Effectiveness of natural adsorbents in reducing Cu and Pb content of chemistry laboratory’s wastewater treatment

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Abstract. Recently, using natural adsorbent to solve wastewater problem is considered as environmentally step that supporting nature sustainability. Zeolite and rice husk charcoal are potential natural adsorbent which easily found surround human being. The aim at this research are to determine the effectiveness of weight ratio of zeolite and rice husk charcoal weight (RHCW) in lowering Cu and Pb parameter of liquid waste chemical laboratory and determine the adsorption isotherm models weight ratio of zeolite and RHCW. Data were analysed using Randomized Completely Block Design (RCBD), 5 treatments and 5 replications. As a block is the time analysis. As the treatment is different variations on the weight ratio of zeolite and RHCW (g/g). The treatment of its adsorbent was given separately and both of the treated with stirring. To test the difference between treatment means, the Honestly Significant Differences (HSD) was used with 5% level of significance. The results showed that the effectiveness of giving 8 grams of zeolite for 240 minutes is 68.78% (Cu) and 94.53%(Pb), respectively. While the effectiveness of giving 2 grams RHCW in the next 180 minutes is 70.75% (Cu) and 84.30% (Pb), respectively. The maximum adsorption capacity of giving 8 grams of zeolite within 240 minutes is Cu = 0.327 mg/g (followed Freundlich isotherm model); Pb = 0.754 mg/g (followed Langmuir isotherm model), respectively. While the absorption capacity of giving 2 grams RHCW in the next 180 minutes is: Cu = 0.084 mg/g (followed Freundlich isotherm model); Pb = 0.782 mg/g (followed Langmuir isotherm model), respectively.

Keywords: zeolite; rice husk charcoal; adsorbent; adsorption isotherms; laboratory wastewater

1. Introduction
Chemistry laboratory wastewater contain much more heavy metals and other hazardous compounds than industrial waste. The content of heavy metals in chemical laboratory liquid waste comes from practicum and research activities of students and lecturers. Heavy metals that burden chemistry laboratory wastewater among others Cu, Fe, Cr, Mn, Al, Zn, Pb, Cd, Ni, Hg, and As [1]. Revelation to heavy metals, even at trace levels, As is harmful to human beings [2-5]. Thus, removal of undesirable metals from water sources is considered as an important task that is still threatening the environment. Emerging such patterns which have been planned from waste material and can be more used effectively to adsorb contaminants is the new propensity for recent research [6]. Innovative processes of treating industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet technology-based treatment standards and adsorption is one of the methods [7]. Modelling the adsorption isotherm data is an essential way for predicting and comparing the adsorption performance, which is critical of optimization of the adsorption mechanism pathways, expression of the adsorbents capacities, and effective design of the adsorption systems [8]. The adsorbents may be of mineral, organic
or biological origin, zeolites, Industrial by-products, agricultural wastes, biomass, and polymeric materials [9]. Cellulosic agricultural waste materials are an abundant source of significant metal biosorption [10]. The functional groups present in agricultural waste biomass viz. acetamide, alcoholic, carbonyl, phenolic, amido, amino, sulphydryl groups etc. have the affinity with heavy metal ions to form metal complexes or chelates. The mechanism of the bio sorption process includes chemisorption, complexation, adsorption on a surface, diffusion through pores and ion exchange etc. Natural zeolites their selves are abundant and low-cost resources, which are crystalline hydrate aluminosilicates with a framework structure containing pores occupied by water, alkali and alkaline earth cations. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites have been widely used as adsorbents in separation and purification processes in the past decades [11]. Further, it stated that zeolite selectivity with respect to the investigated metal ions, determined on the basis of the percent removal of a given ion from the solution and distribution coefficients, Is the following: Single ion solutions [12]: Pb>Cd>Cu>Zn>Ni mixed solution: Pb>Cu>Zn>Cd>Ni

In relation to risk husk chaff, the experiment results in Nhapi et al. [13] showed that 2 g/L of the material can reduce the heavy metal content of the textile industry waste by following the order for Zn>Pb>Cu>Cd. Based on the above background then the purpose of this study is: determine the effectiveness of weight ratio of zeolite and rice husk charcoal (RHCW) in lowering Cu and Pb parameter of liquid waste chemical laboratory and determine the adsorption isotherm models weight ratio of zeolite and rice husk charcoal.

2. Materials and Methods

2.1. Time and Research Place.
The research was conducted at the Laboratory of Environmental Chemistry, Chemistry Program, Faculty of Science and Mathematics, Satya Wacana Christian University from 2015-2016.

2.2. Materials and Equipment.
Zeolites obtained from chemicals stores and rice husks were obtained from the paddy planting plant in Salatiga. Liquid waste is obtained from the Satya Wacana Christian University, Science and Mathematics Faculty of Chemistry Laboratory. The devices used include reflux, HACH DR/EL 2000 Spectrophotometer, pH meters HANNA Instrument 9812, Analytical Balance (Mettler H80), Atomic Absorption Spectroscopy (AAS) Perkin Elmer 3110.

2.3. Activated Zeolite Preparation [14]
Zeolites are washed with distilled water over and over again, then dried in an oven at 110°C for 24 hours and further put in a desiccator. 100 g of Zeolite was soaked in 2000 mL of 1 M HCl. The mixture was stirred with a magnetic stirrer for 3 hours, then rinsed with distilled water to neutral pH and dried in an 110°C oven to dry.

2.4. Preparation of Rice Husk Charcoal Weight/RHCW [15]
Rice Husk (RH) washed with distilled water repeatedly until clean and then activated with 0.5 M NaOH for 3 hours then filtered and washed until clean and come to neutral pH then dried in 110°C oven to dry.

2.4.1. Treatments. Five (5) beaker glasses of 1 L each filled with wastewater of 1 L. The mixtures of the zeolite adsorbent and RHCW ratio is 5:5; 6:4; 7:3; 8:2 and 9:1 (g/g). Next, each of them was given a ratio of zeolite adsorbent weight of 5, 6, 7, 8 and 9. Then, stirred using magnetic stirrers up to 240 minutes. Then followed by the addition of rice husk charcoal with weight 5, 4, 3, 2 and 1 g and stirred using magnetic stirrers up to 180 minutes.

2.4.2. Measurement of Physical-Chemistry Parameters. The changes that occur to the treatment can be known by performing some analysis of physical and chemical parameters (table 1).

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Table 1. Parameters of laboratory liquid waste by method / research tools.

| Parameters                        | Tools                                      |
|-----------------------------------|--------------------------------------------|
| **Physic**                        |                                            |
| ✓ TDS (Total Dissolved Solids) (ppm) | TDS meter (HANNA Instrument 9812)         |
| ✓ TSS (Total Suspended Solid) (mg/L)  | Spectrophotometer HACH DR/EL 2000         |
| **Chemistry**                     |                                            |
| ✓ pH                               | pH meter (HANNA Instrument 9812)          |
| ✓ COD (Chemical Oxygen Demand) (mg/L) | Titrimetric                              |
| ✓ Pb (mg/L)                        | Perkin Elmer AAS 3110                     |
| ✓ Cu (mg/L)                        | HACH DR/EL 2000-Spectrophotometer         |

2.4.3. Zeolite uptake effectivity. Zeolite uptake effectivity was calculated using the equation of zeolite uptake efficiency [12]:

\[
\text{Uptake, } \% = \left( \frac{\text{Co-Ceq}}{\text{Co}} \right) \times 100
\]

(1)

where Co is the initial and Ceq is the equilibrium concentration of pollutant, mg/L.

2.4.4. Isotherm adsorption. In this research used 2 adsorption isotherms namely Langmuir and Freundlich. Langmuir adsorption model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. Langmuir equation can be described by the linearized form as writing down on [16]. While Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent and the concentration of the metal in solution to equilibrium [17].

2.4.5. Data Analysis [18]. Data were analysed using Randomized Completely Block Design (RCBD), 5 treatments and 5 replications. As a block is the time analysis. As the treatment is different variations on the weight ratio of zeolite and RHCW (grams/gram). The treatment of its adsorbent was given separately and both of these treated with stirring. To test the difference between treatment means, the Honestly Significant Differences (HSD) was used with 5% level of significance.

3. Results and Discussions

3.1. Initial characterization of physical-chemistry of liquid waste parameter

The initial characterization results in chemical laboratory wastewater before being treated as follows, TDS (Total Dissolved Solids) 1,210 ppm (Indonesia quality standard is 2,000 ppm), TSS (Total Suspended Solids) 8.6 ppm (Indonesia quality standard is 100 ppm), pH 2.3 (Indonesia quality standard is 6-9), COD (Chemistry Oxygen Demand) 11.184 ppm (Indonesia quality standard is 100 ppm), Cu 3.35 ppm (Indonesia quality standard is 2 ppm), Pb 7.142 ppm (Indonesia quality standard is 0.1 ppm). The result of the analysis showed that TDS and TSS have met the standard before treated. While the chemical parameters of pH, COD, Cu, and Pb did not meet the standard quality standard.

3.2. Chemical physical waste parameters of chemical liquid waste after treating zeolite within 240 minutes.

Physical-chemistry parameter contents of TDS, TSS, pH, COD, Cu, and Pb within 240 minutes are presented in Fig. 1. The figure appears that various variations on zeolite for 240 minutes were able to decrease the mean TDS range of 350±8.78 ppm to 488±5.55 ppm. Conversely, TSS have increased from an average of 9.0±1.96 mg/L to 33.2±12.58 mg/L. pH increments of an average ranging from 3.84±0.142 to 6.48±0.162. Also, giving 8 g of zeolite was able to decrease from COD by 89.6±8 mg/L.
The content of physical-chemistry parameter (±se) of the chemistry laboratory liquid wastes on various additions of zeolite weight in contact time 240 minutes. Note: A = TDS and TSS; B = COD, Cu, and Pb; The numbers followed by the same letters show that the treatments are not significantly different, on the contrary, the numbers are followed by different letters indicate a real difference.

Refer to Lakdawala and Patel [19] argued that zeolites are more effective against the removal of all kind of contaminants from the water and wastewater than the other alumino-silicates as they have a typical feature of the opening of their structure and their ion exchanged character. Further, Chester and Derouane [20] explained that zeolites are naturally occurring crystalline aluminosilicate that has a three-dimensional structure; aluminium, silicon and oxygen which are arranged in a regular structure of [SiO₄]⁻ and [AlO₄]⁻ tetrahedral units that form a framework with small pores (also called tunnels, channels or cavities) of about 0.1-2 nm diameter running through the material.

Cu and Pb decreased at 8 g zeolite with a succession of 1.046±0.110 mg / L and 0.391±0.020 mg/L, respectively. The results of this study are in line with the research Dursun and Pala [21], 2 g zeolite in 100 ml of Pb²⁺ 1.6 ppm for 1 hour can decrease in Pb²⁺ 67% and support the research of Salam et al. [22] which showed that 5 g of zeolite in 1 L of Cu²⁺ 10 ppm solution for 3 hours was able to decrease Cu²⁺ 91-97.5%, as well as Mara et al. [23], showed that zeolite 25 g/100 ml solution to Pb²⁺ 75 ppm could decrease Pb²⁺ by 96.7%. Basically, Panayotova and Velikov [12] was investigating that lead ions were strongly immobilized by the zeolite.
3.3. Effectivity Zeolite as Adsorbent.

Fig. 2 shows the effectiveness of liquid chemical laboratory treatment of various zeolite (g) weights in contact time 240 minutes range from 68.78% - 94.53%. Adding of 9 g zeolites effectively decreased TDS by 71.07% effectiveness, while adding of 6 g zeolites effectively increased the pH from 2.3 to 6.20. The results of this study are in line with Holub et al. [24] showing that 1 g of zeolite in 100 ml of Pb\textsuperscript{2+} 10 ppm solution was able to increase the pH from 5 to 7.1 with the effectiveness of 29.58%. On the administration of 8 g zeolites effectively decrease COD 99.20% and in line with research Bazrafshan et al. [25] which shows that 25 g of zeolite in 100 ml of chemical laboratory waste for 1 hour can decrease COD 54.61%. The exposure to 8 g of zeolite effectively decreased Cu\textsuperscript{2+} and Pb\textsuperscript{2+} by 68.78% and 94.53% respectively. The results of this study are in line with the research of Dursun and Pala [21] which showed that 25 g of zeolite in 1 L of Cu\textsuperscript{2+} 10 ppm solution to 3 hours was able to decrease Cu\textsuperscript{2+} 91-97.5% and Mara et al. [23] showed that zeolite 25 g/100 ml of solution of Pb\textsuperscript{2+} 75 ppm could decrease Pb\textsuperscript{2+} by 96.7%. Based on Al-Anber [26], the slightly soluble metal ions in water will be more easily removed from water (i.e., adsorbed) than substances with high solubility. Also, non-polar substances will be more easily removed than polar substances since the latter have a greater affinity for adsorption. If the surface of adsorbent is slightly polar, the non-polar substances will be more easily picked up by the adsorbent than polar ones, it means the opposite is correct [26].
Parameters of Chemistry Laboratory Liquid Waste after Treating HRCW in Time 180 Minutes. Next, Fig. 3 appears that variations in the addition of HRCW were able to decrease TDS from 320±8.78 ppm to 460±12.41 ppm and TSS also decreased in from 4.6±0.68 mg/L to 18.2±2.69 mg/L. For pH, there was an increase in from the range of 6.24±0.242 to 7.78±0.162. Giving 2 g of the HRCW is able to decrease from COD to be 76.8±5.44 mg/L. The results of this study are in line with the study of Swathi et al. [27], which showed that 2 mg of HRCW in 250 ml of tanneries was able to reduce the COD content from 1,400 mgs/L to 506.6 mg/L. Adding 2 gs of HRCW is able to decrease to Cu²⁺ and Pb²⁺ by successively 0.306±0.007 mg/L and 0.087±0.007 mg/L. The results of this study are in line with research Oliveira and Rubio [15] showing that 0.5 g of HRCW in 10 ml of laboratory chemistry wastewater was able to decrease from Cu²⁺ 78.57% for 2.5 hours and able to decrease 99.38% Pb²⁺ in multi component wastewater for 3 hours.

Figure 3. The content of physical-chemistry parameters (±SE) of chemistry laboratory liquid waste on various additions of HRCW in contact time 180 minutes. Note: A = TDS, B = TSS, C = Cu, Pb and COD as well as pH.
Figure 4. The effectiveness of various of hrcw in liquid waste treatment of chemistry laboratory within 180 minutes’ contact time on reference parameters.

Figure 5. Physical-chemistry parameter content (±SE) of liquid waste of chemistry laboratory at addition of HRCW on the next 180 minutes.
Effectivity HRCW as Adsorbent. Fig. 4 and Fig. 5 show that the addition of 5 g of HRCW effectively decreased TDS and TSS with effectiveness ranging from 31.91% to 48.89%. While the addition of 4 g of HRCW effectively increased the pH from 6.20 to 7.22. In addition, 2 gs of HRCW effectively reduced COD 42.34%. The results of this study are in line with Swathi et al. [27] indicating that 10 gs of HRCW effectively reduced COD on textile wastewater with the effectiveness of 59%. In addition, 2 gs of HRCW is also able to decrease Cu$^{2+}$ and Pb$^{2+}$ with the effectiveness of 70,75% and 84,30% respectively. The results of this study are consistent with study Muneer et al. [28]. Shown that 1 g of HRCW in 100 ml of heavy metal mixed solution (at 1-20 ppm) of Cu, Pb and Zn can decrease the ion metal content in Zn>Pb>Cu sequence and the successive effectiveness 96.64%, 96.45% and 96.31% respectively.

3.4. Isotherm adsorption (using zeolite and HRCW in contact time 420 minutes).
The results of Langmuir and Freundlich adsorptions calculation presented in table 2. It shows that the COD adsorption isotherm follows the Langmuir model on 8 gs of zeolite with the $R^2$ value of 0.999 and the adsorption capacity of 166.670 mg/g. While on HRCW follow Freundlich model with value $R^2$ 0.996 and adsorption capacity 3,490×10$^3$ mgs/g. The results of this study are in line with the study of Abuzar et al. [29] showing that the COD adsorption isotherm models using a corn peels powder followed the Langmuir model with a value of $R^2$ 0.987 and adsorption capacity of 27.75 mg/g. Research Estiaty [30] indicates that the COD isotherm model using to fly ash follows the Freundlich model with the $R^2$ value of 0.93 and an adsorption capacity of 0.4360.

Table 2. Isotherms adsorption Langmuir and Freundlich chemistry parameter of chemistry laboratory liquid waste.

| No | Parameter | AR (g/g) | Langmuir | Freundlich |
|----|-----------|----------|-----------|------------|
|    |           |          | b         | Q (mg/g)   | n          | Kf        |
| 1  | COD       | Z (8)    | y = 0.006x - 0.463 | 166.67 | 0.007 | y = -0.020x + 3.183 | 1.540×10$^3$ |
|    | HRCW (2) | R$^2$ = 0.999 | r=0.999 | 9.144 | 0.151x - 9.144 | 0.791 | y = -2.162x + 5.544 | 3.490×10$^3$ |
| 2  | Cu        | Z (8)    | y = 0.151x - 11.71x - 10.17 | 0.017 | 0.930 | y = 11.71x - 0.151 | 0.085 | -0.35 | y = -1.011x + 0.486 | 0.989 | 0.327 |
|    | HRCW (2) | R$^2$ = 0.964 | r=0.999 | 4.771 | 1.327x - 4.771 | 0.375 | y = -1.273x + 1.077 | 0.946 | 0.084 |
| 3  | Pb        | Z (8)    | R$^2$ = 0.998 | r=0.999 | 27.48x | 0.059 | 22.479 | 0.754 | 0.006 | y = -0.975x + 0.049 | 0.993 | 0.119 | 0.782 |
|    | HRCW (2) | R$^2$ = 0.986 | r=0.999 | 2.101 | 13.076 | 0.036 | 0.16 | y = -0.975x + 1.813 | 0.906 | 1.026 | 0.015 |

Note: AR = Adsorbent Ratio; Z = Zeolite, HRCWW = Rice Husk Charcoal Waste; R$^2$ = Determination Coefficient; r = Correlation Coefficient; b = Langmuir Constant; Q = Maximum Adsorption Capacity (mg/g); RL = Separation Factor; n = Freundlich Constant; Kf = Adsorption Capacity

The isotherm adsorption model of Cu$^{2+}$ follows the Freundlich model on adding of 8 gs of zeolite with the R2 value of 0.964 and adsorption capacity of 0.327 mg/g. Likewise, the addition of 2 gs of HRCW followed the Freundlich’s model with the R2 value of 0.895 and the adsorption capacity of 0.084
mg/g. The results of this study are in line with Estiaty [30] which shows that the Cu$^{2+}$ isotherm model uses zeolite following Freundlich model with the R2 value 0.996. The Pb$^{2+}$ adsorption’s model to follow the Langmuir isotherm’s model on adding of 8 gs of zeolite with a value of R$^2$ 0.998 and adsorption capacity of 0.754 mg/g. Similarly, the 2 gs of HRCW followed the Langmuir isotherm model with the R2 value 0.986 and adsorption capacity of 0.036 mg/g. The results of this study are in line with research of Hanjanattri et al. [31] showing that the zeolite adsorption isotherm model of the Pb$^{2+}$ follows the Langmuir model with a 5.057 mg/g adsorption capacity. Supporting [32] that Pb$^{2+}$ HRCW isotherm’s model to follow the Langmuir’s model with an adsorption capacity of 0.62 mg/g.

Langmuir isotherm’s type based on separation factor (RL) values on COD, Cu and Pb parameters (table 2) cannot be indicated because the RL value is negative. In order to determine more suitable isotherm’s equation, the standard deviation (SD) value must be determined [33]. The results of further calculations show that the addition of zeolite for removal COD follows Langmuir adsorption isotherm’s model with SD=22.82; Cu to follow Freundlich adsorption isotherm’s model with SD=0.0175, and Pb to follow Langmuir adsorption isotherm’s model with SD=0.0046. HRCW for decreasing to COD to follow Freundlich adsorption isotherm’s model with SD=376.26; Cu follows Freundlich adsorption isotherm’s model with SD=0.0050, and Pb follows Langmuir adsorption isotherm model with SD=0.0187.

4. Conclusions
The maximum adsorption capacity of giving 8 grams’ zeolite within 240 minutes is Cu=0.327 mg/g (followed Freundlich isotherm model); Pb=0.754 mg/g (followed Langmuir isotherm model), respectively. The absorption capacity of giving 2 grams RHCW in the next 180 minutes is: Cu=0.084 mg/g (followed Freundlich isotherm model) and Pb=0.782 mg/g (followed Langmuir isotherm model), respectively.

Acknowledgements
Chemistry Laboratory of the Faculty of Science and Mathematics, Satya Wacana Christian University-Salatiga, which allows its liquid waste to be investigated.

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