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Adsorption Isotherm Studies of Co (II) Metal Ion Using Activated Carbon Adsorbent from Lai *Durio kutejensis* (Hassk) Becc. Immobilized in Clay from East Kalimantan

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Abstract: *The stages of the method in this research are the production of fractionated clay, activation of carbon from lai skins and immobilization of Lai Durio kutejensis (Hassk) Becc. in Clay. Then, adsorption of Co (II) metal ions was carried out using activated carbon adsorbents which were immobilized on clay using a batch method using concentration parameters of 5, 15, 30, 50 and 65 mg/L. The concentration of the remaining heavy metal ions was analyzed using Atomic Absorption Spectroscopy (AAS). Optimum percentage of adsorbed metal ions was obtained at a concentration of 50 mg/L for 30 minutes. The adsorption type of* Co^{2+} *metal by immobilized adsorbent is Freundlich isothermal because the* R^2 *value is 0.9009, while the adsorption capacity is 0.00945 mg/g and the adsorption energy is 11.704 kJ/mol so it is classified as a physical adsorption type.*

Key Word*: Adsorption, Activated Carbon, Clay, Lai, Co (II)*

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I. Introduction

At present, the main problem arising from industrial development is environmental pollution through heavy metal ions contained in industrial waste. Most heavy metal ions can pollute the environment through waterways, such as cobalt metal (Co). Cobalt (Co) is widely used in the coloring of ceramics, glass and paint industries. Cobalt silicate compounds and cobalt (II) alumina ($CoAl_2O_4$, cobalt blue) can produce a deep blue color that is typical of ceramics, glass, ink, paints and varnishes. In addition to pollute the aquatic environment in the form of sediment or mud, if these metal ions enter the body in large numbers it can damage the thyroid gland, change red blood cells, increase blood pressure and the onset of heart failure [1]. To protect the life of aquatic organisms, a threshold of cobalt (Co) levels in sediments was determined, namely 50.57-158.13 mg/L [2].

Some methods that can be used to reduce the concentration of heavy metal ions in liquid waste are precipitation, ion exchange with resin, filtration and by adsorbent absorption in the form of synthetic resins and activated carbon [3]. In general, the adsorption method is used for the process of removing heavy metal ions from polluted environments or liquid waste. This method is very effective in removing heavy metals even though it is only done by a simple and economical adsorption process [4]. The adsorption process has been carried out using various types of adsorbents, such as activated carbon from corn cobs, sugarcane bagasse, coconut shells and others. Even many who modify the two types of adsorbents in various ways such as trapping, immobilization, intercalation and making adsorbents in the form of membranes.

One method for removing Co (II) metal ions in industrial waste, namely the adsorption method using natural clay or activated carbon because it is more economical. The adsorption process with immobilized Saccharomyces cerevisiae biomass adsorbent on clay has been carried out on Ni^{2+} metal ions and an optimum adsorption power of 19.4 mg/g was obtained at a concentration of 50 mg/L metal solution and a contact time of 120 minutes [5]. Still with the same adsorbent, but for a different metal, Pb^{2+}, the optimum adsorption power of 7.352 mg/g was obtained at a concentration of 50 mg/L metal solution and a contact time of 30 minutes [6]. The adsorption process uses the Atomic Absorption Spectroscopy (AAS) method. The basis of the analysis using the Atomic Absorption Spectroscopy (AAS) technique is to measure the amount of light absorption by the analyte atoms at a specific wavelength, then the concentration of the analyte can be determined [7].

In this study used clay adsorbents because they contain active sites in the form of silanol (Si-OH), siloxane (Si-O-Si), and aluminol (Al-OH) which have an active role in adsorbing metal ions. Meanwhile, activated carbon is used because it has an effective pore in absorbing or binding heavy metal ions from solution [8]. This activated carbon can be obtained from the waste of lai fruit skin (*Durio kutejensis* (Hassk) Becc.) which is a typical fruit of the Kalimantan region. Lai (*Durio kutejensis* (Hassk) Becc.) has the same family as durian (*Durio zibethimus*), so it has several similarities such as the skin content [9]. Durian peels contain high cellulose (50-60%), lignin (5%) and low starch (5%). In addition, it also contains high carbon so that it can be used as an adsorbent in the form of activated carbon [10]. The adsorbents can be optimized through the immobilization system. Until now, the adsorption of Co (II) metal ions using activated charcoal from lai shell (*Durio kutejensis* (Hassk) Becc.) has never been done. Moreover, which has been immobilized on clay. So, in this research the Co (II) metal ion adsorption will be carried out using activated carbon adsorbent from lai shell (*Durio kutejensis* (Hassk) Becc.) which is immobilized in the fractionated clay.

II. Material and Methods

Materials

Fruit skin of lai (*Durio kutejensis* (Hassk) Becc.) as shown in Fig.1, Clay, HCl, $KMnO_4$, H_2SO_4, HNO_3, $CoAl_2O_4$, distilled water. All the reagents were used as received without further purification.

Figure 1. Lai Fruit (*Durio kutejensis* (Hassk) Becc.)

Synthesis of Adsorbent

Step 1: Synthesis of Activated Carbon

Lai shell with a size of 1x2 cm^2 is dried and carbonized using a furnace at 400°C for ± 15 minutes. Then the charcoal is cooled and ground and then sieved with a 100mesh sieve. Then activated using HCl solution for 24 hours. Then filtered and washed. After that, it is dried at 100°C for 3 hours. Then 1 g of activated carbon is cooled in a desiccator to calculate its water content [11].

Step 2: Synthesis of Fractionated Clay

Dry clay was sieved using a 100mesh sieve and mixed with $KMnO_4$ while stirring for 4 hours at 80ºC. The results are filtered and washed and then roasted for 12 hours at 80ºC. Then this clay was added H_2SO_4 with the same procedure and HCl with the same procedure.

Step 3: Immobilization of Lai *Duriokutejensis* (Hassk) Becc. in Clay

Activated carbon from laishell is mixed with clay using a ratio of 2.5: 5 (g activated carbon: g clay).

Adsorption of Co (II)

For the variable effect of concentration, as much as 40 mL of Co (II) metal ion solution with a concentration of 5, 15, 30, 50 and 75 mg/L is shaken with 0.1 gram of adsorbent at 175 rpm for 30 minutes. The filtrate was filter and its absorption was analyzed by Atomic Absorption Spectroscopy (AAS). All experiment was carried out at room temperature (302 K).

Adsorption Isothermal

The adsorption power of Co (II) is calculated by the following equation:

$$q_t = (C_0 - C_t)\frac{V}{m} \tag{1}$$

where C_0 (mg/L) is the concentration of the initial solution, C_t (mg/L) is the concentration after contact time, V (L) is the volume of the solution, and m is the mass of the adsorbent (gr) [12].

The percentage of metal ions adsorbed (Ads%) in the solution is calculated using the following formula [13]:

$$\text{Ads}(\%) = \frac{\text{initial concentration} - \text{final concentration}}{\text{initial concentration}}\ x\ 100\% \quad (2)$$

The Langmuir isotherm states that the adsorption occurs over a uniform adsorbent surface at a single layer [14]. The Langmuir isotherm equation is as follows:

$$\frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{qm} \quad (3)$$

where Ce is the equilibrium concentration of the adsorbate (mg/L) and q_e is the amount of adsorbate adsorbed while q_m is the adsorption capacity (mg/g) and b is the Langmuir constant [13,15]. The adsorption capacity and Langmuir constant are calculated from the slope and intercept of the plot Ce/q_e versus Ce.

The Freundlich equation assumes that the adsorption process occurs on a heterogeneous surface [16]. The Freundlich parameter value can be calculated by plotting the log q_e versus log Ce obtained using the following formula [13]:

$$\log qe = \log K_f + \frac{1}{n} \log Ce \quad (4)$$

where K_f and n are Freundlich's constants which can be obtained from the slope and intercept of the straight sections of the linear plot.

Characterization

Scanning electron microscopy (SEM) was applied to analyze the morphology of adsorbent. Co (II) concentration was determined using atomic absorption spectroscopy (AAS).

III. Result

AAS Analysis

To determine the adsorption power of the immobilized adsorbent against a solution of Co^{2+} metal ions, a solution of Co^{2+} metal ions with various concentrations is needed, namely 5, 15, 30, 50 and 65 mg/L. The relationship between the adsorption power of Co^{2+} metal ions by immobilized adsorbents to the concentration of Co^{2+} metal ions is shown in Figure 2. While Freundlich and Langmuir isothermal data is shown in Tables 1 and 2 and Figures 3 and 4.

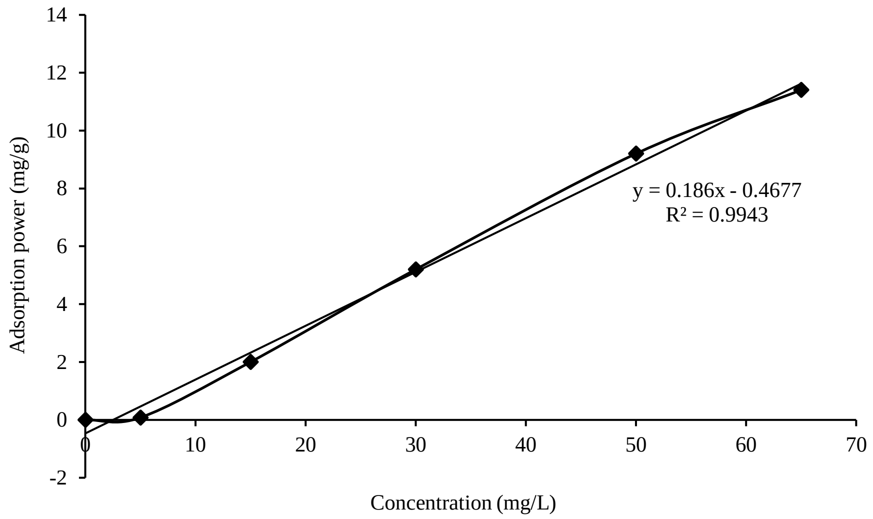

Figure 2. Effect of concentration on adsorption power of immobilized adsorbent

Table no 1: Shows the results of AAS data analysis based on Freundlich adsorption isotherms

C_0 (mg/L)	Ce (mg/L)	q_e(mg/g)	Log Ce	Log q_e	% adsorbed	Adsorbed weight(mg)	Adsorption Power(mg/g)
5	4.8	0.2	0.6812	-0.6989	4	0.008	0.08
15	10	5	1	0.6989	33.3333	0.2	2

30	17	13	1.2304	1.1139	43.3333	0.52	5.2
50	27	23	1.4313	1.3617	46	0.92	9.2
65	36.5	28.5	1.5622	1.4548	43.8461	1.14	11.4

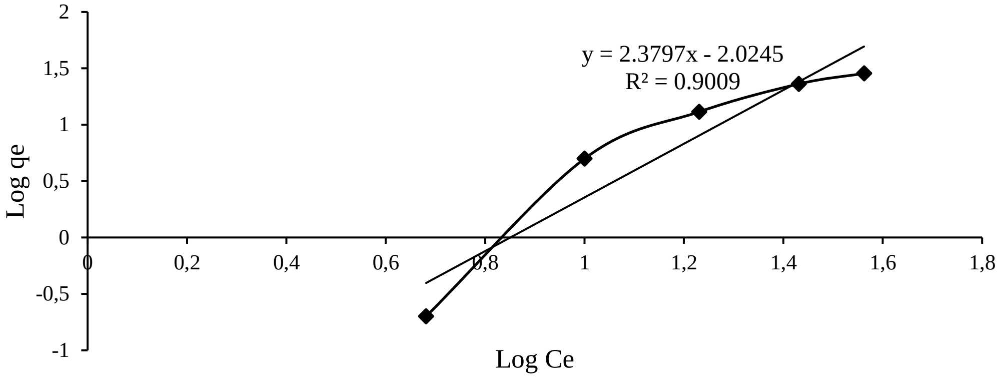

Figure 3. Freundlich adsorption isotherm of Co^{2+} metal ion by immobilized adsorption

Table no 3. Shows the results of AAS data analysis based on Langmuir adsorption isotherms

C_0 (mg/L)	Ce (mg/L)	q_e (mg/g)	Ce/q_e	% adsorbed	Adsorbed weight (mg)	Adsorption Power (mg/g)
5	4.8	0.2	24	4	0.008	0.08
15	10	5	2	33.3333	0.2	2
30	17	13	1.3076	43.3333	0.52	5.2
50	27	23	1.1739	46	0.92	9.2
65	36.5	28.5	1.2807	43.8461	1.14	11.4

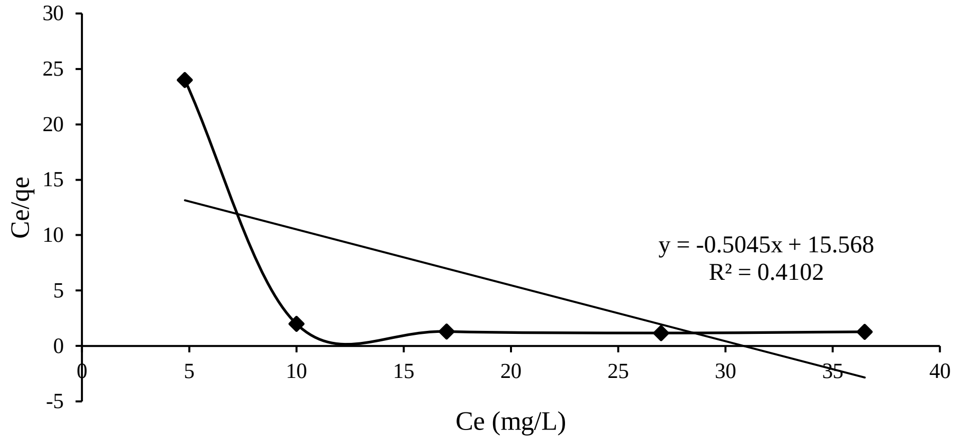

Figure 4. Langmuir adsorption isotherm of Co^{2+} metal ion by immobilized adsorption

IV. Discussion

The adsorption power of Co^{2+} metal ions increased from a concentration of 5 to 65 mg/L as shown in Figure 6. Results of this study identified that the higher the concentration of Co^{2+} metal ions, the more Co^{2+} metal ions adsorbed by the adsorbent, which is influenced by the increasing number of Co^{2+}metal ion particles in the metal solution. This adsorption process is also supported by the excellent adsorption properties of the clay due to its very small colloid particle size and the mineral structure that makes up the clay in the form of layers that are not tightly bound so that it easily expands when interacting with water molecules and causes the clay volume to double. The ability of clay to expand and deflate causes the minerals that make it easy to capture and trap metal ions into its structure [17]. The ability of this clay is supported by the ability of activated carbon adsorbent which also has good adsorbing properties because its surface area, adsorption capacity and surface reactivity are quite large, and its microstructure is porous, so it is easy to embed metal ions into its structure [8].

The adsorbed metal ion percentage also increased with increasing concentration of the metal solution, but after passing the 50 mg L concentration, the adsorbed metal ion percentage began to decline, namely right at the concentration of 65 mg/L as seen in Table 1. This happened because adsorbent has a saturation point which causes metal ions to no longer be adsorbed. So, from these results it is known that the best concentration at the best adsorption is at a concentration of 50 mg/L because it can absorb up to 46% of Co^{2+} metal ions. From these data it can be concluded that the higher the concentration, the smaller the absorption of Co^{2+} ions, this is because the adsorbent has a saturation point which causes metal ions to no longer be adsorbed.

The adsorption process that occurs can be analyzed using Freundlich and Langmuir's isothermal theory. These two theories are the isotherm theories most common used to analyze the adsorption system at equilibrium [18-19], so that it can be seen whether it includes physical adsorption (physisorption) or chemical adsorption (chemisorption). Freundlich isothermal is an adsorption process that takes place physically on heterogeneous surfaces and layered structures and cannot determine the adsorption capacity in a single layer, while Langmuir isothermal is an adsorption process that occurs chemically in a single layer by a very strong active side between the surface and the adsorbate molecule. Because it is influenced by use of electrons between the adsorbent and the adsorbate [18].

The type of adsorption isotherm, adsorption capacity and adsorption energy can be determined by observing the isothermal curve of the adsorption of Co^{2+} metal ions by immobilized adsorbents with varying metal ion concentrations. Figures 7 and 8 present Freundlich and Langmuir adsorption isothermal curves of Co^{2+} metal ions by adsorbents with concentrations of 5, 15, 30, 50, 65 mg/L, where qe is the amount of adsorbed adsorbed and Ce is the adsorbate concentration at the adsorption equilibrium. The type of adsorption isotherm can be determined by analyzing the linear regression rates of the two isotherms. This value is shown from the value of R^2 and the value of the largest adsorption capacity [20]. If the resulting isotherm graph is a straight line, the adsorption process is Freundlich's isotherm, but if the resulting graph has an inverted L shape, the adsorption process is included in the Langmuir isotherm type [21]. Based on Figures 7 and 8, it is known that the adsorption carried out obtained the Freundlich and Langmuir linear regression equations with R^2 values of 0.9009 and 0.4102, respectively, which means that the R^2 value for the Freundlich equation is greater than the Langmuir equation. This indicates that the adsorption type of metal ion Co^{2+} by immobilized adsorbent is Freundlich isotherm.

In addition, the adsorption capacity obtained from calculations using the Freundlich equation is 0.00945 mg/g and the adsorption energy is 11.704 kJ/mol. Meanwhile, using the Langmuir equation, the negative adsorption capacity is -1.9821 mg /g. This happens because between the adsorbent and the adsorbate a fair large hydrogen bond is formed. If an adsorption process has an adsorption energy of more than 20.92 kJ/mol then the adsorption is a chemical adsorption type, but if it is less than that value it is considered physical adsorption [22]. While the adsorption energy obtained in this study was below this value, namely 11.704 kJ/mol, so that the adsorption that took place in this study was classified as a type of physical adsorption.

V. Conclusion

The adsorption power of Co^{2+} metal ions continues to increase from a concentration of 5 to 65 mg/L. While the optimum percentage of adsorbed metal ions was obtained at a concentration of 50 mg/L for 30 minutes. The adsorption type of Co^{2+} metal by immobilized adsorbent is Freundlich isothermal because the R^2 value is 0.9009, meanwhile the adsorption capacity is 0.00945 mg/g and the adsorption energy is 11.704 kJ/mol so it is classified as a physical adsorption type.

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