Utilization of wood sawdust as heavy metal adsorbent in paint industry waste

Y Sukmawardani1*, Pitriani1, P Pitriana2, and C Z Subarkah1

1UIN Sunan Gunung Djati Bandung, Departement of Chemical Education. Jl. Cimencrang, Panyileukan, Kota Bandung 40292, Indonesia.
2UIN Sunan Gunung Djati Bandung, Departement of Physics Education. Jl. Cimencrang, Panyileukan, Kota Bandung 40292, Indonesia.

*yulia.sukmawardani@uinsgd.ac.id

Abstract This study aims to utilize wood sawdust waste in the paint industry waste treatment. The first thing to do is a qualitative analysis of heavy metals before and after the processing. Furthermore, the parameters measured are temperature, pH, TDS, and dissolved oxygen (Dislove Oxgen). The use of wood sawdust as a heavy metal adsorbent in paint industry wastes is able to provide efficient results with no sediment formation when conducting qualitative analysis of Cu²⁺ and Cd²⁺ metal ions and raising the waste parameters to be environmentally friendly. This shows that the adsorption process works optimally.

1. Introduction
One of the environmental pollution caused by emergence of many industries. Along with the continued increase and development of the industry today, unwittingly began to emerge various environmental pollution impacts, which come from byproducts or waste that is wasted, especially in the waters [1]. If the waste is not treated properly it will cause a negative impact, because of the various contents in it, one of which is heavy metal content. Heavy metals are classified as hazardous (B3) if they are present in wastes with an amount of more than 5g/cm³. To deal with this before it is disposed of into the environment, special handling of waste in the factory needs to be done first. This is done so that there is no ongoing pollution, so that it poses a serious danger to human health and the environment [2]. In addition, it can also result in aquatic life slowly decreasing, because the pollutants contained in industrial waste can pollute the aquatic ecosystem as a whole. Heavy metals such as Copper (Cu), Lead (Pb), Zinc (Zn), and Cadmium (Cd) can be easily found in paint industry wastes. If industrial waste enters the aquatic environment, it can contribute serious problems to living things. Monitoring of waste containing heavy metals above can be done on a laboratory scale, one of them by conducting qualitative cation analysis [1].

The methods commonly used in handling heavy metal contaminated waste are precipitation chemically, membranefiltration, ion exchange with resins, and adsorption of active metals. These processes require substantial costs with tools that are rarely used on a small scale, so it is very difficult to be done in an integrated laboratory within an agency [3]. The use of environmentally friendly materials would be better if used in this waste treatment process, one of which is using biosorbents obtained from the side production of the furniture industry, namely sengon sawdust [4]. It is hoped that using this biosorbent in waste treatment will be able to minimize costs. Wood waste has an advantage
in its high absorption, because it contains lignin and cellulose as the main components of wood composition [5]. Previous studies discussing cation analysis have been carried out using sawdust as an adsorbent, to test the effectiveness of its absorption, first chemically activated by acetylation, sulfonation, or the use of certain acids such as HNO$_3$ to obtain optimum adsorbent absorption.

2. Method

2.1 Qualitative analysis

Waste samples are diluted using distilled water, for identification of Cu metal ions carried out by adding Fe (CN)$_6^{3-}$ which will form a red precipitate of the [Cu$_2$Fe(CN)$_6$] complex. Identification of Cd metal ions can be done by adding ammonium sulfide and yellow deposits will form.

2.2 Quantitative analysis

Metal ion adsorption experiments on paint industry waste were carried out using batch equilibrium techniques. This batch equilibrium technique is the technique of choice for conducting experiments in adsorption studies because it allows studying the adsorption process under various experimental conditions of pH, temperature, time, and so on. 1 gram of sawdust is treated for adsorption of 100 ml of the waste sample. After equilibration for the required time interval, the solution is filtered and the filtrate is analyzed for metal ion concentration. The concentration of adsorbed metal ions was calculated by subtracting the concentration of metal ions in the filtrate from the initial metal ion concentration. The concentration of metal ions is determined by spectrophotometer (Hitachi, Japan Model - 180 - 80).

The effect of contact time on the number of adsorbed metal ions is analyzed by taking 300 ml of a waste sample in a beaker mixed with magnetic stirrer with activated wood sawdust adsorbent and not activated (with separate operation) for different time intervals, for example, 5, 7, 10, 20, and 30 minutes. After a certain time interval, the mixture is filtered and analyzed for the final metal ion concentration using atomic absorption spectrophotometer.

To find out how optimally the sengon sawdust in adsorbing heavy metals in the paint industry wastes it is necessary to do a qualitative analysis on the cation analysis sub-material. This analysis is done by testing the presence of metal ions using inorganic solvents. This test was carried out on paint waste samples before adsorption and after adsorption.

3. Results and Discussion

The process resulting from the application of the adsorption method in paint industry waste samples is carried out in stages. Paint industry wastes were obtained from one of factories in Bandung, West Java, seen from the results of a preliminary study that paint industry waste shows the presence of heavy metals contained. The following parameters were tested for physical and chemical characteristics of the paint industry waste, namely: pH, temperature, TSS, TDS, metal content and chemical oxygen levels needed (COD). Table 1 and 2 represent the results of the test parameters before and after the adsorption.

| Parameter     | Research result | Quality standard (kepmen LH No. 05 2014) |
|---------------|-----------------|----------------------------------------|
| Temperature   | 26°C            | 25-26°C                                |
| pH            | 5.8             | 6-9                                    |
| TDS           | 672 mg/l        | 500 mg/l                               |
| COD           | 320 mg/l        | 200 mg/l                               |
| Cu level      | 2.07 mg/l       | 1.00 mg/l                              |
| Cd level      | 0.23 mg/l       | 0.10 mg/l                              |

Based on Table 1, the characteristics of the paint industry waste have levels of pollution above the quality standard. So that it will cause danger if discharged directly to the environment.
Table 2. Measurement results of waste characteristics after adsorption

| Parameter | Research result | Quality standard Minister of Environment Decree No.5 of 2014 |
|-----------|-----------------|--------------------------------------------------------------|
| Temperature | 26°C | 25-26°C |
| pH | 7.2 | 6.9 |
| TDS | 348 mg/l | 500 mg/l |
| COD | 120 mg/l | 200 mg/l |
| Cu level | 0.08 mg/l | 1.00 mg/l |
| Cd level | 0 mg/l | 0.10 mg/l |

Based on Table 2, shows that the characteristics contained in the paint industry waste are in accordance with quality standards and can be said to be categorized as environmentally friendly waste. The electrocoagulation stage is carried out to remove the color contained in the waste.

Optimization results of the utilization of sengon sawdust as a heavy metal adsorbent based on the preliminary test results in Table 1, it can be seen that the paint industry waste clearly contains heavy metals. This shows that paint waste has a role in polluting the environment, especially in waters. The water is the most important element in the life of all living things such as plants, animals and humans. If the water has been contaminated with heavy metals, all living things will be affected. Based on these reasons the author took the initiative to conduct a qualitative analysis of the paint industry waste, the aim is to find out what metal ions are contained in the waste. Qualitative analysis of Cu\(^{2+}\) and Cd\(^{2+}\) metal ions in paint industry wastewater was carried out on a semi micro scale by adding excess concentrated NH\(_3\) precipitating. This is done because the metal ions of Cu\(^{2+}\) and Cd\(^{2+}\) will precipitate at pH > 7 and form complexes \([\text{Cu} (\text{NH}_3)_4]^2+\) and \([\text{Cd} (\text{NH}_3)_4]^2+\). The process of forming complex compounds such as Figure 1.

**Figure 1.** Reaction of the formation of Ion coppertetraamino (II)

However, during the experimental process the complex compounds that are formed cannot be seen visually through the colour of the formed solution. The statement is in accordance with what the previous researchers did about the metal ion Cu\(^{2+}\) in river water. The next step to do is to add hydrogen sulfide. This process is done very carefully. Surely enough after evaporation for ±10 seconds the Cd\(^{2+}\) ion was identified by the formation of a slight yellow precipitate in the waste sample, the yellow color was due to the formation of CdS. The accuracy of hydrogen sulfide in identifying metal ions of Cu\(^{2+}\) and Cd\(^{2+}\) up to 1 mg /l. The reaction of the formation of CdS is as follows:

\[
\text{[Cd(NH}_3)_4]^2+_{(aq)} + \text{H}_2\text{S}_{(g)} \rightarrow \text{CuS}_{(s)} + \text{NH}_4^+_{(aq)} + \text{H}^+_{(g)}
\]

The step to identify the metal ion Cu\(^{2+}\) is not the same as the metal ion Cd\(^{2+}\), because before the waste sample is evaporated with hydrogen sulfide first 1 drop of K\(_4[\text{Fe(CN)}_6]\) solution is added. The precipitate that will be formed is a reddish-brown precipitate of a compound of Cu\(_3[\text{Fe(CN)}_6]\). The adsorption process was carried out for 20 minutes then separate the filtrate from the adsorbent using 1.0 µm porous filter paper. The filtrate obtained is then analyzed again as above. The results obtained as expected, did not form yellow deposits and reddish brown deposits in the adsorption waste sample. This indicates that the adsorption process is carried out optimally because the metal ions of Cu\(^{2+}\) and Cd\(^{2+}\) present in the waste sample become less than 1 mg /l.
The binding process of Cu\(^{2+}\) and Cd\(^{2+}\) metal ions during the adsorption process occurs because of the attractive forces between molecules on the surface of an unbalanced solid. The existence of this force causes the solid to tend to attract other molecules that come in contact with the surface of the solid. So it can be concluded that the adsorption process is a symptom on the surface, so that the greater the surface area, the more substances are adsorbed. This is also the reason why during the adsorption process the stirring is carried out not to exceed 150 rpm. The stirring speed was also carried out by previous researchers in the use of wood sawdust as a heavy metal adsorbent, only the waste that the previous researchers used was synthetic waste\[6\].

Physical changes in the waste sample that has been adsorbed for 20 minutes occurs in the color of the waste that was dark yellow to yellowish cream. The distinctive odor of paint which was initially quite pungent turned into the smell of wet wood. This resulted in the waste being reprocessed by electrolysis. Electrolysis process is carried out to remove the color that is still present in the adsorption waste sample.

The waste electrolysis process is carried out using aluminum electrodes. Optimum condition occurs with the reaction that occurs is the oxidation reduction reaction due to an electric current that is flowed to the waste sample. The aluminum oxidation reaction becomes Al\(^{3+}\) and the reduction of water to OH\(^-\) and the two ions combine to form Al(OH)\(_3\) in the form of large colloids such as coagulants \[8\]. This identifies that Al\(^{3+}\) ions successfully optimally bind the remaining pollutants and impurities in the adsorption wastewater and waste that is obtained becomes colorless. It is also in accordance with previous researchers regarding the treatment of detergent waste using the electrocoagulation method. In the study of the use of wood sawdust as a heavy metal adsorbent, the authors do not prioritize the electrocoagulation method, because the utilization of wood sawdust adsorbent has taken place optimally even though it cannot eliminate color completely.

Parameter test results before and after adsorption and electrolysis based on the results of the experimental treatment of paint industry waste by using wood sawdust as a heavy metal adsorbent are presented in Table 4.9. All parameters are in accordance with the quality standard in the Minister of Environment Decree No.5 of 2014. It is proven that adsorption has a high efficiency in treating waste by binding to impurities or pollutants both organic and inorganic, such as test parameters for pH, temperature, TDS, COD and metal content in the paint industry waste.

The first parameter test for pH, based on the results of large laboratory tests of pH before and after the adsorption process has decreased. From 5.8 to 7.2 in accordance with quality standards. The second parameter test for temperature, based on the results of laboratory tests obtained a fixed temperature and in accordance with the quality standards of liquid waste. The third parameter test is Total Dissolved Solid (TDS). This test was carried out using the gravimetric method, so that the TDS value in waste that has not been carried out by the adsorption process was 672 mg/l while the TDS value of the paint industry waste that had been adsorbed was 348 mg/l. Fourth parameter test for Chemical Oxygen Demand (COD), this chemical oxygen demand for oxidizing substances is one of the important characteristics in the analysis of waste parameters. Laboratory test results for the analysis of oxygen demand have decreased after adsorption was carried out from 348 mg / l to 150 mg / l, through the analysis of oxygen demand levels performed by laboratory scale permanganometry titration method. Finally, to test the parameters of the metal, this stage is carried out using atomic absorption spectrophotometry (AAS), the metal content measured is copper (Cu\(^{2+}\)) and cadmium (Cd\(^{2+}\)). Obviously decreased after adsorption. Which is the level of copper which was 2.07 mg / l to 0.08 mg / l and cadmium level which was 0.23 mg / l to 0.72 mg / l.

The waste parameter test that has been done above shows that the paint industry waste that we use has become an environmentally friendly waste, according to previous researchers related to waste treatment \[9\], the thing to do is to adjust the parameters of the waste to its quality standards. Thus the waste from the process of adsorption of sawdust which has been electrolyzed is safe to be disposed of the environment without damaging the waters.
4. Conclusion
Research on sawdust as an absorbent of heavy metal materials in paint industry waste has been carried out using qualitative analysis of Cd and Cu content. The qualitative analysis of parameters measurement in the paint industry waste after adsorption such as temperature, pH, TDS, COD, Cu level and Cd level are in accordance with quality standards and can be said to be categorized as environmentally friendly waste.

5. References
[1] Heryando P 2017 Pencemaran dan Toksikologi Logam Berat. (Jakarta: Rineka Cipta)
[2] Bakkaloglu I, Butter T J, Evison L M, Holland F S, and Hancockt I C 1998 Water science and technology 38 269
[3] Rahayuningsih, Susilowati E, and Mahardani L 2012 Pemanfaatan Serbuk Gergaji Kayu Sengon Sebagai Adsorben Ion Logam Pb\(^{2+}\). Prosiding Seminar Nasional Seminar SNKPK IV, 2, 75–81.
[4] Hao L, Liu Q, Li X, Du Z and Wang P 2014 RSC Advances 4 49569
[5] Yusminar E, 2009 Jurnal sains dan teknologi 77
[6] Chang R 2004 Kimia Dasar Konsep - Konsep Inti, Jilid 1. Ed. Ketiga (Jakarta: Erlangga)
[7] Andrabi S M A 2011 Eur.J.Wood.Prod. 69 75
[8] Susetyaningsih R, Kismolo E, and Prayitno 2008 Kajian Proses Elektrokoagulasi untuk Pengolahan Limbah Cair. Seminar Nasional IV SDM Teknologi Nuklir Yogyakarta.
[9] Dwiki I M, Indah R S, and Salami 2012 Jurnal Teknik Lingkungan 18 130

Acknowledgement
We would like to thank to Laboratory of Chemical Education where we did the research. We also thank to LP2M UIN Sunan Gunung Djati Bandung who have motivated and provided an opportunity in writing this article.