Biosorbent Prepared from Calotropis Gigantean Stems for Adsorption of Cu(II) Ions from Aqueous Solution

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Abstract
Calotropis gigantea stems (CGS) has the potential to use as biosorbent for adsorption of Cu(II) ions. In this study, the CGS biosorbent (CGSB) was prepared by drying and grounding. The effect of independent variables on adsorption capacity were investigated. As the result, the maximum adsorption capacity of 53.457 mg/g was obtained when initial Cu(II) ions concentration of 356.74 mg/L, CGSB size of less than 230 mesh, CGSB mass of 1 g, temperature of 27 °C, pH 5, and contact time of 60 min. The CGSB surface morphology was analysed using SEM. The adsorption of Cu(II) ions fitted well with pseudo first-order adsorption kinetic (PFO-AK) model (R²=0.99), and the PFO-AK adsorption capacity and rate constant obtained were 70.194 mg/g and 0.0877 g/mg.min, respectively. The adsorption isotherm of Cu(II) ions was in accordance with Freundlich model (R²=0.99), and the intensity and volume constants attained were 0.876 and 1.017 L/mg, respectively. This result showed that physical adsorption occurred dominantly than chemical adsorption. The application of CGSB on the wastewater of initial Cu(II) ions concentration of 389.31 mg/L from ex-mine pool of acid mine drainage (AMD) in Jantang village, Lhoong District, Aceh Besar, Aceh Province resulted in adsorption capacity of 37.52 mg/g with adsorption efficiency of 66.13%.

Keywords: Calotropis gigantean, copper, adsorption, kinetic, isotherm, acid mine drainage

1. Introduction
Various sources for coastal pollution can be identified, such as domestic sewage to ditches and rivers in coastal cities, industrial effluents from upstream and downstream of the river, and the outlet of ships in rivers and seas. Among other pollutants, certain toxic heavy metals were added to mixture pollutants (Vikasa and Dwarakish, 2015). One of the most abundant examples of heavy metals ions in industrial effluent is copper ions. Its mine plants capacity is 10 times higher than other non-ferrous metals plants (Miličević et al., 2020). Cu(II) ions in wastewater can come from mining operation, petroleum and agricultural industries, chemical and electrical industries, and even household domestic (Biswajit and Sudip, 2013).

Ions concentration cannot be more than 1.3 mg/L in customer taps of drinking water (USEPA, 2008) because accumulation of excess Cu(II) ions in the human body can cause disorders and various diseases including cancer due to its redox activity and mobilization in the human metabolic activity (Theophanides and Anastassopoulou, 2002). Several methods have been applied for the treatment of wastewater containing Cu(II) ions, such as electrochemical technologies, ion exchange, chemical precipitation, flotation, coagulation and membrane filtration (Fu and Wang, 2011) including adsorption method which have been carried out in various studies. Among other methods, adsorption is a proficient method for reduction of heavy metal including Cu(II) ions in industrial effluent because of its simplicity and cost-effectiveness (Wang et al., 2014).

The agricultural solid wastes which was readily available resources and cheap such as tree fern (Ho, 2003), wheat bran (Ozer et al., 2004), waste sugar beet pulp (Aksu and Işoglu, 2005), leaves of saltbush (Sawalha et al., 2007), pine cone powder (Ofomaja et al., 2010), palm oil fruit shells (Hossain et al., 2012), Spirulina platensis biomass (Ali et al., 2014), fermented corn stalk (Ren et al., 2018), sesame seed, groundnut seed, and coconut cake (Kumar et al., 2019), green vegetable waste (Sabela et al., 2019), cocoa cortex (Fotsing et al., 2020), Paesonia ostii seed coats (Liu et al., 2020), and spent biomass of Gelidiella acerosa (Dulla et al., 2020) have been proposed as raw material of biosorbent for adsorption of Cu(II) ions in aqueous solution. The basic components of

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these raw material consisted of some chemical functional groups as active sites for adsorption of Cu(II) ions.

Calotropis gigantea stems (CGS) have not been proposed for removal of Cu(II) ions in the previous studies. This plant generally grow in coastal areas, which has many benefits from its stems, leaves and roots. The plant is also upright wild plant which can grow in the dry season and dry land. The plant is classified as an annual plant, and it has height of 0.5-3 m. Each leaf blade is oval or elliptical with pinnate leaves. Single leaf shape with short stalks attached directly to the stem (Ahmed et al., 2005). The CGS has carbon content and chemical functional groups as the active sites, and the CGS carbon was applied in Lithium/Sodium ion batteries (Sahu et al., 2020).

The purpose of this study was to prepare biosorbent from the CGS, and to use it for the adsorption of Cu(II) ions in aqueous solution. The effect of independent variables, such as contact time, initial Cu(II) ions concentration, initial pH and biosorbent size on adsorption capacity were investigated to obtain an optimal condition. A scanning electron microscope (SEM) analysis was completed to show the CGSB surface layer, and to associate it with the effect of biosorbent size on adsorption capacity. Adsorption kinetic and isotherm studies were carried out based on optimal condition attained, the related constants were obtained. The CGSB were applied for Cu(II) ions in wastewater from examine pool of acid mine drainage (AMD) in Jantang village, Lhoong District, Aceh Besar, Aceh Province in order to obtain the adsorption capacity and efficiency.

2. Materials and Methods

2.1. Materials

CuSO$_4$.5H$_2$O (99%, Sigma-Aldrich) was diluted in aquades to prepare 1000 mg/L of stock Cu(II) ions aqueous solution. Then, it was diluted in aquades according to determined Cu(II) ions concentration at the range of 5.5-550 mg/L, and the real concentration was obtained using an Atomic Adsorption Spectrophotometer (AAS, 7000 AA, Shimadzu Japan). It was 5.52, 26.49, 57.01, 115.9, 251.5 and 567.47 mg/L according the AAS result and dilution factor, which was still in the range of previous studies (Kurniawan et al., 2006).

The raw material of biosorbent used in this study was Calotropis gigantea stem (CGS). To utilize the CGS biosorbent (CGSB), the CGS was taken from coastal Peukan Bada of Aceh Besar District, Aceh Province. The CGS was sliced into small pieces then washed using tap water, and aerated at room temperature. It was dried in an oven at 150 °C and 1 atm for 8 hours until the dried CGS mass being constant. Then, dried CGS was grounded to powder and divided into 4 (four) sizes, namely the CGSB-A (less than 230 mesh), the CGSB-B (in between 120-230 mesh), the CGSB-C (in between 60-120 mesh) and CGSB-D (more than 60 mesh).

2.2. Batch Adsorption

A preliminary adsorption experiment was conducted in batch mode to determine the equilibrium time of adsorption (Muslim, 2017). It was stirred at 75 rpm (Compact HI 180-2, Hanna Instruments Pte Ltd.), 1 atm, 30 °C and initial pH of 5. The CGSB-A (smallest size, less than 0.063 mm of diameter) was chosen for this test because it was expected that the smallest size biosorbent has the highest adsorption capacity, as reported in the previous study of eucalyptus-based biosorbent (Gebretsadik et al., 2020). It was compared to the CGSB-D (the biggest size). The bath mode run consisted of 1 g of CGSB-A, 100 mL of the solution at 567.47 mg/L of Cu(II) ions concentration. Using variable volume pipettes, 2-mL solution samples were taken at 0, 20, 40, 60 and 80 min of contact time. Each sample was diluted in 10 mL of aquades, and the diluted filtrate sample was filtered using syringe filter. It was finally analysed using AAS. Adsorption capacity at certain time was obtained by Equation (1) which was modified from previous study (Naswir et al., 2020):

$$q_t = \frac{(C_0 - C_t)V_{st}}{m_{AC}}$$

where $C_0$ (mg/L) is the Cu(II) ions concentration in aqueous solution (C) at the initial contact time of 0 min; $C_t$ (mg/L) represents the $C$ value at the contact time of $t$ (min); $q_t$ labels the adsorption capacity at $t$; and $q_t$ becomes $q_e$ when $t$ reach an equilibrium time; $V_{st}$ (L) is the aqueous solution volume (L) at the contact time of $t$; and $m_{AC}$ (g) is the CGSB mass. $V_{st}$ should be different at any contact time except at $t$ = 0 min and $t$ = 20 min because the aqueous solution volume decreased by 2-mL after taking each sample for AAS analysis.
Adsorption experiments were conducted after the equilibrium time was obtained, and the experiments were run until reaching the equilibrium time with independent variables i.e. $C_0$ (5.52–567.47 mg/L), initial pH (3–5) and CGSB sizes. The initial pH of adsorption was set by adding HCl and NaOH aqueous solution at 0.01–0.5 M prepared from a standard solutions (99%, Aldrich). The initial pH was obtained by Cobra3 Chem-Unit (12153, PHYWE, Western Germany). An optimal condition was obtained at the end of these bath experiments. A screen study was done at the end of this section and the result was highlighted in a table.

2.3. Analysis of Surface Morphology

Surface morphology of CGSB was analysed using a Scanning Electron Microscopy (SEM, TM-3000, 500 VA, 1 Phase 50/60 Hz, Hitachi Japan) with a magnification of 1500x to show the layer and pores distribution of CGSB. The SEM result was linked with the Cu(II) ions adsorption capacity of biosorbent over the CGSB size.

2.4. Adsorption Kinetic and Isotherm

Adsorption kinetic experiment was conducted in an optimal condition found in the previous procedure. Adsorption kinetic of Cu(II) ions onto the CGSB represented the amount of this heavy metal ions being adsorbed by CGSB per unit of time, which was counted by measuring the difference between $C_e$ and $C$ at equilibrium time, which can be presented by the adsorption rate constant. Pseudo first-order adsorption kinetic (PFO-AK) model by Lagergren et al. (1898) and pseudo second-order adsorption kinetic (PSO-AK) model by Ho et al. (1996) are presented by Equations (2) and (3), respectively (Muslim et al., 2017a):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where $q_t$ (mg/g) denotes as the adsorption capacity (q) at the time of $t$ (min); $q_e$ (mg/g) is $q$ value at the equilibrium time; and $k_1$ (/min) represents the rate constant of linearized PFO-AK model; and $k_2$ (g/mg.min) is the rate constant of linearized PSO-AK model.

Adsorption isotherm experiments were also conducted in an optimal condition found in the previous procedure. Linearized model of Langmuir adsorption isotherm (Langmuir, 1918) and Freundlich adsorption isotherm (Freundlich, 1906) which are commonly used to determine the adsorption isotherm parameters, can be expressed as Equations (4) and (5), respectively (Syahiddin and Muslim, 2018):

$$C_e = \frac{1}{q_e} \frac{1}{q_m K_L} + \frac{1}{C_e}$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_F$$

where $q_m$ (mg/g) represents the mono-layer adsorption capacity of Langmuir model; $K_L$ (L/mg) is the Langmuir pore volume constant; $K_F$ (mg/g) and 1/n are the adsorption capacity and intensity of adsorption based on Freundlich model, respectively.

2.5. Application of Biosorbent

A batch mode experiment was conducted in an optimum condition using 1 g of CGSB-A and 100 mL of wastewater consisting Cu(II) ions. The wastewater was taken from the AMD pool of ex-mine in Jantang Village, Lhoong District, Aceh Besar. The adsorption capacity and efficiency were obtained.

2.6. Comparison of Adsorption Capacity

The maximum adsorption capacity of Cu(II) ions from aqueous solution by CGSB in the optimal condition and the $q_e$ value based on the appropriate adsorption kinetic and isotherm constants were compared with the ones by other biosorbents, the adsorption capacity of Cu(II) ions from wastewater of AMD pool was also compared with the ones by other biosorbents.

3. Result and Discussion

3.1. Effect of Contact Time

The effect of contact time on the adsorption capacity in a preliminary adsorption study was shown clearly in Figure 1. The time range was based on the previous study wherein the Cu(II) adsorption capacity started steady at 80 min of contact time (Muslim et al., 2017a). The $q_e$ value for the CGSB-A at 20, 40, 60 and 80 min was 37.731, 51.056, 53.457 and 53.737 mg/g, respectively, and it was 13.795, 31.046, 36.713 and 36.738 mg/g, respectively for the CGSB-D. The adsorption
capacity of CGSB-A increased sharply for the first 20-min contact time was reasonable because it was expected to be initial adsorption stage. This stage is controlled by the diffusion of adsorbate onto adsorbent where the driving force becoming higher when the gap between concentration of adsorbate in solution and on adsorbent is higher (Medhi et al., 2020). However, this stage was different for the CGSB-A, which increased moderately. This result caused by reducing the size of CGSB which will be highlighted in the following discussion on effect of biosorbent size.

The adsorption capacity inclined slowly after 20-min. The Cu(II) ions adsorption might be driven by the electrostatic attraction, Van der Waals interaction, or active site binding. The strongest intraparticle interaction results the most dominant adsorption of adsorbate onto adsorbent taking place (Marlina et al., 2020). Cu(II) ions adsorption reached steady stage when it stopped at equilibrium time. As can be observed in Figure 1, the equilibrium time for both the CGSB-A and CGSB-D was obtained at 60 min.

### 3.2. Effect of Initial Concentration

Figure 2 shows the effect of $C_0$ on the adsorption capacity of CGSB-A under a condition of pH 5. It can be seen that it increased with increasing $C_0$ value. The highest adsorption was obtained at the concentration of 567.47 mg/L, which was 53.457 mg/g. While the lowest adsorption capacity of 0.520 mg/g was obtained at the lowest $C_0$ of 5.52 mg/L. This trend is common because more metal ions presented in the aqueous solution results in more diffusion of metal ions on adsorbent (Marlina et al., 2020). As viewed in Figure 2, a saturation has not been reached yet because there might be still free active site not being occupied by adsorbate. It expected to be saturation when increasing initial concentration of adsorbate in the solution (Liu et al., 2014).

![Figure 1. Adsorption capacity over contact time](image1)

![Figure 2. Adsorption capacity over initial Cu(II) ions concentration](image2)

### 3.3. Effect of Initial pH

Effect of initial pH on adsorption capacity under a condition as the $C_0$ value of 567.47 mg/L and 1 g of the CGSB-A was shown in Figure 3. The pH range of 3-5 was based on the previous studies wherein a maximum Cu(II) adsorption capacity was obtained at the initial pH of 4.5, in a range of 3-6 (Syahiddin and Muslim, 2018), and it increased when initial pH reduced from 6 (Givianrad et al., 2013).

As can be observed in Figure 3, the optimum adsorption obtained was at pH 5 with the adsorption capacity of 53.457 mg/g. It was 53.379 and 52.585 at pH of 4 and 3, respectively. When the initial pH declined, Cu(II) ions on CGSB-A was lower because the adsorbent surface might be surrounded by H$^+$ ions to compete Cu(II) ions to adsorb on the CGSB-A at lower pH. This trend was in line with previous study (Lee and Davis, 2001).

![Figure 3. Adsorption capacity over initial pH](image3)

The repulsion occurs between Cu(II) ions and the CGSB-A so that the Cu(II) ions adsorption reduced because of the acidic condition of the
adsorbent surface which was also positively charged (Aldov et al., 1995). Other study concluded that adsorption of metal ions onto some adsorbents starts decreasing when pH reduces from 6 (Givianrad et al., 2013).

3.4. Effect of Biosorbent Size

One of the factors influencing the adsorption of Cu(II) ions using CGSB was the biosorbent size. The difference in adsorption capacity under a condition as initial Cu(II) ions concentration of 567.47 mg/L and pH 5 can be seen in Figure 4. The results showed that CGSB-A, CGSB-B and CGSB-C had almost the same of adsorption capacity, which was 53.457, 52.895 and 52.253 mg/g, respectively.

The adsorption capacity was 36.713 mg/g for CGSB-D. It could be because the smaller CGSB size resulting the more surface area and pores on the adsorbent, causing the more Cu(II) ions were absorbed (Liese and Hilterhaus, 2013). The same trend was also highlighted by the previous studies for different metal ions adsorbed on adsorbent prepared from eucalyptus with the size ranged from 0.063 to 1.2 mm (Gebretsadik et al., 2020), and adsorbent prepared from sawdust with the size ranged from 1.18 to 2.36 mm (Nnaji and Emefu, 2017).

53.457 mg/g was obtained in an optimum conditions at equilibrium time ($t_e$) of initial Cu(II) ions concentration of 567.47 mg/L, adsorbent size of less than 230 mesh (A) and pH of 5 at 1 atm and 30 °C.

3.5. Biosorbent Surface Morphology

The previous result and discussion showed that CGSB-A had the highest adsorption capacity, and CGSB-B had the smallest one. Hence, only surface morphology of these biosorbents were analysed, and the results were viewed in Figure 5. As shown in Figure 5, CGSB-A surface had open, larger and much more pores, and it had also the layers covering visible pores. In contrast, CGSB-D surface had closed and less pores. This result was justifiable because grounding might cause shear, collision and friction resulting particle size reduction (Zorica et al., 2019), It can also break the adsorbent surface to open internal pores (Lee et al., 2018). Therefore, CGSB-A might have larger surface area compared to CGSB-D leading to the more Cu(II) ions were absorbed on CGSB-A compared to CGSB-D as highlighted in the previous discussion. However, this study did not cover Brunauer–Emmett–Teller study to determine CGSB surface area.

![Figure 4](image1.png)

**Figure 4.** Effect of the CGSB size on adsorption capacity

![Table 1](table1.png)

**Table 1.** Screening of an optimum condition for maximum adsorption capacity

| Biosorbent | $q_e$(mg/g) | $q_e$(mg/g) | $q_e$(mg/g) |
|------------|-------------|-------------|-------------|
| A          | 52.585      | 53.379      | 53.457      |
| B          |             |             | 52.895      |
| C          |             |             | 52.253      |
| D          |             |             | 36.713      |

Batch Adsorption: $C_0 = 567.47$ mg/L, 1 atm and 30 °C

A result of screen study was listed in Table 1. As listed in Table 1, a maximum capacity of

![Figure 5](image2.png)

**Figure 5.** Surface morphology of (a) CGSB-A and (b) CGSB-D
3.6. Kinetic and Isotherm Studies

Kinetic study was carried out under an optimal condition listed in Table 1 wherein the maximum adsorption capacity was obtained with an adsorption condition consisting of 1 g of CGSB-A, highest C<sub>0</sub> value of 567.47 mg/L and highest pH of 5 and the contact time ranged from 0 to equilibrium time (60 min) which was presented in the previous discussion.

As shown in Figure 6, the correlation coefficient (R<sup>2</sup>) value of linearized PFO-AK model was higher than R<sup>2</sup> value of linearized PSO-AK model, indicating the adsorption of Cu(II) ions onto CGSB-A followed the pseudo first-order adsorption kinetic. The R<sup>2</sup> value of linearized PFO-AK model also indicated that physical adsorption might control dominantly the adsorption of Cu(II) ions onto the CGSB-A (Pal and Deb, 2014, Li et al., 2020). The values of q<sub>e</sub> and k<sub>L</sub> were 70.194 mg/g and 0.0877 g/mg.min, respectively which were calculated from the slope and intercept of trendline, respectively.

Isotherm study was conducted under an optimal condition listed in Table 1 where the maximum adsorption capacity was obtained at the equilibrium time of 60 min at highest pH of 5, 1 g of CGSB-A and C<sub>0</sub> value of 5.52-567.47 mg/L. As can be calculated from the slope and intercept of trendline in Figure 7, the adsorption of Cu(II) ions on CGSB-A was very well defined by Freundlich isotherm model, and the values of K<sub>F</sub> and 1/n obtained were 1.017 L/mg and 0.876, respectively. Freundlich isotherm indicated the physical adsorption involving Cu(II) ions and CGSB-A took place dominantly which was in line with the previous study (Muslim et al., 2017b). However, chemical adsorption might also occur as expected in the kinetic study, since the n value was less than 1 (Ajenifuja et al., 2017).

The CGSB-A was applied for the adsorption Cu(II) ions in wastewater taken from the AMD pool of ex-mine in Jantang Village, Lhoong District, Aceh Besar, Aceh Province. An experiment of adsorption was also conducted in batch mode under optimal condition with 1 g of CGSB-A, 100 mL of the wastewater with an initial Cu(II) concentration of 389.31 mg/L based on AAS analysis. It was stirred at 75 rpm, 1 atm, 30 °C initial pH of 5 for 60 min of equilibrium time. As the result, adsorption...
capacity obtained was 37.521 mg/g and the adsorption efficiency achieved was of 66.13%.

3.8. Comparison of Adsorption Capacity

Table 2 displays a comparison maximum adsorption capacity ($q_{max}$) of Cu(II) ions from aqueous solution by different lignocellulosic-based biosorbents reported in present and previous studies. The $q_{max}$ value in present study based on optimal condition screened using independent variables and the appropriate adsorption kinetic are symbolized as PSAS-M and PSAS-K, respectively. Meanwhile PSWW-M stands for $q_{max}$ value for the adsorption capacity of Cu(II) ions from wastewater of AMD pool.

Table 2. Comparison of adsorption capacity of Cu(II) ions by CGSB and other biosorbents

| Biosorbents                          | $q_{max}$ (mg/g) | Ref.          |
|--------------------------------------|------------------|---------------|
| Tree fern                            | 11.7             | Ho, 2003      |
| Wheat bran                           | 51.5             | Özer et al., 2004 |
| Sugar beet pulp                      | 28.50            | Işoglu, 2005  |
| Palm oil fruit shell                 | 60.0             | Hossain et al., 2012 |
| Pine cone powder                     | 26.32            | Ofomaja et al., 2010 |
| Fermented Corn stalk                 | 12.47            | Ren et al., 2018 |
| Groundnut, sesame and coconut seed   | 4.24             | Kumar et al., 2019 |
| cake powder                          |                  |               |
| Green vegetable waste                | 75.0             | Sabela et al., 2019 |
| Cocoa cortex                         | 76.92            | Fotsing et al., 2020 |
| Paeonia ostii seed coats             | 25.5             | Liu et al., 2020 |
| CGSB-A                               | 53.457           | PSAS-M        |
| CGSB-A                               | 70.194           | PSAS-K        |
| CGSB-A                               | 37.52            | PSWW-M        |

As listed in Table 2, $q_{max}$ value of CGS-A was higher than $q_{max}$ value of biosorbents prepared from tree fern, sugar beet pulp, pine cone powder, fermented corn stalk, groundnut and sesame and coconut seed cake powder. Biosorbents utilized from green vegetable waste and cocoa cortex had higher $q_{max}$ value compared to CGS-A. Overall, biosorbent in present study would a biosorbent for the adsorption of Cu(II) ions.

4. Conclusion

The CGS biosorbent was able to absorb rapidly Cu(II) ions in the first 20 min of contact time, and the adsorption reached the equilibrium time at 60 min. Adsorption of Cu(II) ions CGS biosorbent with the size of less than 230 mesh (CGSB-A) followed pseudo first-order adsorption kinetic under an optimal condition, indicating a physical adsorption of Cu(II) ions occurred on CGSB-A. The expectation of physical adsorption was also in line with the result of adsorption isotherm study whereas it was favorable adsorption to Freundlich isotherm model. The equilibrium adsorption capacity and rate constant obtained were 70.194 mg/g and 0.0877 g/mg.min, respectively based on the kinetic study where the adsorption fitted well to the pseudo first-order adsorption kinetic. The experimental studies in bath mode using Cu(II) ions aqueous solution and ex-mine wastewater showed that CGS could be a promising raw material of biosorbent for the future.

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