Utilization of reject material in raw grinding mill unit as industrial wastewater adsorbent

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Abstract. The technology of handling industrial wastewater adopted by the industry is quite expensive with high costs in its operation, so that wastewater treatment technology that is cheap and easy to adopt and under strict environmental regulations is an important thing to consider. Innovative adsorption-based technology developed using industrial waste and agricultural waste offers an easy and economical solution for polluted environments. Raw grinding mill as one part of the cement industry production equipment serves to grind or soften cement raw material, some waste material which is known as reject material during the process and has not been used optimally. This research aims to determine the effect of reject material as an adsorbent on decreasing metal content and pH of industrial wastewater. The method used in processing, namely the wastewater sample, is put into a reservoir (tub I), then flowed continuously into tub II, which is filled with reject material as an adsorbent. The sampling technique was carried out after the wastewater flowed from tub II and then collected in a storage container and ready to be analyzed for heavy metal content and pH of wastewater in the laboratory. The results of the research showed that reject material of Raw Grinding Mill as an adsorbent of PT. Bosowa cement can reduce metal material PO₄ = 94.63%, NO₃ = 81.82%, NH₃ = 22.41%, As = 76.67%, Zn = 73.23%, Ni = 100%, Ag = 60% .

1. Introduction
In the current era of industrialization, the development of the industry has become very rapid. The progress in the industrial sector, in addition to causing positive impacts, also has a negative effect. The process of producing wasted or failed materials that contain hazardous metals and organic matter is one of the adverse effects that can pollute the environment and will ultimately disrupt the balance of the environmental ecosystem if it is not appropriately handled [1, 2]. The remaining raw paper derives from solvent residue, washing and rinsing equipment, kettle boilers and cooling water systems, and sanitary wastes [1, 2].

The technology for handling wastes and industrial wastes that are adopted by the industry is quite expensive, with high costs in operation so that waste handling technology that is cheap and quickly adopted and following strict environmental regulations is an important thing to consider [3, 4]. Various studies have been carried out to develop wastewater handling technology. Innovative adsorption-based technology developed using agricultural waste and cheap industrial waste is a technology that has the potential to exclude suspended or dissolved organic and inorganic materials in the wastewater.

The adsorption by utilizing industrial waste material offers an easy and economical solution for polluted environments. Raw grinding mill as a part of cement production equipment has an important...
role. Besides functioning to grind or smooth cement, raw material, as well as drying material that is milled with a raw grinding mill machine, has a composition of limestone, clay, silica sand, and iron sand [5]. During the production process, several reject materials have taken place that has not been utilized optimally by the industry, so further handling is needed so as not to cause environmental problems. One effort that can be done is to use the rejected material as an adsorbent to replace zeolite. Reject material has a composition similar to zeolite. According to [6], zeolite is a porous material with the principal constituent components, which are silica (SiO₂), iron oxide (Fe₂O₃), aluminum oxide (Al₂O₃), calcium oxide, and magnesium oxide. A study conducted by [6] natural zeolite could reduce chromium metal (Cr) wastewater with an absorption value of 99.725%. [7] in his research that natural zeolite can reduce COD and heavy metal textile wastewater by 88%. It is what encourages the conduct of research by utilizing reject material as an adsorbent to polluted wastewater.

2. Methods

2.1. Tools and Materials
The tools used in this research are wastewater treatment tanks, mesh sieves, electric ovens, burettes, funnels, desiccators, Erlenmeyer, volume pipettes, buckets, Jergens, measuring flasks, incubators, filter paper, analytic balance. For analysis using a spectrophotometer instrument, namely XRF and pH meter. Water Pump (PGB Water Pump), ½ 60 cm pipe, stop tap, hose. The material used in this study was wasted material from the industry of PT. Bosowa, a sample of industrial laboratory wastewater from PT. Bosowa, aqua dest, quartz sand.

2.2. Data Collection Techniques
2.2.1. Processing Tub
The processing tub made of PVC type plastic material consists of 2 tubs with the size of each tub is 20 cm long, 30 cm wide and 40 cm high (laboratory scale) consisting of:

The tub I as a wastewater reservoir before the wastewater has flowed into the processing tub, Tub II, as a processing tank filled with reject material.

![Figure 1. Processing tub.](image)

2.2.2. Procedures
The procedures in the study are as follows:
3. Methods

Based on the research conducted, the results of the analysis are as follows:

3.1. Effect of solid waste (rejected material) Raw Grinding Mill as an adsorbent and ion exchange for laboratory wastewater.

Table 1. Results of analysis of inorganic (metal) materials in samples of PT Semen Bosowa laboratory wastewater.

| Sample Type         | Adsorbent Mass (g) | Al  | P   | Cr  | Mn  | Fe  | Co  | Cu  | Hg  | Pb  | pH  |
|---------------------|--------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Wastewater (100 mL) | 0                  | 0.656| 1.047| 0.073| 0.106| 0.749| 0.454| 0.050| 0.030| 0.039| 1.6 |
| Sample 1 (100 mL)   | 10.7752            | 0.806| 0.798| 0.000| 0.000| 0.593| 1.381| 0.134| 0.108| 0.115| 2.18|
| Sample 2 (100 mL)   | 20.885             | 0.000| 0.944| 0.212| 0.240| 1.211| 2.042| 0.077| 0.207| 0.123| 5.78|
| Sample 3 (100 mL)   | 30.0578            | 0.683| 1.102| 0.092| 0.081| 0.354| 0.564| 0.048| 0.042| 0.019| 6.96|
| Sample 4 (100 mL)   | 40.2495            | 0.000| 1.187| 0.231| 0.186| 0.711| 1.223| 0.224| 0.277| 0.184| 6.15|
| Sample 5 (100 mL)   | 50.8845            | 0.394| 0.920| 0.102| 0.192| 0.871| 1.597| 0.035| 0.152| 0.034| 6.25|
Figure 2. The graph of the mass effect of raw grinding mill adsorbent (rejected material) on decreasing element content and heavy metals.

Figure 3. The graph of the mass effect of rejected material on increasing pH.

3.2. Analysis of the reduction of inorganic and organic laboratory wastewater materials.

The reduction of inorganic and organic laboratory wastewater materials at PT. Bosowa Maros Cement concerning PERGUB SUL-SEL No. 69 Tahun 2010 about quality standards and criteria for environmental damage can be shown in table 2.

4. Discussions

4.1. The effect of solid waste (reject material) Raw Grinding Mill as an Adsorbent and ion exchanger

4.1.1. As an adsorbent

The reject material in the Raw Grinding Mill process unit is waste material that is wasted during the process. This solid waste contains several components, including limestone, clay, iron sand, and silica sand. The reject material can function as an adsorbent wherein its components there are zeolites, namely clay (Al₂O₃·SiO₂).

In this research, how is the effect of reject material from the Raw Grinding Mill process unit as an adsorbent, which sees the effect of changes in the mass of reject material on the absorption of elements and heavy metals in the laboratory wastewater? The research was conducted with changes in the mass of reject material 10 g, 20 g, 30 g, 40 g, and 50 g, concerning laboratory wastewater without mass
addition of the adsorbent. The study was carried out by inserting reject material into 100 ml of each laboratory wastewater, then stirring and allowed to stand for one hour aimed at stirring where the adsorbent merged with laboratory wastewater. Stirring is intended to give material particles the chance to intersect with absorption compounds. After that, it is left to stand until all rejected material settles. Then, after all, precipitates, filtering is carried out using filter paper after filtering laboratory wastewater, which is initially pink and can turn into transparent. It proves that the reject material in the Raw Grinding Mill process unit can absorb the color of laboratory wastewater. The silica element contained in the material is a level of material that is hard and is not easily soluble in water, serves as a purifier of particles contained in turbid water to obtain clear water [7, 8].

Table 2. Results of analysis of organic and inorganic laboratory wastewater.

| Parameters | Unit | Inlet | Outlet | Standard | Efficiency (%) |
|------------|------|-------|--------|----------|----------------|
| Physical   |      |       |        |          |                |
| TSS        | mg/L | 25    | 26     | 100      | -              |
| TDS        | mg/L | 2110  | 2030   | 4000     | 3.79           |
| Chemical   |      |       |        |          |                |
| Colour     | -    | Pink  | Colorless | -      |
| pH         | -    | 1.68  | 6.25   | 6-7      | -              |
| BOD        | mg/L | 40    | 16.67  | 50       | 58.33          |
| COD        | mg/L | 60    | 24.99  | 100      | 58.35          |
| PO₄        | mg/L | 21.43 | 1.15   | 94.63    |
| NO₃        | mg/L | 0.11  | 0.02   | 15       | 81.82          |
| NH₃        | mg/L | 6.47  | 5.02   | 8        | 22.41          |
| CN         | mg/L | 0.03  | 0      | 0.05     | 100            |
| Pb         | mg/L | 0.0161| 0.0029 | 1.1      | 81.99          |
| As         | mg/L | 0.003 | 0.0007 | 0.1      | 76.67          |
| Hg         | mg/L | 0.263 | 0.0092 | 0.02     | 96.50          |
| Cr         | mg/L | 0.03  | 0.01   | 0.5      | 66.67          |
| Zn         | mg/L | 0.263 | 0.0704 | 4        | 73.23          |
| Ni         | mg/L | 0.01  | 0      | 0.2      | 100            |
| Ag         | mg/L | 0.05  | 0.02   | -        | 60             |
| Cu         | mg/L | 0    | 0      | 2        | -              |
| Mn         | mg/L | 0.6   | 0.87   | 2        | -              |

Table 3. Results of analysis of rejected material components
(X-ray Lab of PT. Semen Bosowa Maros)

| No | Component | Concentration (%) |
|----|-----------|-------------------|
| 1  | SiO₂      | 7.26              |
| 2  | Al₂O₃     | 0.62              |
| 3  | Fe₂O₃     | 0.43              |
| 4  | CaCO₃     | 48.57             |
| 5  | MgO       | 0.88              |

The levels of elements and heavy metals obtained using Omnian X-RF instrumentation. After the adsorption process, it then compared to the metal content value without adsorption treatment, and there is an increase in the value. As a result, it occurs because the adsorbents used has not been activated, so that many impurities affect the adsorbent [8, 9, 10, 11]. Besides that, the size of reject material granules has not been uniformed.
Significant absorption of P element occurred in sample 1, where the mass of the adsorbent was 10.7752 g with a concentration difference of 0.249 mg / L with a percentage decrease of 28.5% in the concentration of wastewater without treatment. Also, there was a decrease in samples 2 and 5 of each concentration difference of 0.103 mg / L (percentage reduction of 14.51%) and 0.127 mg / L (16.8%), the more significant the difference in concentration, the higher the absorption. Other than that, the level of P elements relatively increases. It proves that the reject material in the Raw Grinding Mill process unit can absorb P elements.

Significant absorption of Cr metal occurred in sample 1 with an adsorbent mass of 10.7752 g, were in the sample, there was no metal Cr concentration (100% absorption), only in sample 1 there was a decrease in concentration. As a result of not decreasing the concentration in other samples, the Raw Grinding Mill reject material is not activated so that there are still various impurities and granules of discarded material that even vary.

Significant absorption of Mn metal occurred in sample 1 with the adsorbent mass of 10.772 g, wherein the sample there was no Mn metal concentration (100% absorption). In sample 3, there was a concentration difference of 0.025 mg / L (23.71%) against laboratory wastewater without treatment, which means that the absorption of Mn metal by using the Raw Grinding Mill process reject unit material as the adsorbent can absorb well. Absorption of Fe occurs in sample 1, sample 3, and sample 4 with mass adsorbent respectively 10.772 g, 30.0578 g, and 40.2495 g, wherein these samples the concentration difference is 0.157 mg / L respectively. (20.91%), 0.395 mg / L (52.69%), and 0.038 mg / L (5.1%) against untreated laboratory wastewater meaning that the absorption of Fe metal by using reject unit material in the Raw Grinding Mill process as the adsorbent can absorb properly.

In the identification of Co metal, the absorption that occurred or did not affect the increase in the mass of the adsorbent and Co concentration tended to be unstable. Co metal cannot be absorbed by reject material, so reject material in the Raw Grinding Mill process unit as an adsorbent does not function to absorb Co metal in laboratory liquid waste.

Absorption of Cu elements occurs in samples 3 and 5 decreasing - each concentration difference of 0.002 mg / L (2.7%) and 0.015 mg / L (29.86%), the greater the concentration difference, the greater the absorption. Other than that, the concentration of Cu elements has relatively increased. It proves that the reject material in the Raw Grinding Mill process unit can absorb Cu elements.

In the identification of Pb metal, the absorption that occurs or does not affect the increase in the mass of the adsorbent and Pb concentration tends to be unstable. Pb metal cannot be absorbed by reject material, so reject material in the Raw Grinding Mill process unit as an adsorbent does not function to absorb Pb metal in laboratory wastewater.

Absorption of Hg elements occurred in samples 3 and 5 decreased - each concentration difference was 0.020 mg / L (51.87%) and 0.005 mg / L (13.26%), the greater the concentration difference, the greater the absorption. Other than that, the concentration of Hg elements relatively increased. It proves that the reject material in the Raw Grinding Mill process unit can absorb Hg elements.

From the above discussion, two heavy metals cannot be absorbed by the Raw Grinding Mill reject unit material in laboratory wastewater, namely Co and Pb metals.

4.1.2. As an ion-exchange

The reject material in the Raw Grinding Mill process unit is waste material that is wasted during the process. This solid waste contains several components, including limestone, clay, iron sand, and silica sand. Rejected material can function as an ion exchanger wherein its components there is limestone (CaCO₃).

In this research, how is the effect of reject material unit of Raw Grinding Mill process as an ion exchanger, which sees the impact of changing the mass of reject material on increasing pH in laboratory wastewater? The study was conducted with changes in the mass of reject material 10 g, 20 g, 30 g, 40 g, and 50 g, concerning laboratory wastewater without mass addition of the adsorbent. The research was carried out by removing filtered liquid waste by 30 mL. Furthermore, measuring the pH of each waste using a pH meter.
The research of wastewater used acidic with an initial pH of 1.6. Ion exchange occurs because limestone (CaCO$_3$) reacts with HCl acid so that pH increases, where H$^+$ elements will exchange with Ca$^{2+}$, so that water (H$_2$O) is formed with CO$_2$ gas, and CaCl$_2$ with chemical reactions as follows:

$$\text{CaCO}_3(s) + 2\text{HCl}(l) \rightarrow \text{CaCl}_2(l) + \text{H}_2\text{O(aq)} + \text{CO}_2(g)$$

The changes in pH of wastewater with increasing mass of reject material as ion exchangers are increasing. Still, in the reject material mass of 30 g to 50 g, the increase in pH of wastewater tends to be constant, with the final pH of wastewater is 6.25.

The research of the effect of reject material from the Raw Grinding Mill process as an ion exchanger, the impact of the addition of the reject material mass, greatly affected the pH rise of laboratory wastewater, according to No. Pergub Sulawesi Selatan No. 69 Tahun 2010, the maximum level of pH of wastewater released from the environment is 6.0 – 8.5, the pH of water obtained is following that range, which is 6.25.

![Figure 4. WWTP laboratory using the primary reject material of the Raw Grinding Mill process unit.](image)

5. Conclusion

Based on the results of the research, the data showed that reject material of Raw Grinding Mill as an adsorbent of PT. Bosowa cement can reduce metal material PO$_4$ = 94.63%, NO$_3$ =81.82%, NH$_3$=22.41%, As=76.67%, Zn=73.23%, Ni=100%, Ag=60%. Data obtained according to the quality standard set by Pergub Sulawesi Selatan No. 69 Tahun 2010.

References

[1] Tangahu B V, Ningsih D A, Kurniawan S B and Imron M F 2019 Study of BOD and COD Removal in Batik Wastewater using Scirpus grossus and Iris pseudacorus with Intermittent Exposure System *Journal of Ecological Engineering* **5** 130-134

[2] Yusuf H, Pallu M H, Samang L and Tjaronge M W 2012 Characteristical analysis of unconfined compressive strength and CBR laboratory on dredging sediment stabilized with Portland cement *International Journal of Civil & Environmental Engineering* **04** 25-31

[3] Bagastyo A Y Anggrainy A D and Nindita C S 2017 Electrodialytic removal of fluoride and calcium ions to recover phosphate from fertilizer industry wastewater *Sustainable Environment Research* **5** 230-237

[4] Warmadewanthi W, Pandebesie E S, Herumurti W, Bagastyo A Y and Misbachul 2017 Phosphate recovery from wastewater of fertiliser industries by using gypsum waste *Chemical Engineering Transactions* **56** 1765-1770

[5] Bhatnagar A 2007 Removal of bromophenols from water using industrial wastes as low cost adsorbents *Journal of Hazardous Materials* **1** 93-102
[6] Harianto T, Hamzah S, Nur S H, Abdurrahman M A, Latief R U, Fadliah I and Walenna A 2013 September Biogrouting stabilization on marine sandy clay soil In Proceedings of the 7th International Conference on Asian and Pacific Coasts (APAC 2013) Bali Indonesia September 24-26

[7] Lee J S, Kim J H, Kim J T, Suh J K, Lee J M and Lee C H 2002 Adsorption equilibria of CO2 on zeolite 13X and zeolite X/activated carbon composite Journal of Chemical & Engineering Data 5 1237-1242

[8] Purwanti I F, Titah H S, Tangahu B V and Kurniawan S B Design and Application Of Wastewater Treatment Plant For Pempek Food Industry Surabaya Indonesia

[9] Kurniawan S B, Purwanti I F and Titah H S 2018 The Effect of pH and aluminium to bacteria isolated from aluminium recycling industry Journal of Ecological Engineering 3

[10] Setiyana B 2005 Analisis Efisiensi Raw Griding Mill Pada Proses Pembuatan Semen Rotasi 1 60-65

[11] Todingrara Y T, Tjaronge M W, Harianto T and Ramli M I 2017 Performance of Laterite Soil Stabilized with Lime and Cement as a Road Foundation International Journal of Applied Engineering Research 14 4699-4707