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Biosorption of Pb and Cd using gambir leaf (uncariagambirroxb) with silica gel immobilization technique

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Abstract. The Gambir plant (*Uncariagambir*Roxb) is one of the largest commodities in West Sumatera. The Gambir plant contains high cellulose, lignin and tannin compounds which can be utilized as adsorbents to absorb dissolved metals in water. Biosorbents produced from Gambir plants contain tannin compounds that do not have strong bond structures and are so easily degraded, that it is necessary to strengthen the structure by immobilization using silica gel. The biosorbent made consists of BiosorbentWithout Treatment (BWT) and Biosorbent Treatment Silica Gel (BTSG). This research was conducted to determine the ability of leaves of Gambir in absorbing cadmium (Cd). This study was conducted using a batch system. Characteristics of bisorbent obtained for BWT type with moisture content 1.27%, volatile 10.77%, ash content 2.62% and bound carbon content of 85,48%. As for biosorbent type BTSG obtained water content value 5.19%, volatile 21%, ash content 53% and carbon content bound by 24,6%. The optimum conditions obtained are the type of BTSG. Where is the size,concentration of initial waste, dosage and contact time of biosorbent are very influential on the adsorption process. Where the optimum condition are with the biosorbent size of 60 mesh, the concentration of 25 ppm, bisorbent dosage of 5 mg/L and contact time of 30 minutes. The reaction rate runs on the second order and the isotherm adsorption is Freundlich. The recovery rate obtained is 6.39%,energy free Gibbs is -0.068 kJ/mol.

1. Introduction

Nowadays the existence of industry in Indonesia is growing rapidly, both large-scale industry and home industry. This is in line with population growth and the increasing needs of the community. But the negative impacts caused by industrial activities can endanger the environment and human health, such as waste that produces heavy metals. The presence of heavy metals in the environment is quite common now. Heavy metals that were found in environments are Pb, Cd, Cr, Co and Mn.

Gambir (UncariagambirRoxb) is one of the export-oriented smallholder plantation commodities. Nearly 90% of Gambir's production is produced in West Sumatra. The main content of Gambir is 7-13% catechins and 20-55% tannins [1]. Tannin compounds are astringent compounds that have a bitter taste from their polyphenol groups which can bind and precipitate or shrink proteins. On research [2]Pb (II) can be adsorpted by biosorbent from plant spikes. Loquat leaf potential has also been proven that is able to absorb Cd in [3]. Biosorbent from mangoes can absorb metals Pb as much as 69% on research [4]. The high tannin content in Gambir plant can be used as an adsorbent. In the study of [5], Tannin and Flavonoids were reported to have an -OH group that can bind heavy metals through ion exchange. However, the tannin in the water will dissolve easily, therefore it is necessary to modify it using silica gel immobilization technique. Therefore, conducted a study on the use of Gambir leaves as an adsorbent to absorb heavy metals Pb and Cd as the most common and toxic metals in the environment with modification of silica gel immobilization.

2. Methodology

2.1. Biomass preparation
Gambir leaves (UncariagambirRoxb) are collected from the Gambir tree in the gambir plantation in the area of Lima Puluh Kota regency, West Sumatra. Gambir leaves are washed thoroughly with distilled water to remove sticking dust. The leaves were dried in an oven at temperature of 105°C for 16 hours, then cooled at room temperature in a desiccator. The dried leaves are smoothed using a blender to become a fine powder without treatment. Leaf powder is separated into 600 micron, 300 micron and 250 micron using mechanical sieve analysis to be used in optimization of size variation.

2.2. Biosorbent process
Biosorbent used in this study consisted of two types of manufacturing processes: native biosorbent and biosorbent with immobilization. The immobilization process with silica gel was carried out by mixing 9 grams of Gambir leaf powder with a gel formed from a mixture of 25 ml of sodium silica, 25 ml of distilled water, and 50 ml of 3 N sulfuric acid to become a paste. Leaf paste was left for one night, then the remaining water was dried using a waterbath then dried with a temperature oven of 105ºC for 4 hours, then pounded again into a fine size 250 micron.

2.3. Biosorbent characterization
Characterization of biosorbents consists of two types, namely physical and chemical characterization and structural characteristics. Physical and chemical characterization analysis includes water content, volatile content, ash content and fix carbon content. This functional group analysis for biosorbent uses Fourier Transform Infrared (FTIR) at the time before and after the adsorption process. For the analysis of the structure of the biosorbent morphology, using crystal form analysis with X-Ray Diffractometer (XRD) and biosorbent surface shape analysis using Screening Electron Microscopy (SEM).

2.4. Biosorbent performance
The testing process of heavy metal adsorption using Gambir leaf biomass was carried out with various biosorbent sizes, initial concentration of maximum waste, biosorbent dose, contact time to obtain the optimum value. Artificial waste is made by diluting the standard Cd^{2+} which is derived from $Cd(NO_3)_2.4H_2O$ with a concentration of 1000 ppm to obtain the required concentration variation. Performance testing was carried out by agitating biosorbent of Gambir leaves in 100 mL of Cd^{2+} solutions with an initial concentration off 50 ppm in 250 mL Erlenmeyer glass at 24ºC and pH 4.3. The sample was filtered with whatman filter size of 42 then 1 drop of HNO_3 was added to the filter to maintain the ionic strength of the solution. The concentration of metal which is still contained in the filtrate is known by using the Atomic Absorption Spectrophotometer (AAS).

2.5. Determination of adsorption isotherms

The absorption mechanism was analyzed through the adsorption isotherm test based on the Langmuir model and Freundlich model. Based on isotherm parameters can be known the absorption mechanism of Pb and Cd by biosorbent. Determination of Langmuir isotherm is used [2]

$$qe=\frac{QmKaCe}{1+Ka\ Ce} \tag{1}$$

While the determination of Freundlich's isotherm uses [2].

$$qe = KfCe^{1/n} \tag{2}$$

2.6. Determination of adsorption kinetics

Adsorption kinetics describe the absorption rate of solute, where the adsorption mechanism depends on the physical and chemical characteristics of the adsorbent in the mass transfer process. To determine the adsorption kinetics using the Lagergren equation [6].

$$log(qe - qt) = log\ qe\left(\frac{k1}{2.303}\right)t \tag{3}$$

The linear equation graph is made by connecting log (qe-qt) with t. If the data generated in the study is not linear then the next order kinetic rate is used. For the second order, it can be linearized as the following [2].

$$\frac{1}{qt}= \frac{1}{(k2\ qe)}+ \frac{1}{qe}\ t \tag{4}$$

Thermodynamics is the study of energy changes that occur in physical and chemical processes. Thermodynamic parameters in the form of changes in Gibbs energy (ΔG^o) can provide information regarding the mechanism of adsorption of contaminants in an adsorbent. Where the calculation of free energy is calculated using the following.

$$\Delta G^o = -RT\ ln(Kc) \tag{5}$$

2.7. Desorption

The desorption process is carried out to see how much metal ions are absorbed on the surface of the adsorbent. For the Pb metal cation desorption process, it is carried out by collecting biomass (adsorbent) into the column which is eluted 10 ml of 0.1 M HNO_3 solution with a flow rate of 1.5 ml/minute with 3 times elution. Eluet is stored 5 ml each in the vial to determine the concentration Cd^{2+} metal which is desorbed.

3. Results and discussion

3.1. Biosorbent characteristic

The biosorbent characteristic test was carried out to determine the physical, chemical and structural properties of the biosorbent used. The biosorbent characteristic test included moisture content, volatile content, ash content, fix carbon content (in Table 1), Fourier Transform Infrared (FTIR), X-Ray Diffractometer (XRD) and Screening Electron Microscopy (SEM) test.

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Table 1. Physics and chemistry characterization of biosorbent

Parameters	Native	SNI 06-3730-1995
Water content	1.27 %	Max 15 %
Volatile content	10.77 %	Max 25 %
Ash Content	2.62 %	Max 10 %
Fix Carbon Content	86.61 %	Min 65 %

3.2. Water content
The water content test aims to determine the hygroscopic properties of biosorbent, namely the ability to absorb water and surrounding air in the pores on the surface of the adsorbent. In general, the greater the surface area will increase biosorbent absorption to a substance, so that more molecules of water vapor from the air will be adsorbed and result in increased moisture content. Based on Table 1 the water content value of native biosorbent is 1.27% which has met SNI.

3.3. Volatile content
Volatile levels show that volatile substances are lost at 950℃ heating. The evaporating substances are carbon, sulfur and nitrogen compounds that can cover the adsorbent pores. Based on Table 1 it can be seen that the value of volatile content for native biosorbent is in accordance with SNI, with a value of 10.77%.

3.4. Ash content
Ash levels indicate the amount of metal oxides remaining in high heating. The ash that is formed comes from minerals that are strongly bound to charcoal, such as calcium, potassium, and magnesium. Excessive ash can cause blockage of activated carbon pores, it's make that the surface area of activated carbon becomes reduced. In accordance with the results of the study shown in Table 1 where the ash content value for native biosorbent is 2.62%.

3.5. Fix carbon content
The fix carbon content is the carbon fraction (C) which is bound in the sorbent in addition to the water fraction, evaporating substances and ash. The high and low levels of bound carbon in sorbent are influenced by the value of ash content, volatile substance content, and hydrocarbon compounds that are still attached to the charcoal surface research on[7]. Based on Table 1 the value of fix carbon content for native biosorbent is 85.48% where this value is in accordance with SNI which is a minimum of 65%.

3.6. Biosorbent performance
Biosorbent performance test was carried out to determine biosorbent size, biosorbent dosage, contact time, and maximum concentration of artificial waste on Cd removal. The optimum condition is a condition where the removal efficiency and absorption capacity of the metal is greatest for each optimization experiment.

3.7. Effect of Biosorbent Size
In this study the biosorbent size used was 600, 300 and 250 μ using native biosorbent with 1 gram of biosorbent, 60 minutes contact time, the concentration of artificial waste was 50 ppm pH 4.2 which

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was carried out at room temperature, at 24ºC with a stirring speed of 200 rpm, and in volume of 100 mL. All parameters remain for each biosorbent size variation. The results of the biosorbent size variation experiment can be seen in Figure 1.

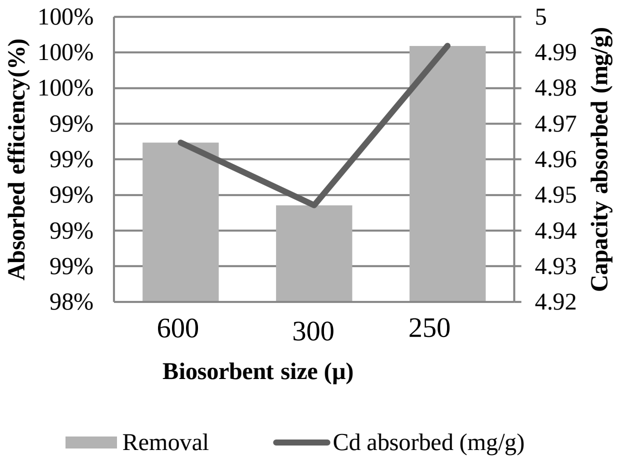

Figure1. Effect of biosorbent size on metal absorption

Biosorbent with size in 250 μ showed the highest efficiency compared to 300 and 600 μ sizes, where absorption occurred for Cd, where the highest absorption efficiency is 250 μ with a value of 99.84% and for biosorbent sizes of 300 and 600 μ respectively is 99.29% and 98.84%. Where this result can shows that biosorbent can absorb Cd metals very well. The level of adsorption will increase with the decrease in particle size. Based on the results of the research that has been done it can be seen that the absorption Cd^{2+} is most effective at 250 μ sizes. It is possible to link the total surface area and molecular size of hydrolyzed metal ions.

3.8. Effect of initial concentration of artificial waste

Variation of concentration were carried out to see at what concentration the biosorbent could work better considering that the solution used was artificial waste. Determination of optimum initial concentration was carried out on both types of biosorbent namely native and immobilization biosorbent with optimum size of 250μ, dosage of biosorbent of 10 g/L, contact time of 60 minutes and variations in waste concentration ranging from 0.05-125 ppm for Cd. The experimental results graph can be seen in Figure 2.

In Figure 2 it can be seen that both types of biosorbent for Cd tend to experience a decrease in efficiency along with the increase in initial concentration. In Cd, which is seen when the concentration of 75 ppm shows a constant state. The maximum initial concentration of artificial waste for native and immobilization biosorbent obtained for Cd is 25 ppm.

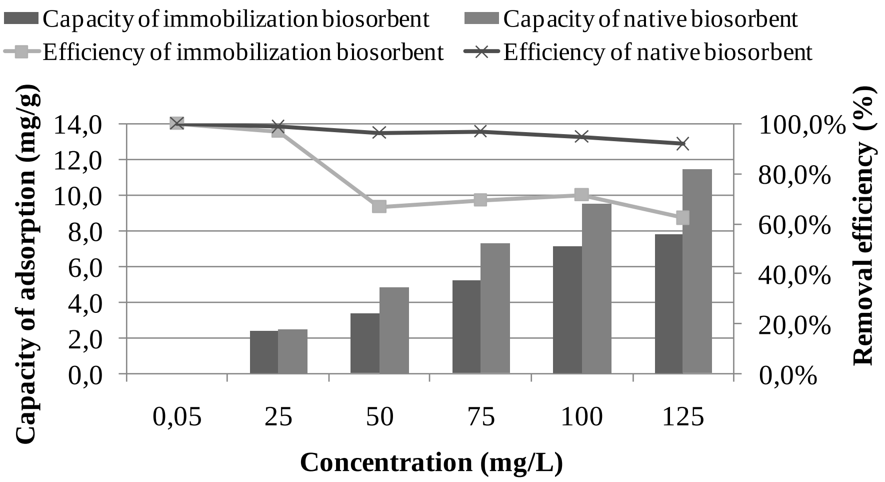

Figure 2. Effect of initial concentration on metal adsorption

3.9. Effect of biosorbent dosage

Experiments on the effect of biosorbent dosage occur with a variation of 0.5 g/L to 25 g/L. The experiment was conducted using biosorbent with 250 μ size, 60 minutes contact time and uses a concentration of 25 ppm for both types of biosorbent. In Figure 3 it can be seen that the optimum biosorbent dosage for Cd metal obtained the optimum biosorbent dosage for Cd at 10 g/L for native biosorbent and 5 g/L for immobilization biosorbent.

If the surface is saturated or near saturated with adsorbate, there are two possible phenomena. First, a second adsorption layer will be formed and another layer above the adsorbate that has been bound to the surface, this symptom is called *multilayer* adsorption. Second, the second layer and so on are not formed so that the adsorbate that has not been adsorbed will diffuse out of the pore and return to the fluid current.

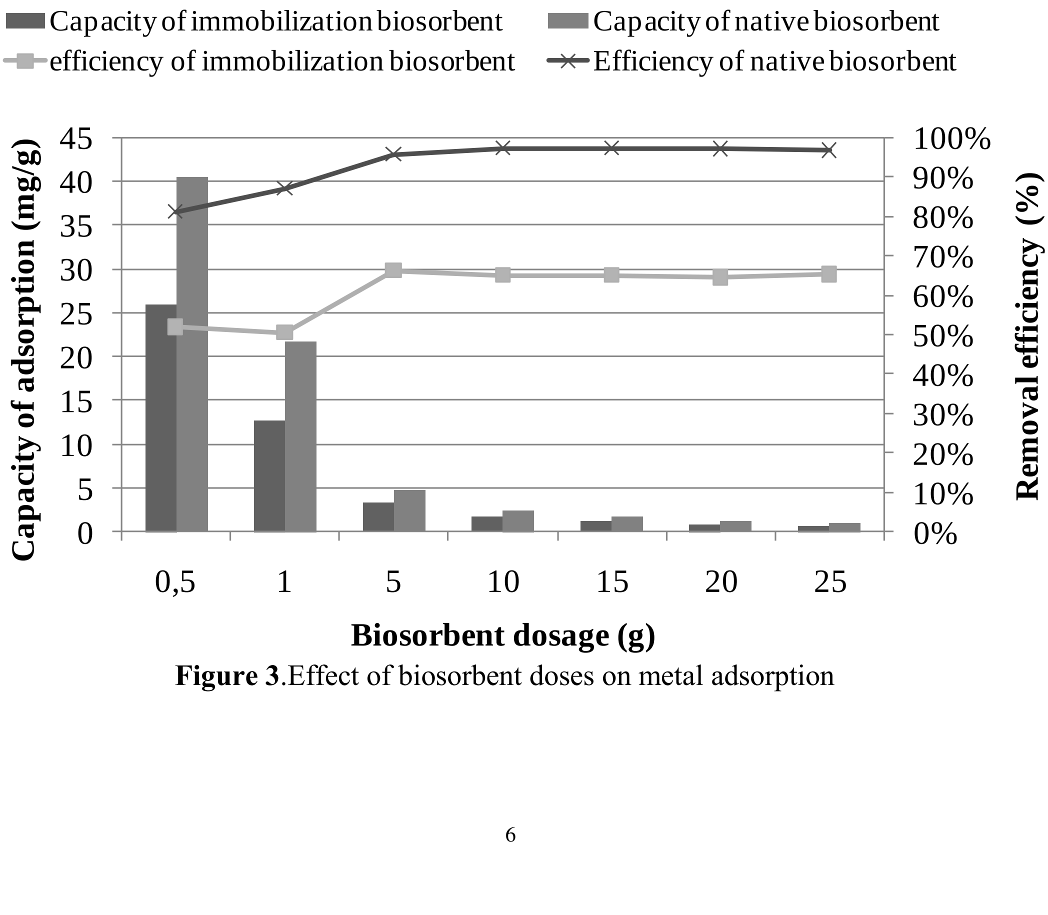

Figure 3.Effect of biosorbent doses on metal adsorption

3.10. Effect of contact time

The research on the optimization of the contact time aims to find out how much time is needed to achieve optimum equilibrium while the adsorption process. Determination of the optimum contact time was carried out on both types of biosorbent. The Cd metal, biosorbent is used for 250 µ size, 25 ppm of waste concentration, biosorbent dosage in 10 mg/L for native biosorbent and 5 mg/L for immobilization biosorbent. The contact time variation used is from 0-90 minutes. The experimental results graph is in Figure 4 and obtained the optimum contact time for native and immobilization are 60 minutes and 30 minutes.

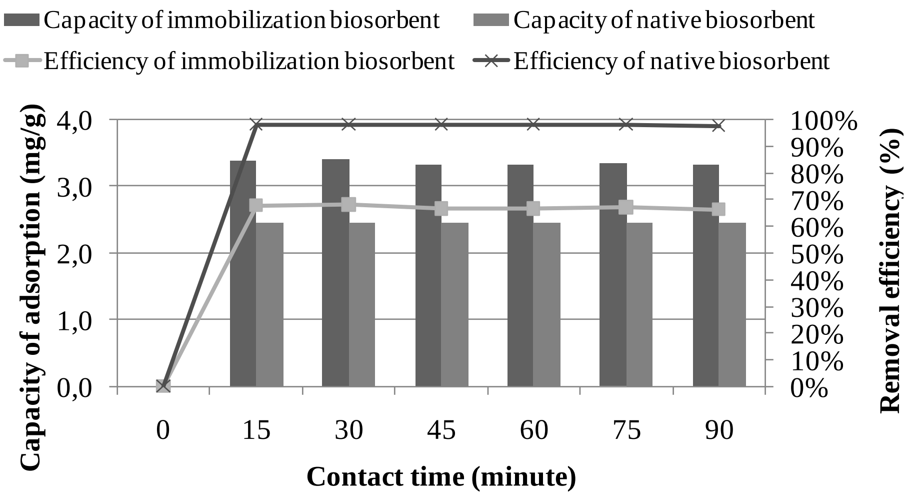

Figure 4. Effect of contact time on metal adsorption

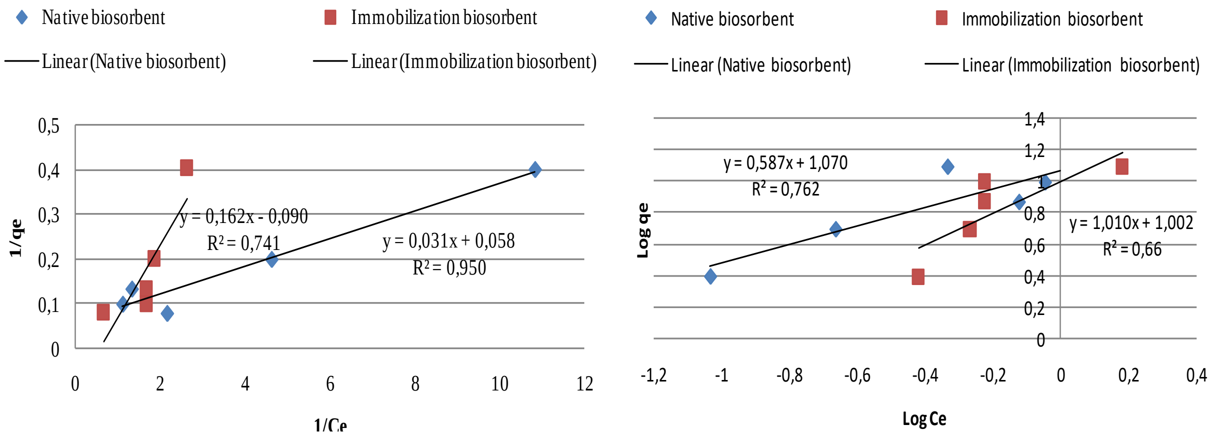

Figure 5. Metal adsorption isotherm curve Cd (a) langmuir (b) freundlich

Table 2. Parameters of langmuir and freundlich isotherms

Cd	**Langmuir**					**Freundlich**				
	1/qm	qm	1/(qmaks *K_L)	K_L	R^2	1/n	n	Log Kf	Kf	R^2
Native	0.101	9.901	0.098	1.031	0.945	0.458	2.183	0.625	4.217	0.961
Immobilization	0.182	5.494	0.177	1.028	0.703	0.263	3.802	0.378	2.388	0.749

Based on Table 2 it can be seen for Cd metal with biosorbent type native and immobilization follows Freundlich isotherms. Isotherm Langmuir shows that the sorption process takes place *monolayer* while Freundlich runs *multilayer*. In the Langmuir isotherm the KL value of 1 indicates strong affinity between the metal and the adsorbent surface. Whereas for the smaller 1/n value, it shows the great strength between the adsorbent and the adsorbate. This is found in the type of native and immobilization for Cd and native biosorbent for Pb metal.

3.11. Adsorption kinetics
The adsorption kinetics of Pb and Cd metals by biosorbent were evaluated Lagergren equation in the variation of contact time from 0 to 120 minutes. The results of the study are presented in Table 3.

Table 3. Recapitulation of parameters of the metal kinetics model on Cd

Heavy Metal	**Biosorbent**	**1st orde**		**2st orde**	
		k_1 (menit^{-1})	R^2	k_2 (gmg^{-1}menit^{-1})	R^2
Cd	Native	0.032	0.112	0.901	0.976
	Immobilization	0.020	0.141	0.221	0.999

The data in Table 3 obtained the greatest R^2 value and close to 1 in the second order reaction. This shows that the adsorption of Cd metals by biosorbent of gambir leaves follows the second order kinetics model. Where the second-order reaction shows that the reaction that occurs in the early minutes is fast but at equilibrium at one point in time the reaction will run slowly and even tends to decrease. Research study [8] kinetics of the second order describe a decrease in the concentration of metal Pb^{2+}, Cd^{2+}, and Ni^{2+} using adsorbent of cherry and sour beans that produce active carbon.

3.12. Thermodynamics
In this study, the thermodynamic parameters determined include changes in Gibbs free energy (ΔG^o). The parameters associated with the adsorption process can be predicted through the relationship between the adsorption equilibrium constant and temperature. The Gibbs free energy value can be seen in Table 4 below.

Table 4. Thermodynamic parameters of metal adsorption Cd

Adsorbent	**Cd**	
	Kc	ΔG^o (kJ/mol)
Native	1.031	-0.075
Immobilization	1.028	-0.027

Based on Table 4 it can be seen that generally the biosorbent used to adsorb Cd metals is negative value, which shows a spontaneous reaction.

3.13. Desorption
Desorption aims to release the metal that is bound or absorbed by biosorbent during the adsorption process. Where the main purpose of desorption in this study is to prove that biosorbent made from Gambir leaves can indeed absorb Cd cadmium can see in Table 5.

Table 5. Desorption of Cd metals from gambir leaf adsorbent

Adsorbent	Conc. After adsorption (ppm)	Equilibrium conc (ppm)	*Recovery* (%)
Native Cd	24.546	17.948	73.12
Immobilization Cd	17.020	1.087	6.39

Based on Table 5 it can be seen that for native biosorbentwith recovery rate is higher when compared to the immobilization. Where the level of recovery for immobilizationbiosorbentis below 10%. This is because the modification by silica gel on the adsorbent makes the absorbed metal bound in the surface of the adsorbent containing silica gel and it is make the strong bond and difficult to detach.

4. Conclusion

Based on research on experiments and calculations it can be concluded that Gambir leaf biomass has the potential as a biosorbent. Absorption is strongly influenced by biosorbent size, concentration of artificial waste, adsorbent dosage and contact time. The optimum condition obtained in the study is the type of immobilization for Cd metals. The reaction rate runs on the second order and meets the Freundlich for Cd. Gibbs. Free cadmium, positive for The recovery rate of the two types of metals with BTSG biosorbent is below 10%.

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