      | 10.99   | 23.9    | 16.4        |
|                        | n-Hexane         | 10.58   | 11.39   | 19.5    | 13.3        |
| 15                     | Dichloromethane  | 9.03    | 8.56    | 31.3    | 34.9        |
|                        | Ethanol          | 8.77    | 9.93    | 33.3    | 24.4        |
|                        | n-Hexane         | 8.63    | 10.91   | 34.3    | 17.0        |
| Control                |                  | 13.14   |         |         |             |
Figure 4. Cuprum content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length.

Table 4. Cuprum content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length; and its reduction to control.

| Lauryl Amine Dose (gr) | Solvent    | Concentration (mg/kg) | Reduction to control (%) |
|------------------------|------------|------------------------|--------------------------|
|                        |            | 4 hours | 8 hours | 4 hours | 8 hours |
| 5                      | Dichloromethane | 25,35   | 25,44   | 34,8    | 34,6    |
|                        | Ethanol    | 28,19   | 31,39   | 27,5    | 19,3    |
|                        | n-Hexane   | 31,07   | 35,22   | 20,1    | 9,5     |
| 15                     | Dichloromethane | 24,98   | 23,65   | 35,8    | 39,2    |
|                        | Ethanol    | 25,41   | 29,72   | 34,7    | 23,6    |
|                        | n-Hexane   | 26,18   | 33,28   | 32,7    | 14,4    |
| Control                |            | 38.9    |          |          |         |

Figure 5. Ferrum content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length.
Table 5. Ferrum content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length; and it reduction to control.

| Lauryl Amine Dose (gr) | Solvent       | Concentration (mg/kg) | Reduction to control (%) |
|------------------------|---------------|-----------------------|--------------------------|
|                        |               | 4 hours  | 8 hours  | 4 hours  | 8 hours  |
| 5                      | Dichloromethane | 7939    | 9131    | 31.8     | 21.6     |
|                        | Ethanol       | 9475    | 10725   | 18.6     | 7.9      |
|                        | n-Hexane      | 9166    | 10615   | 21.3     | 8.8      |
| 15                     | Dichloromethane | 8777    | 6814    | 24.6     | 41.5     |
|                        | Ethanol       | 7952    | 9169    | 31.7     | 21.2     |
|                        | n-Hexane      | 7841    | 10363   | 32.6     | 11.0     |
| Control                |               | 11642   |          |          |          |

3.6. Nickel
Nickel reduction occur in all treatments and the pattern of Nickel reduction figureis quite similar with Ferrum reduction figure, where except in Dichloromethane solvent, the Lauryl Amine at 15 gram dosage produce higher Nickel reduction compared than 5 gram in both 4 hours and 8 hours process time (Figure 6). The 4 hours process time reduce higher Nickel content than 8 hours, except in Dichloromethane solvent (Table 6). The highest Nickel reduction at 41.7% shown by 15 gram Lauryl Amine in Dichloromethane solvent with 8 hours process time.

3.7. Zinc
Both 5 gram and 15 gram Lauryl Amine collector in Dichloromethane, Ethanol and n-Hexane solvents will be reducing Zinc content after the treatment (Figure 7 and Table 7). The 15 gram Lauryl Amine at 4 hours process time give the highest reduction of Zinc content at 48.4%, 46.3%, 37.9% for n-Hexane, Ethanol and Dichloromethane solvents respectively.

Figure 6. Nickel content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length.
**Table 6.** Nickel content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length; and it reduction to control.

| Lauryl Amine Dose (gr) | Solvent       | Concentration (mg/kg) | Reduction to control (%) |
|------------------------|---------------|------------------------|--------------------------|
|                        |               | 4 hours | 8 hours | 4 hours | 8 hours |
|                        | Dichloromethane | 11.09   | 12.31   | 34.3    | 27.1    |
|                        | Ethanol       | 12.82   | 14.3    | 24.1    | 15.3    |
|                        | n-Hexane      | 12.76   | 14.27   | 24.5    | 15.5    |
| 15                     | Dichloromethane | 12.04   | 9.84    | 28.7    | 41.7    |
|                        | Ethanol       | 10.86   | 12.55   | 35.7    | 25.7    |
|                        | n-Hexane      | 10.74   | 13.7    | 36.4    | 18.9    |
| Control                |               |          |          |          | 16.89   |

**Figure 7.** Zinc content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length.

**Table 7.** Zinc content on Lauryl Amine collector and three different solvent at 4 and 8 hours process length; and it reduction to control.

| Lauryl Amine Dose (gr) | Solvent       | Concentration (mg/kg) | Reduction to control (%) |
|------------------------|---------------|------------------------|--------------------------|
|                        |               | 4 hours | 8 hours | 4 hours | 8 hours |
|                        | Dichloromethane | 31.68   | 31.11   | 38.4    | 39.5    |
|                        | Ethanol       | 36.86   | 43.99   | 28.3    | 14.4    |
|                        | n-Hexane      | 47.965  | 41.73   | 6.7     | 18.8    |
| 15                     | Dichloromethane | 31.89   | 30      | 37.9    | 41.6    |
|                        | Ethanol       | 27.59   | 35.6    | 46.3    | 30.7    |
|                        | n-Hexane      | 26.52   | 43.76   | 48.4    | 14.8    |
| Control                |               |          |          |          | 51.39   |
Within the 5 gram dosage of Lauryl Amine collector, the Dichloromethane solvent consistently showed higher heavy metal reduction in all elements including Cd, Co, Cr, Cu, Fe, Ni and Zn both in 4 hours and 8 hours process time (Table 8). Within the 15 gram dosage, only the Dichloromethane solvent at 8 hours process time consistently as the highest treatment to reduce heavy metal, 4 hours process time, it shown that not consistently as the highest solvent in reducing heavy metal, the percentage reduction of Dichloromethane solvent is not so different with other solvents. In term of process time, it is obvious that 4 hours reduce more heavy metal than 8 hours. Based on these results, the most effective and efficient treatment combination is 5 gram Lauryl Amine collector in Dichloromethane solvent for 4 hours process time.

Table 8. Summary of heavy metal reduction.

| Lauryl Amine Dose (gr) | Solvent       | Cd     | Co     | Cr     | Cu     | Fe     | Ni     | Zn     |
|------------------------|---------------|--------|--------|--------|--------|--------|--------|--------|
|                        |               | 4h     | 8h     | 4h     | 8h     | 4h     | 8h     | 4h     | 8h     | 4h     | 8h     | 4h     | 8h     |
|                        | Dichloromethane| 42.5   | 42.5   | 32.7   | 32.0   | 32.3   | 28.7   | 34.8   | 34.6   | 31.8   | 21.6   | 34.3   | 27.1   | 38.4   | 39.5   |
|                        | 5             | 42.5   | 42.5   | 32.7   | 32.0   | 32.3   | 28.7   | 34.8   | 34.6   | 31.8   | 21.6   | 34.3   | 27.1   | 38.4   | 39.5   |
|                        | Ethanol       | 33.6   | 27.4   | 25.9   | 16.7   | 23.9   | 16.4   | 27.5   | 19.3   | 18.6   | 7.9    | 24.1   | 15.3   | 28.3   | 14.4   |
|                        | n-Hexane      | 26.8   | 27.1   | 24.0   | 15.7   | 19.5   | 13.3   | 20.1   | 9.5    | 21.3   | 8.8    | 24.5   | 15.5   | 6.7    | 18.8   |
|                        | 15            | 41.5   | 39.8   | 31.4   | 40.9   | 31.3   | 34.9   | 35.8   | 39.2   | 24.6   | 41.5   | 28.7   | 41.7   | 37.9   | 41.6   |
|                        | Ethanol       | 42.0   | 36.6   | 35.7   | 28.4   | 33.3   | 24.4   | 34.7   | 23.6   | 31.7   | 21.2   | 35.7   | 25.7   | 46.3   | 30.7   |
|                        | n-Hexane      | 40.1   | 28.7   | 33.9   | 18.5   | 34.3   | 17.0   | 32.7   | 14.4   | 32.6   | 11.0   | 36.4   | 18.9   | 48.4   | 14.8   |

4. Conclusion

Lauryl amine collector in Dichloromethane, Ethanol and n-Hexane solvent may reduce heavy metal such as Cd (26.8%-42.5%), Co (15.7%-40.9%), Cr (13.3%-34.9%), Cu (9.5%-39.2%), Fe (7.9%-41.5%), Ni (15.3%-41.7%), and Zn (6.7%-48.4%) from boiler ash. the most effective and economically efficient treatment used to reduce the heavy metal content of boiler ash from pulp and paper mill waste is 5 gram Lauryl Amine collector in Dichloromethane solvent for 4 hours process time.

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