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# MODIFICATION LEAF DREGS OF LEMONGRASS WITH CITRIC ACID FOR Cd(II) REMOVAL

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Penulis Korespondensi

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***A B S T R A C T***

*The present research was studied the capability of leaf dregs lemongrass (LDLG) and modified LDLG by Citric Acid (LDLGCA) for Cd(II) removal. The optimum conditions for both biosorbents at pH 5, stirring speed 200 rpm, contact time 60 minutes, and temperature 25 °C. The optimum concentration LDLG was 120 mg/L and 160 mg/L LDLGCA with adsorption capacity 10.63 mg/g and 11.66 mg/g, respectively. Isotherm models revealed that the adsorption of LDLG and LDLGCA followed Langmuir isotherm model with coefficient determination ($R^2$) 0.98 LDLG and 0.93 LDLGCA. Both biosorbents were fitted to pseudo-second-order indicating that adsorption process chemically occurring. Adsorption Cd(II) LDLG spontaneous reactions and exothermic, meanwhile for Cd(II) removal LDLGCA not spontaneous and exothermic. The characterization biosorbents was done using FTIR, XRF, SEM – EDX and BET. The adsorption capacity of both biosorbents decreased after 3 times adsorption-desorption cycles. Applications biosorbents to the real wastewater (Laboratory wastewater) indicated that LDLG can remove Cd(II) up to 46.88 % and LDLGCA reached the peak at 52.14 %. Based on XRF data, the percentage of Cd(II) in both adsorbents increased up to 21.12% for LDLG and 24.04 % for LCGA. The result indicated that Citric Acid was quite effective as modifier for Cd(II) removal.*



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## Introduction

Industrial development has caused advantages and disadvantages for Indonesian citizens. It increases economic, education and health values, but produces liquid, solid, and gas waste. The liquid waste contains hazardous substances such as pesticides, dyes, and heavy metals. When mentioned, waste contacted with a living thing in exceeding it can cause health problems and even death. The qualities of water should be determined, the facts causing the pollution should be taken to minimize the pollution. Therefore, the studies involved with the tracing of wastewater treatment and water quality all over the world have increased every passing day (Kalipci, 2019). Heavy metals are the elements of chemical compounds with an atomic mass of 66.8 g/mol and low biodegradability, which are one of the most toxic contaminants in the environment . Cadmium is the seventh most dangerous heavy metal ions with the permissible limit of 0.002 mg/L according to the Toxic Agent and Disease Registry (ATSDR) and the United States Environmental Protection Agency (USEPA). Meanwhile, the World Health Organization (WHO) stated that the threshold value of the metal ion Cd(II) in drinking water is 0.003 mg/L (Alakhras, 2019).

Due to its disadvantages, some technologies which are efficient, environmentally friendly, and short-time operation are required to remove Cd(II) in the environment. Several methods have been used to remove Cd(II) ions from the environment, namely coagulation, oxidation, chemical reduction, electrochemical treatment, and reverse osmosis. However, these methods suffer from several drawbacks such as cannot remove ions completely, need more reagents, high costs, and high energy consumption. Moreover, the process also produces toxic sludge so that it can harm the environment (Nasution, Aziz, et al., 2019). The adsorptions method is a technology using agricultural by-products or geomaterial as an adsorbent. This method is preferred due to its high efficiency and being environmentally friendly.

Most of the agricultural waste mainly consists of components such as cellulose, hemicelluloses, and lignin, and they provide effective removal of a wide range of pollutants through functional groups such as hydroxyl, carboxyl, phenols, methoxy, etc. As a result, agricultural wastes can be used as an economical and eco–friendly adsorbent since it is abundant and renewable source. Lemongrass (*Cymbopogon nardus* L. Rendle) is an aromatic plant with a distinctive scent which is widely cultivated in Indonesia. It is harvested three times a year in the age range of 6 months. This lemongrass is widely used in perfume industries, cosmetics, and as a flavoring agent. The increase of essential oils production from lemongrass leaf results in increasing Leaf dregs of lemongrass. Leaf dregs of lemongrass contain lignocellulose 39.50%, cellulose, 22.60% hemicellulose, and 28.50% lignin (Haque et al., 2018). Several other studies also stated that lemongrass leaves contain citronella 32 – 45% , geraniol 12 – 18 %, citronellol 11 – 15%, geranyl acetate 3 – 8%, lemongrass acetate 2 – 4 %, Limone 2 – 4% and other components 1 – 36%. Lemongrass leaves (Cymbopogon citrus) consist of some functional groups such as O – H stretching, C – N stretching, C – O stretching (carboxylic), C = O stretching. Those functional groups play an important role in the adsorption process.The process of modifying leaf dregs of lemongrass using citric acid occurs against the O – H cellulose group contained in the leaf dregs of lemongrass with the carboxylic group contained in the citric acid, which will later form an ester bond between the two to add a hydroxyl group to the biosorbent to increase the Cd(II) capacity.

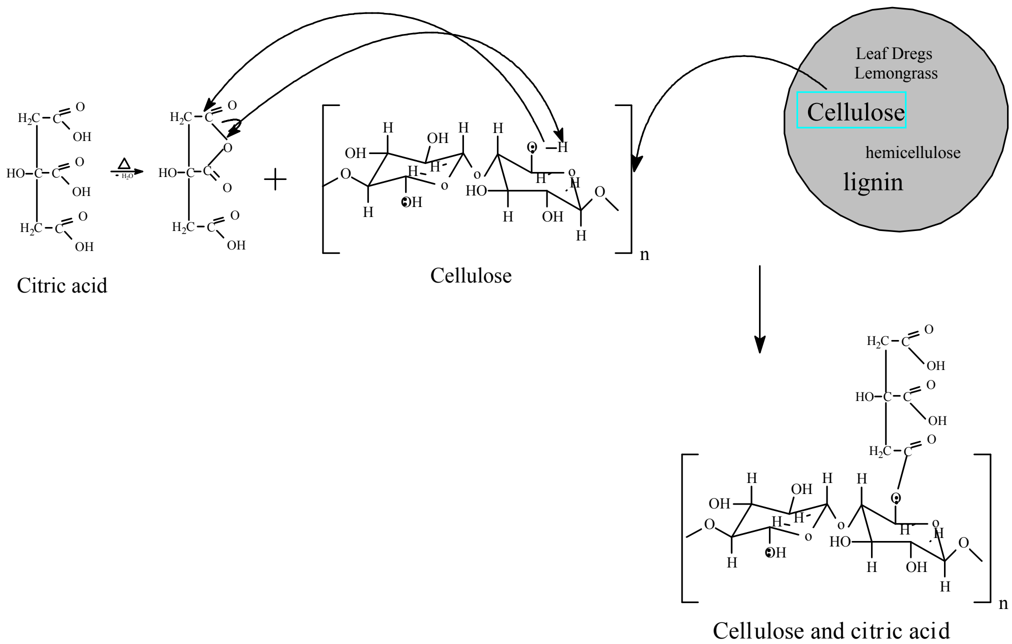



**Figure 1. Possible mechanisms between cellulose and citric acid**

To increase the adsorption capacity of adsorbent, leaf dregs of lemongrass was modifier by citric acid. The use of citric acid as a modifier was due the presence of plenty of hydroxyl groups in the compound, which can interact with Cd(II) for enhancing adsorption capacity. A research that has been done by (Ranasinghe et al., 2018) which compared citric acid (CA) and phosphoric acid (PA) as a modifier found that CA was more effective for increasing the adsorption capacity of adsorbents. The previous research by (Leyva-Ramos et al., 2012) has employed citric acid-modified corn cobs and revealed that the adsorption capacity of mentioned adsorbent was 26.5 times more efficient than those without modification with citric acid. Citric acid consists of three carboxylic (tricarboxylate) groups, which can contribute to the adsorption process. Thus, the aim of this research was to study lemongrass leaf dregs and citric acid-modified lemongrass leaf dregs ability for Cd(II) ion removal.

## *Material and Methods*

### Material

The LDLG (*Cymbopogon nardus* R.Lendle) was obtained from the agricultural area of the Andalas University Limau Manis, Padang City, West Sumatra, Indonesia. Cadmium Acetate Dihydrate $(CH_3COO)_2Cd_2H_2O$ (Merck), $HNO_3$ pa (Merck). NaOH (Merck), Citric Acid ($C_6H_8O_7$) (Merck), Monobasic Sodium Phosphate ($NaH_2PO_4$) (Merck), Dibasic Sodium Phosphate ($Na_2HPO_4$) (Merck), Sodium Citrate Dihydrate ($C_6H_5Na_3O_7.2H_2O$) (Merck), and Acetic Acid ( $CH_3COOH$) (Merck). All the reagents were analytical grade.

**Sample Preparation**

The LDLG was washed with tap water to remove dirt and dried at the room temperature. The dried leaves was grinded into a small size and sieved with the size of 36 µm. The powder of LDLG was activated using 0.01 M HNO3 in 1: 6 w/v and let it sit for 24 hours. Then, it was rinsed until the neutral pH was reached and then air-dried.

**Modification of Ldlg With Citric Acid (CA)**

Modification LDLG with CA was adopted from (Leyva-Ramos et al., 2012). 20 gram LDLG powder was added in to 100 ml citric acid 1 M. The mixture was heated at 60°C for 2 hours. The mixture was filtered and let sit to cool down before putting it in the oven at temperature 50°C for 24 hours. Then the temperature was raised to 120°C for 3 hours and let it cool down. Then the powder was washed with distilled water until the pH was neutral. The modified leaf dregs of lemongrass was dried in an oven at 50 °C for 24 hours to remove the remaining water.

**Point of Zero Charge ($pH_{pzc}$)**

0,5 g of LDLG and LDLGCA was added into 0.1 M KCl solution (25 mL). The pH was adjusted within 2,3,4,5,6,7 and 8 using NaOH or $HNO_3$ 0.01 M. The mixture was shaken for 24 hours with a stirring speed of 100 rpm. The solution was filtered, and the final pH was determined. The point of zero of charge was determined by plotting a curve of ΔpH against the initial pH.

***Adsorption of Cd(II) using LDLG and LDLGCA***

Determination of optimum adsorption capacity for Cd(II) removal using LDLG and LDLGCA was carried by batch method. 0.1 g biosorbents was contacted with Cd(II) solutions (10 mL) at different parameters such as pH (2, 3, 4, 6, and 7), metal ion concentration (20 – 180 mg/L), stirring speed (50 – 250 rpm), contact time (45 – 125 minutes) and heating temperature of biosorbent ( 25 - 150°C). The concentration of Cd(II) that remained in the solution was measured by AAS (Atomic Absorption Spectrophotometry). The adsorption capacity and % removal were calculated by the following equation :

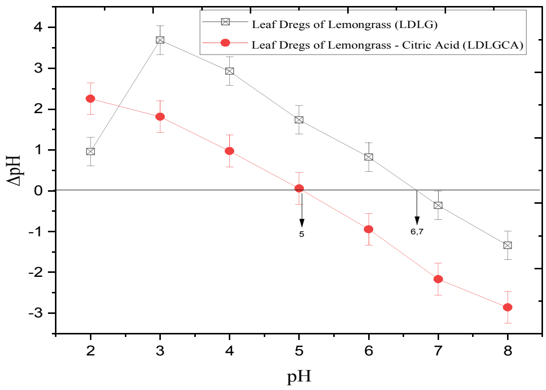
$$qe = \frac{C_0 - C_e}{m} \, x \, v \qquad (1) \qquad\qquad \%\ Removal = \frac{Co - Ce}{Co} \times 100\% \qquad (2)$$

Where $C_o$ is the initial concentration of Cd(II) (mg/L). $C_e$ is final concentration Cd(II) (mg/L). $V$ is the volume of solution (L). $m$ is the mass of biosorbent used (g). The biosorbents were characterized by FTIR, XRF, SEM – EDX and BET.

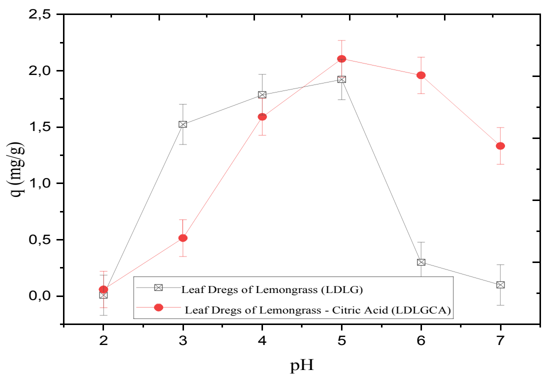
## Result and Discussion

### Point of Zero Charge (pHpzc) and Effect of pH

pHpzc was a parameter used to decide the pH value of the LDLG and LDLGCA has a neutral pH(Rahmiana Zein et al., 2018).




(a)




(b)

**Figure 2 (a) pHpzc of LDLG and LDLGCA, (b) Effect of pH on adsorption of Cd(II) onto LDLG and LDLGCA concentration Cd(II 20 mg/L ; the mass of the biosorbent 0.1 g; stirring speed 100 rpm; contact time 60 minutes**

Figure 2 (a) showed that pHpzc of LDLG and LDLGCA were 6.7 and 5 respectively. At pH < pHpzc, the surface charge of the biosorbent tended to be positive, and at pH > pHpzc the surface charge of the biosorbent tended to be negative. Therefore, the higher pH there was an increase in the affinity of cations for functional groups in biosorbents resulting in increasing Cd(II) adsorption and vice versa. The obtained result showed that PHpzc for LDLG was higher than LDLGCA due to acid modification with high concentration. The same result also reported by (Sharma, 2008). The effect of pH was an important parameter for the adsorption of Cd(II) which was related to the electrostatic properties of Cd(II) on the biosorbent. The optimum pH of both biosorbents was pH 5 with adsorption capacity 1.92 mg/g for the LDLG and 2.11 mg/g for LDLGCA (Figure 2(b)).

Figure 2(b) showed that the higher the pH (up to 5) the higher the adsorption capacity obtained because the lower pH led a competition between metal ions and $H^+$ for occupying the active sites so that the adsorption capacity was reduced (Rahmiana Zein et al., 2018). At pH > 5 the capacity for Cd(II) sorption tended to decrease because Cd(II) ions will form $Cd(OH)_2$ precipitates preventing Cd(II) to be bonded by the active sites and reduced the adsorption capacity.

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**Effect of Concentration and Isotherm Model Evaluation**

The effect of concentration was study in variations of 20 – 180 mg/L.

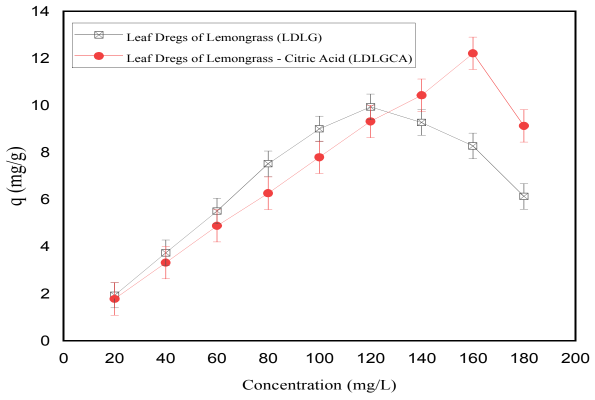


**Figure 3 effect of Cd(II) concentrations on LDLG and LDLGCA sorption pH 5 ; the mass of the biosorbent 0.1 g; stirring speed 100 rpm; contact time 60 minutes**

Figure 4 showed that the optimum concentration of LDLG was 120 mg/L with an adsorption capacity of 9.94 mg/g. Meanwhile, for the adsorption Cd(II) ion with LDLGCA the optimum concentration was 160 mg/L with an adsorption capacity of 12.22 mg/g. The result showed the higher the concentration the higher the amount of Cd(II) that can be bound by the active site so that the adsorption increased until the equilibrium was reached. It was obvious the modification of LDLG with citric acid enriched the number of O – H groups which increased the number of active sites as well.

The isotherm model was determined to describe the relationship between the Cd(II) and biosorbent. The Langmuir isotherm and the Freundlich isotherm models were employed to evaluate the adsorption phenomenon of LDLG and LDLGCA. The Langmuir isotherm model stated that the interactions that occurred between Cd(II) and biosorbent took place on a homogeneous surface, chemical interactions and monolayer (Adeniyi & Ighalo, 2019). The following equation was used to determine the Langmuir isotherm :

$$qe = \frac{q_m b_l C_e}{1 + b_l C_e} \quad (3), \qquad \frac{C_e}{q_e} = \frac{1}{q_m} Ce + \frac{1}{k_l q_m} \quad (4)$$

Where $q_m$ = maximum adsorption capacity (mg/g). $q_e$ = concentration of adsorbate substance per grams of adsorbent (mg/g). $c_e$ = equilibrium concentration and $k_L$= equilibrium constant (adsorption affinity).

The Freundlich isotherm model stated that the interactions between the Cd(II) and biosorbent took place on a heterogeneous surface. The physical sorption occured and formed

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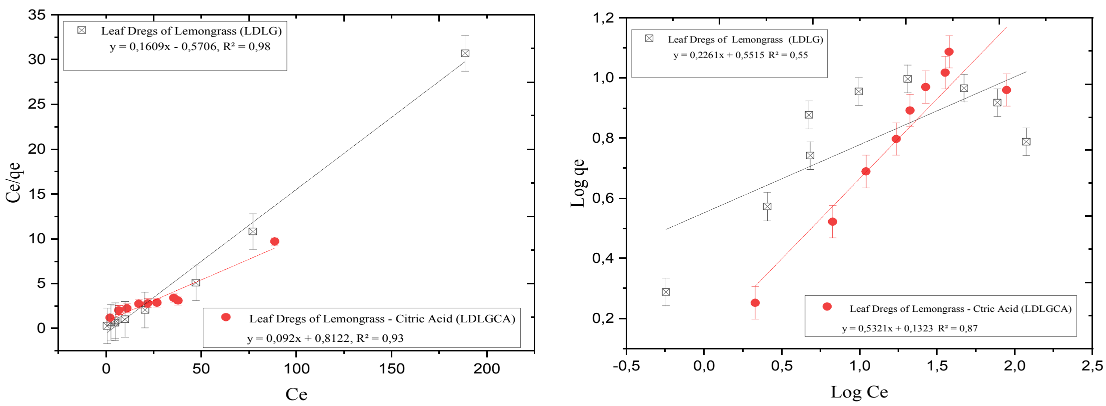
a multilayer. The determination of the Frendluich isotherm model can be obtained by the following equation:

$$qe = K_f C_e^{1/n} \quad (5), \qquad \log qe = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

$K_f$ = Frendluich constant, $qe$ = concentration of adsorbate substance per grams of adsorbent (mg/g).




(a) (b)

**Figure 5. (a) Langmuir ; (b) Freundlich isoterm models of Cd(II) sorption onto LDLG and LDLGCA**

The results obtained showed that the adsorption of Cd(II) onto LDLG and LDLGCA fitted to Langmuir isotherm model. In the adsorption of Cd(II) using the LDLG, y = 0.16x - 0.57 , $R^2$ = 0.98, $K_L$ = 0.28 and qm = 6.25 mg/g. While for LDLGCA obtained y = 0.09 x + 0.81, $R^2$ = 0.93, $K_L$ = 0.11 and qm = 10.87 mg/g. The $K_L$ stated the affinity of Cd(II) sorption for biosorbent. The higher value of $K_L$ caused a higher affinity of biosorbent for to Cd(II). The $K_L$ values for LDLG and LDLGCA were 0.28 and 0.11, respectively which were quite low indicated that the adsorption affinity of the biosorbent for Cd(II) was low. The obtained RL value can also explain the adsorption process favorable or unfavorable. The $R_L$ indicated whether the interaction was favorable or irreversible. If $R_L$ = 0 , the adsorption was irreversible. 0 < $R_L$ < 1 indicated the interaction was favorable, $R_L$ = 1 indicated the interaction was linear and if RL > 1, it was unfavorable (R. Zein et al., 2018). The results of $R_L$ obtained for both biosorbents showed that the interactions were favorable.

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**Table 1. Isotherm parameters for LDLG and LDLGCA**

| Langmuir Isotherm | | | Frenduilch Isotherm | | |
|---|---|---|---|---|---|
| Adsorbent | LDLG | LDLGCA | Adsorbent | LDLG | LDLGCA |
| $R^2$ | 0.98 | 0.93 | $R^2$ | 0.55 | 0.87 |
| $K_L$ | 0.28 | 0.11 | $K_f$ | 0.28 | 0.74 |
| $q_m$ | 6.25 | 10.87 | n | 4.423 | 1.88 |

**Effect of Contact Time and  Kinetic Model**

The contact time was required to see how long the biosorbent and Cd(II) can interact optimally before it became saturated. The length of contact time will be directly proportional to the adsorption of Cd(II) (Ranasinghe et al., 2018). The longer the contact time the more Cd(II) can interact with the active site on the biosorbent.

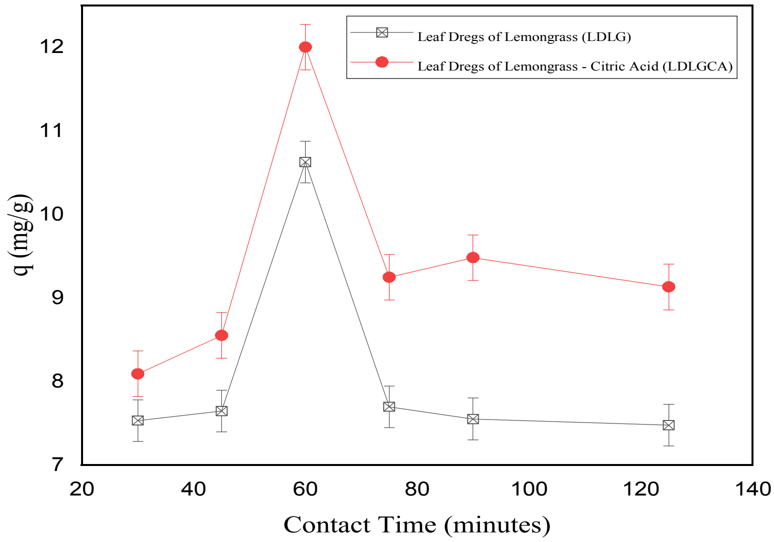


**Figure 6. Effect of contact time on adsorption of Cd(II) LDLG  at concentration 120 mg/L and LDLGCA with a concentration of 160 mg/L; the mass of the biosorbent 0.1 g; stirring speed 200 rpm.**

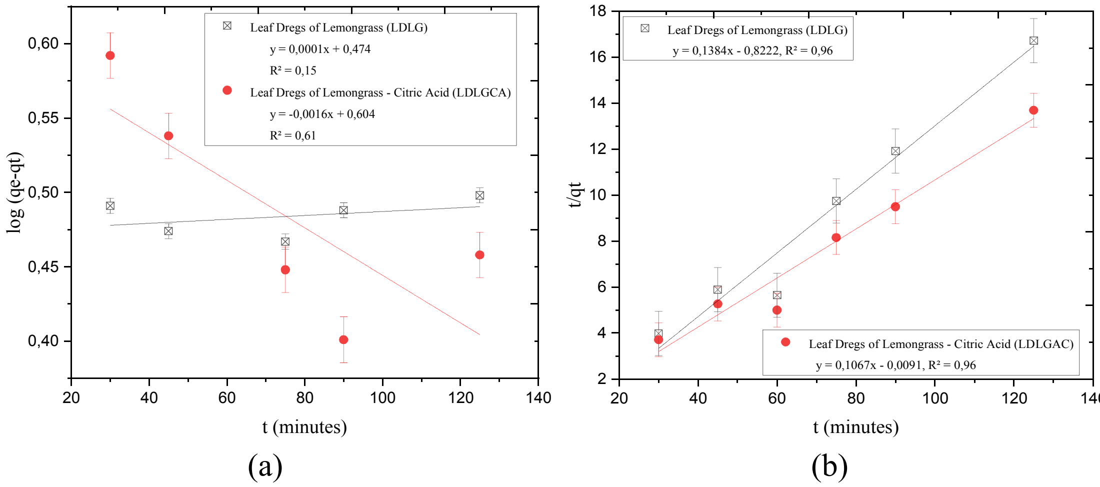


**Figure 7. (a) Pseudo first-order; (b) second-order pseudo curve of Cd(II) LDLG and LDLGCA**

Figure 6 showed that the longer the contact time increased the adsorption capacity of biosorbent until the equilibrium was reached. The LDLG and LDLGCA achieved the optimum condition at contact time of 60 minutes with adsorption capacity 10.63 mg/g and 12.00 mg/g. respectively. As the further time stage, the adsorption capacity of biosorbents decreased because the active site of the biosorbent has bound Cd(II). So that the number of active sites on the biosorbent also decreased causing competition between Cd(II) to interact with the active site on the biosorbent. Since the bond was formed between Cd(II) and the biosorbent were unstable causing the re-release of Cd(II) into the solution(Rahmiana Zein et al., 2019). The kinetic model determined the reaction rate, reaction mechanism and efficiency of Cd(II) sorption onto LDLG and LDLGCA. Kinetic models were usually carried out using two methods namely pseudo-first-order and pseudo-second-order(Rahmiana Zein et al., 2020).

Figure 7 indicated that the coefficient determination for the pseudo–first–order ($R^2$) was 0.15 for LDLG and 0.61 for LDLGCA and pseudo – second – order coefficient determination was $R^2$ = 0.96 and $R^2$ = 0.96 for the LDLGCA. The obtained result showed that the adsorption of Cd(II) with the two biosorbents followed the pseudo – second – order model indicated that the interaction between Cd(II) and biosorbents was chemical interaction. This was also confirmed by the result obtained from isotherm model evaluation.

### *Effect Of Temperature And Thermodynamics Analysis*

The effect of temperature described the capability of biosorbents to withstand high temperatures. The results of the effect of temperature can be seen in Figure 8.

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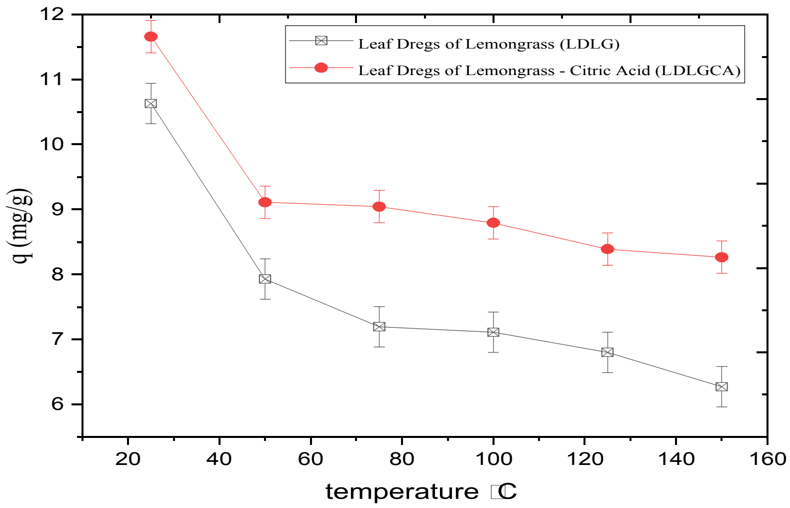


**Figure 8. Effect of temperature on adsorption of Cd(II) onto LDLG at a concentration of 120 mg/L and LDLGCA with a concentration of 160 mg/L; pH 5; the mass of the biosorbent 0.1 g; stirring speed 200 rpm; contact time 60 minutes.**

It showed that optimum temperature was obtained at 25°C for the two biosorbents with an adsorption capacity of 10.63 mg/g for LDLG biosorbent and 11.66 mg/g for LDLGCA. The obtained results showed that the adsorption capacity decreased as the temperature increased due to the damage organic compounds contained in the biosorbent resulted in a decrease in the active site in the biosorbent. The thermodynamic model was determined to see the adsorption process that occurs due to effect temperature (Rahmiana Zein et al., 2020). Parameters that could be determined from the thermodynamic were entropy (ΔS), changes in enthalpy (ΔH), and changes in Gibbs energy (ΔG). These parameters indicated whether the process was exothermic or endothermic in nature. The temperatures used in the thermodynamic test were 25, 35 and 45 °C with Cd(II) concentrations of 10-50 mg/L.

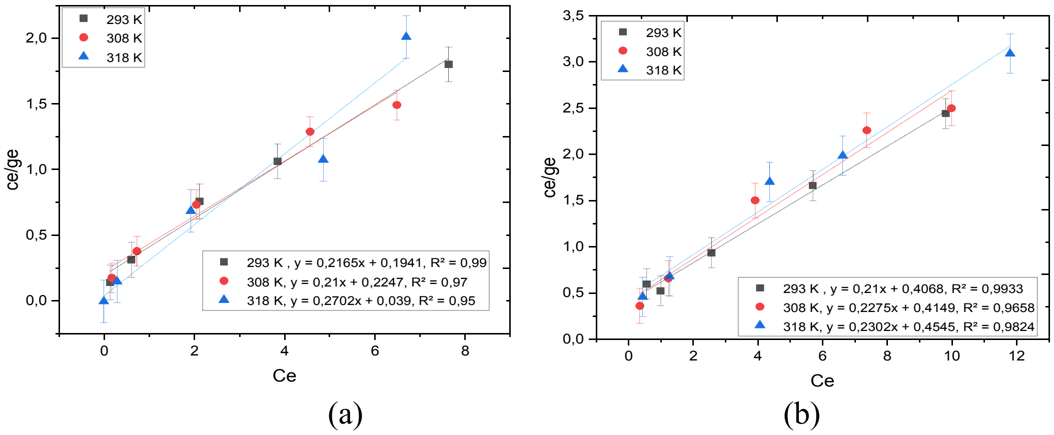


**Figure 9. Thermodynamic evaluation of Cd(II) adsorption (a) LDLG and (b) LDLGCA**

Figure 9. Showed the thermodynamic parameters obtained from Cd(II) adsorption using the LDLG and LDLGCA. It revealed that Gibbs energy value (ΔG) was negative for the LDLG which indicated the reaction was spontaneous and positive (ΔG) indicated non – spontaneously reaction. The value of the entropy change (ΔS) was = -22.66 j/mol.K for the LDLG, ΔS = -15.76 J/mol.K for the LDLGCA and the enthalpy change (ΔH) value = -7.07 kJ/mol for LDLG, (ΔH) = -3.24 kJ/mol for LDLGCA. The ΔS and ΔH values indicated that the two biosorbents went through exothermic reactions.

***Biosorbents Characterization***

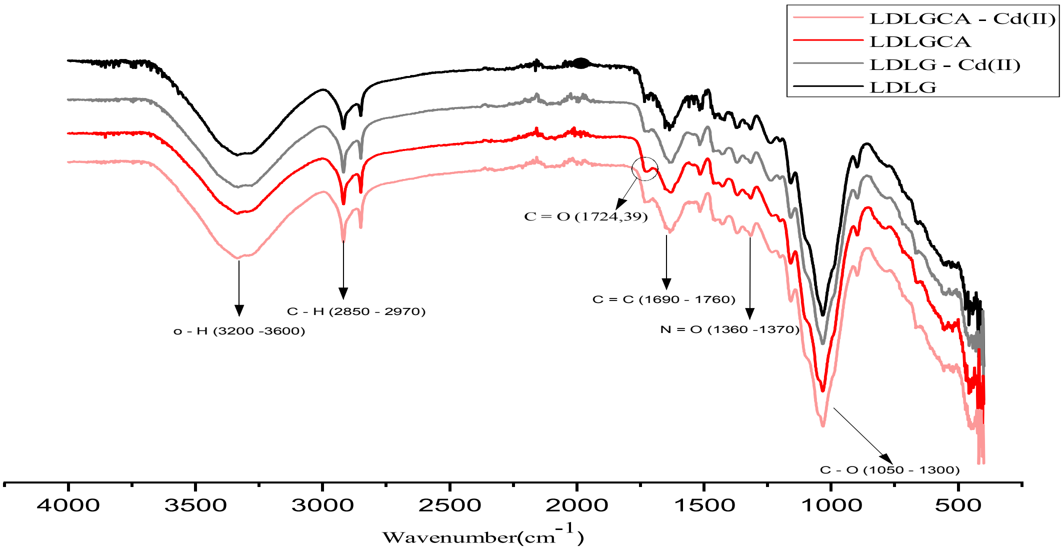


**Figure 10. FTIR spectra of LDLG and LDLGCA with before and after adsorption Cd(II).**

Figure 10. Revealed the functional groups existed in LDLG and LDLGCA including the hydroxyl (O – H) in the range of wavenumber of 3200-3600 cm$^{-1}$, aromatic (C = C) in the wavenumber 3200-3600 cm$^{-1}$, wavenumber 1400 – 1600 cm$^{-1}$, (C = O) at wavenumbers 1690-1760 cm$^{-1}$ and (C – O) group at wavenumber 1050-1300 cm$^{-1}$. The wavenumber has been shifted after adsorption occurred. The functional group of (O – H) shifted from 3330.16 to 3341.75 cm$^{-1}$. The functional group of (O – H) shifted from 3342.70 to 3335.94 cm$^{-1}$ (C = O) from 1627.95 to 1634.70 cm$^{-1}$ and in the functional group (C – O ) from 1031.93 to 1032.90 cm$^{-1}$ (Table 2). The shift in wavenumber indicated an interaction of Cd(II) with the functional group. In the FTIR results, it can also be seen that there was a reaction between the LDLG and LDLGCA namely from the intensity of the carbonyl group that changed because the carboxylic group was bound to the LDLGCA (Leyva-Ramos et al., 2012).

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**Table 2. The wavenumber of LDLG and LDLGCA before and after Cd(II) removal**

| Functional group | LDLG ($cm^{-1}$) | LDLG – Cd(II) ($cm^{-1}$) | LDLGCA ($cm^{-1}$) | LDLGCA – Cd(II) ($cm^{-1}$) |
|---|---|---|---|---|
| O – H | 3330.16 | 3341.73 | 3342.70 | 3335.94 |
| C = C | 1635.66 | 1635.66 | 1627.95 | 1634.70 |
| C – O | 1032.96 | 1032.90 | 1032.90 | 1031.93 |

Characterization with XRF was to determine the chemical composition of biosorbent. The chemical composition of LDLG, LDLGCA, before and after adsorption process were listed in table 3.

**Table 3. Chemical composition of LDLG, LDLGCA before and after adsorptions Cd(II)**

| Element | Contents (%) | | | | Metal Oxide | Contents (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | LDLG | LDLG Cd(II) | LDLGCA | LDLGCA Cd(II) | | LDLG | LDLG Cd(II) | LDLGCA | LDLGCA Cd(II) |
| Si | 59.82 | 55.56 | 77.52 | 40.51 | $SiO_2$ | 69.65 | 67.65 | 82.71 | 54.72 |
| Ca | 15.65 | 2.30 | 3.83 | 9.69 | CaO | 8.48 | 1.30 | 1.83 | 6.46 |
| Mg | 4.51 | 3.09 | 0.86 | 2.15 | MgO | 5.14 | 3.46 | 1.01 | 2.50 |
| Ni | 0.02 | 0.02 | 0.03 | 0.05 | NiO | 0.01 | 0.01 | 0.01 | 0.03 |
| Cu | 0.11 | 0.04 | 0.05 | 0.09 | CuO | 0.05 | 0.02 | 0.02 | 0.05 |
| k | 2.06 | 0.51 | 0.40 | 1.01 | $K_2O$ | 1.01 | 0.26 | 0.18 | 0.64 |
| Cr | 0.05 | 0.05 | 0.05 | 0.09 | $Cr_2O_3$ | 0.03 | 0.03 | 0.02 | 0.06 |
| Cd | 0.00 | 21.12 | 0.00 | 24.04 | CdO | 0.00 | 10.71 | 0.00 | 14.27 |

Table 3 showed that Si was the highest percentage which was 55.58%. then followed by Ca 15.65%, Mg 4.51%, K 2.06%, Cu 0.11 %, and Cr 0.05 % and metal oxides SiO 69.65%, CaO 8.47%, MgO 5.14 % and K2O 1.01% for the LDLG. The element and metal oxide content that decreased after adsorption of Cd(II) were Ca 2.30%. K 0.51%, Cd 21.12% ,CaO 8.48%, $K_2O$ 0.26% and CdO 10.71%. The modified biosorbents contained Si 77.52%, Ni 0.03% metal oxide SiO 54.72%, NiO 0.01% which decreased after the adsorption took place. The presence of Cd(II) in adsorption showed that there was an interaction between Cd(II) and the two biosorbents and a decreasing percentage of several elements and metal oxides was probably due to an exchange with Cd(II) elements on the biosorbent.

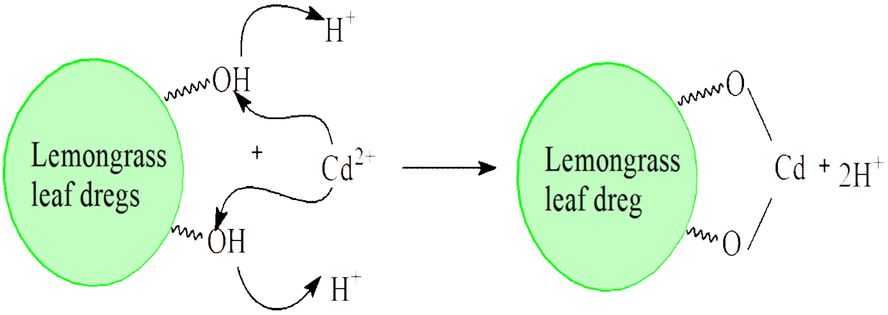
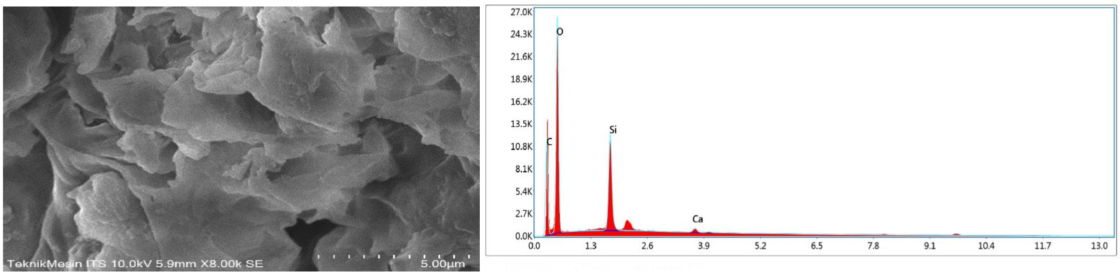
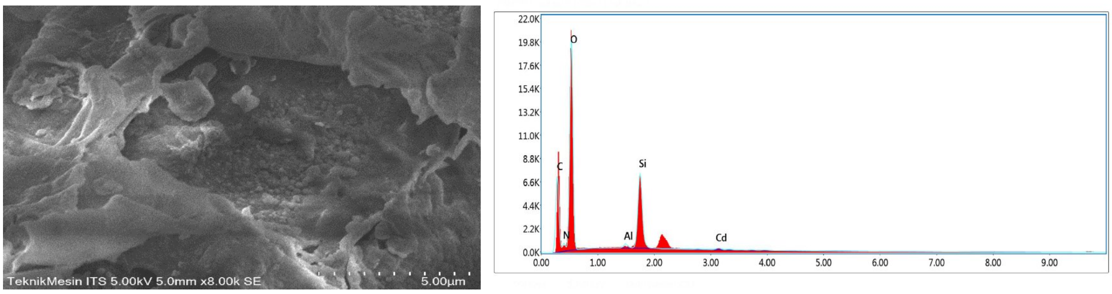



**Figure 11. The possible interaction of Cd(II) with functional groups in leaf dregs of lemongrass**

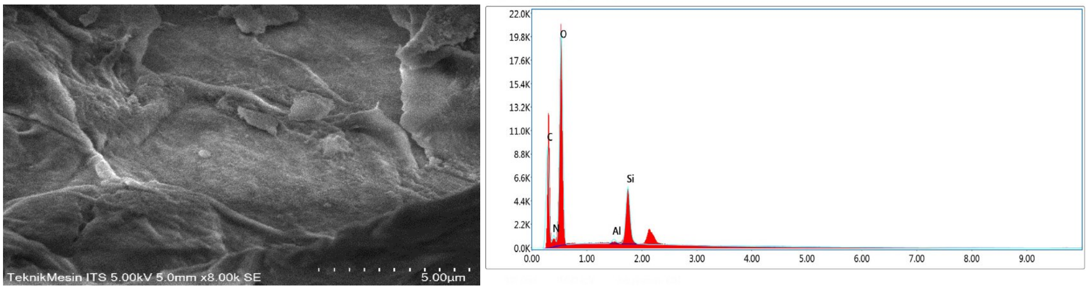
The interactions occurred between Cd(II) and biosorbents were a covalent bond where the $H^+$ group on the OH will undergo a deprotonation process which will cause $O^-$ to be negative charged and attracted positively charged Cd(II) metal ions. Interactions that occurred between metal ions and functional groups on the surface of biosorbents can not only happen covalently but also can occur several interactions such as ion exchange, complex formation, electrostatic interactions, interactions between pores, and several other interactions (Leyva-Ramos et al., 2012).The SEM EDX was mean to see the surface morphology of the biosorbent from LDLG and LDLGCA before and after Cd(II) removal (Figure 12 ).



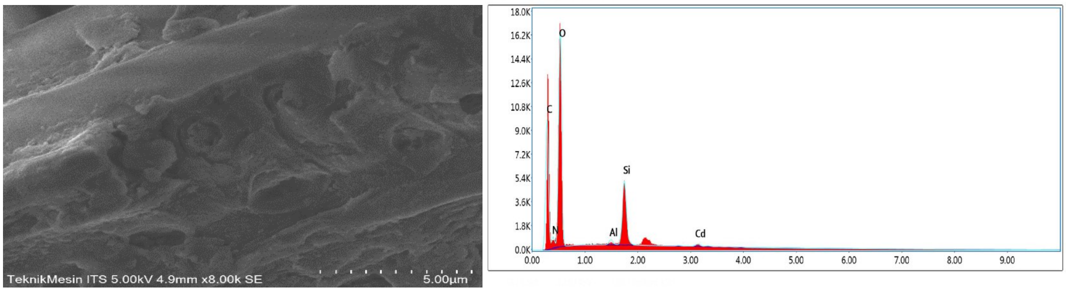
(a)



(b)




(c)




(d)

**Figure 12. SEM and EDX image of LDLG (a), LDLG – Cd(II) (b) LDLGCA (c) and LDLGCA – Cd(II) (magnification : 8000 K)**

The pictures above showed that the surface of the biosorbent before modification has a smooth surface. After adsorption with Cd(II) the surface of the biosorbent became rough indicating a Cd(II) interaction. The SEM results for of LDLGCA before adsorption revealed a smooth and after adsorption slightly rough indicating the presence of citric acid on the surface. The EDX results obtained also showed that before the modification Cd(II) was not showing up and after the adsorption, the Cd(II) was found 0.99% for LDLG and 1.22 % for LDLGCA. Characterization using BET needs to be done because the surface area and pore size significantly affect the binding process of Cd(II) ions with biosorbents . The table 5 showed a summary of the results obtained from the BET test of the biosorbent.

**Table 4. BET results for LDLG and LDLGCA before and after Cd(II) adsorption**

| Biosorbent | surface area ($m^2/g$) | pore diameter ($cm^3/g$) | size pore (nm) |
|---|---|---|---|
| LDLG | 0.92 | 0.01 | 16.83 |
| LDLGCA | 5.79 | 0.02 | 12.93 |
| LDLG – Cd(II) | 3.37 | 0.01 | 16.22 |
| LDLGCA – Cd(II) | 5.37 | 0.03 | 19.14 |

The results showed that the surface area of the biosorbent after being modified with citric acid was more significant, which was 0.92 $m^2/g$ to 5.79 $m^2/g$ (Badri et al., 2021). The decrease in particle size after being modified with citric acid indicated that the interaction between citric acid covering the pores of the biosorbent, which made the outer surface to be higher, causing more possibilities of Cd(II) ions to be bind biosorbent. The same results were also obtained by (Badri et al., 2021). After experiencing the adsorption of metal ions Cd(II), the surface area of the biosorbent also increased. This was due to the Cd(II) ion bond with the active site on the biosorbent. This is the same as that obtained by (Handayani et al., 2020). This was due to the Cd(II) ion bond with the active. This is the same as that obtained by (Handayani et al., 2020), where the surface area of the biosorbent increased after undergoing Pb(II) ion absorption, namely from 1.81 $m^2/g$ to 20,08 $m^2/g$. Biosorbent characterization using TGA was carried out to see the ability of the biosorbent to withstand high temperatures. The results of TGA from Leaf dregs of lemongrass can be seen in Fig 16

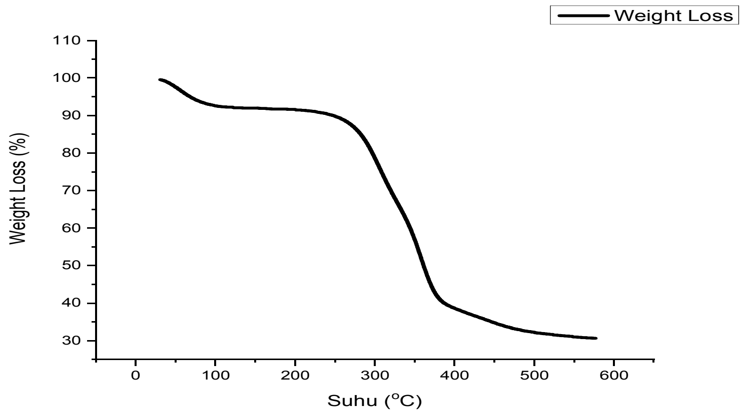



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**Figure 13. Thermogram for leaf dregs of lemongrass**

The TGA results revealed that leaf dregs the leaf dregs of lemongrass can last up to a temperature of 290°C, which indicated that during heating when the process of modifying Leaf dregs of lemongrass with citric acid does not affect the composition and structure of the Leaf dregs of lemongrass itself. Because, during the modification process, the heating temperature used was 120°C. The TGA results also showed that at a temperature of 50-100 °C, a moisture evaporation process occurred, which eliminated the $H_2O$ in the biosorbent. At the temperature 100 – 290 °C hemicellulose depolymerization process occurred. The mass loss of the biosorbent became much higher at the temperature of 290 - 360°C due to the depolymerization and breaking of the cellulose bonds. When the temperature was 400 – 600 °C, the weight loss became significant due to lignin decomposition (Ranasinghe et al., 2018).

## Application Using Laboratory Waste

The application of adsorbent using real waste showed the ability of biosorbent to interact with Cd(II) in a real environment and investigated the effect of other ions on the adsorption of Cd(II) in LDLG and LDLGCA.

  

**Table 5. Condition q and % removal of Cd(II) using LDLG and LDLGCAin laboratory waste**

| Biosorbent | Co dregs | Ce | Qe | % adsorption |
|---|---|---|---|---|
| LDLG | 4.38 mg/L | 2.32 mg/L | 0.20 mg/g | 46.88 |
| LDLGCA | 4.38 mg/L | 2.09 mg/ L | 0.30 mg/g | 52.14 |

The results obtained showed that the adsorption capacity of Cd(II) ions in the LDLG biosorbent was 0.20 mg/g with percent removal of 46.88%, and for the LDLGCA biosorbent, 0.30 mg/g with a percent removal 52.14%. This indicated that LDLGCA was more effective to remove Cd(II) in the real environment. The adsorption capacity of previous adsorbent for Cd(II) removal were listed in table 6.

**Table 6. Comparison of maximum adsorption capacities of several adsorbent for Cd(II)**

| Adsorbent | Adsorbate | $Q_{maks}$ ($mg.g^{-1}$) | Referensi |
|---|---|---|---|
| Sugar palm Arenga pinnata Merr | Cr(III) | 0.28 $mg.g^{-1}$ | (Rahmiana Zein et al., 2014) |
| | Cr(VI) | 0.52 $mg.g^{-1}$ | |
| | Cd(II) | 0.43 $mg.g^{-1}$ | |
| | Zn(II) | 0.58 $mg.g^{-1}$ | |
| Salak fruit skin | Pb (II) | 83.33 $mg.g^{-1}$ | (Rahmiana Zein et al., 2018) |
| | Cd(II) | 27.78 $mg.g^{-1}$ | |
| Kapok fruit peel (Ceiba petandra) | Pb(II) | 223.72 $mg.g^{-1}$ | (Rahmiana Zein et al., 2019) |
| | Cd(II) | 88.70 $mg.g^{-1}$ | |
| Herbal plant of mahkota dewa ( Phaleria macrocarpa ) | Cd(II) | seed : 21.46 $mg.g^{-1}$<br>flesh of fruit : 24.76 $mg.g^{-1}$ | (Nasution et al., 2015) |
| Flesh of fruit | Pb(II) | 31.44 $mg.g^{-1}$ | (Fauzia et al., 2019) |
| Leaf dregs lemongrass (Cymbopogon nardus L.Rendle) | Cd(II) | LDLG : 10.63 $mg.g^{-1}$<br>LDLGCA : 11.66 $mg.g^{-1}$ | Present study |

## Adsorption – Desorption Cycle

Adsorption-desorption cycles were one of an important parameters to investigate the regeneration and reusability of biosorbent. It made biosorbent cost – efective. When the adsorption-desorption process was carried out, there was an elution of Cd(II) ions that have bound to the biosorbent, namely the substitution of $H^+$ ions from $HNO_3$ with Cd(II) so that Cd(II) ion will be released into the solution (Nasution, Zein, et al., 2019). This was done to see the ability of the biosorbent to bind to Cd(II) and how many times the biosorbent can be used before the adsorption capacity was significantly decreased so that the adsorbent must be replaced. The figure 15 was showed that the LDLG and LDLGCA experienced a decrease in adsorption capacity after three times cycles. Although Cd(II) could not be completely eluted, the adsorbent could still be used with a reasonable adsorption rate because the reduction in adsorption during the three times cycles was not considerable.

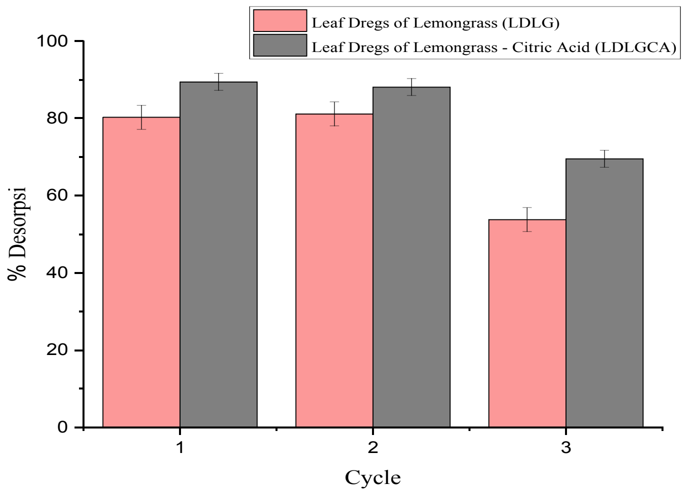


**Figure 14. Graph of Adsorption – desorption cycle results with biosorbents of LDLG and LDLGCA**

## Conclusion

Chemical modification of lemongrass leaf dregs using citric acid as a modifier has proven to be effective as a biosorbent to increase the adsorption of Cd(II) metal ions. The adsorption capacity of Cd(II) ion was increase from 10.63 mg/g to 11.66 mg/g. It had a fast desorption rate, and the equilibrium was achieved within only 60 minutes. The adsorption Cd(II) onto LDLG and LDLGCA experienced both chemical and physical sorption proved by adsorption model and adsorbent characterization. Thus, the utilization of lemongrass as an alternative adsorbent can reduce agricultural solid waste as well as heavy metal waste in the environment.

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**Thanks**

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