The adsorption kinetics and isotherm of activated carbon from Water Hyacinth Leaves (Eichhornia crassipes) on Co(II)

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Abstract. Heavy metal waste can endanger human health and can accumulate in rivers or land. Heavy metals such as Co(II) can be removed or minimized using adsorbents such as activated carbon. The use of activated carbon from water hyacinth leaves (Eichhornia crassipes) has the potential to reduce the concentration of heavy metals in the environment as water hyacinth leaves (WHL) have the ability to adsorb both organic and inorganic compounds. This study aims to determine the appropriate adsorption kinetics and isotherm models in the process of Co(II) adsorption using activated carbon from water hyacinth leaves (ACWHL). The ACWHL can be produced from the carbonization process at 400°C for an hour and two-stage activation process (physical and chemical activation) with 30% H₃PO₄ as an activator and the impregnation ratio of 1:4 (w/w) for 24 hours and then activated at 600°C for 60 minutes. The analytical method used in this study was using a UV-Vis spectrophotometer. The results of the study showed that the ability of ACWHL to adsorb Co(II) followed the pseudo-second-order kinetic model with R² = 0.3086 and the Elovich isotherm with R² = 0.664 with a maximum adsorption capacity of 140.725 mg/g. Fulfillment of this model can be assumed if the adsorption process of Co(II) on the surface of ACWHL occurs in multilayer.

1. Introduction
Activated carbon is amorphous carbon with a surface area varying from 300 to 2000 m²/g. The large surface area that is due to the presence of pore structures cause activated carbon to have the ability to adsorb with an adsorption capacity of 25-100% [1]. Activated carbon is produced through carbonization processes that originate from the breakdown of cellulose into carbon [2]. On the other hand, cellulose is the main component of building plant cell walls. The cellulose content in plant cell walls is about 35-50% of the dry mass of plants [3]. Lignocellulose can be found in leaves, twigs, rice husks, and corn cobs [4]. In addition, lignocellulose is also found in water hyacinth plants (Eichhornia crassipes).

Water hyacinth (E. crassipes) contains lignocellulose which consists of 25% cellulose, 33% hemicellulose, and 10% lignin [5]. At present, the use of water hyacinth is still limited in small areas such as art paper [6], membrane making [5], and bioethanol production [7]. Water hyacinth in the leaves is only used for liquid fertilizer [8], the rest is only weed and discarded. In fact, water hyacinth leaves have the potential to be activated carbon, because water hyacinth leaves have the ability to adsorb organic compounds and inorganic compounds [9].

The application of activated carbon that is often used is as an adsorbent. In the adsorption process, a mass transfer occurs from the fluid (can be a gas or liquid phase) to the solid phase. Adsorption is widely used as a physical separation method that is effective for eliminating or decreasing the concentration of various dissolved (organic, inorganic) pollutants in waste [2]. Adsorption is one of the preferred methods for removing heavy metals because of their efficiency and low costs [10]. However, the adsorption method using activated carbon is quite expensive due to the utilization of synthetic activated carbon.
Therefore, cheaper adsorbents as an alternative as a raw material for the manufacture of activated carbon are becoming very popular and attracting attention among researchers [11].

Water pollution by heavy metal ions is a serious problem for the environment and health, caused by the toxic nature of heavy metal ions at even low concentrations. Several studies on the adsorption of metal ions and natural macromolecules have been carried out [12] by utilizing wood cellulose and sawdust as adsorbent Co(II) with the results of the adsorption capacity of Co(II) on cellulose by $0.55 \times 10^{-4}$ mol/g and $0.09 \times 10^{-4}$ mol/g for wood sawdust. In another study using adsorbent of rice husk to adsorb Cr, Zn, Cu, and Cd, the results showed that rice husk was able to adsorb Cr, Zn, Cu, and Cd by 79%, 85%, 80%, and 85%, respectively [13].

Based on these results, some adsorbents from natural materials can be used as effective adsorbents for heavy metals. Therefore, in this research, a study of appropriate adsorption and kinetic isotherms and models of the Co(II) adsorption using activated carbon from water hyacinth leaves will be carried out. Co(II) was chosen because it is one of the heavy metals that pollutes the aquatic environment and can harm humans because it is toxic and carcinogenic [14].

2. Materials and methods

The water hyacinth leaves (WHL) sample were taken from Rawa Pening, Ambarawa, Jawa Tengah. The materials used include 85% H$_3$PO$_4$, NaOH, and Co(NO$_3$)$_2$•6H$_2$O, all materials used in the degree of PA (Pro-Analysis) were obtained from E-Merck Germany.

The instruments used in this study were spectrophotometer UV-Vis (Shimadzu mini 1240), analytical balance with 0.01 g accuracy (Ohaus TAJ601), analytical balance with an accuracy of 0.1 mg (Ohaus PA214), pH meter (Hanna HI 9812), furnace (Vulcan A-550), as well as a set of glass devices.

2.1. Procedure

2.1.1. Sample preparation [15]

DEG samples were washed with clean water and dried under the sun for ± 48 hours. Next, the sample was cut into small pieces and dried in the oven for 24 hours at 110°C. Then the sample was smoothed with a grinder and sifted using a 30 mesh sieve.

2.1.2. Sample carbonization [16] modified

The sample was put into the furnace (T = 400°C) for 60 minutes followed with impregnation with H$_3$PO$_4$ (30%) with a ratio of 1:4 (w/w) for 24 hours. After that, the sample was filtered and dried in the oven (T = 110°C) for 24 hours, then activated at T = 600°C for 60 minutes. Then, the sample was washed with 1M NaOH and rinsed with distilled water to pH 7. The activation results were dried in an oven (T = 110°C) for 24 hours.

2.1.3. The adsorption kinetics and isotherm of activated carbon from Water Hyacinth Leaves on Co(II)

The adsorption kinetics process was carried out by adding 10 mg of activated carbon from water hyacinth leaves (ACWHL) to 25 mL of Co (II) 50 ppm for 0, 20, 40, 60, 80, 100, and 150 minutes through the stirring method [17]. The adsorption isotherm study was carried out by adding 10 mg of ACWHL to 25 mL of Co (II) solution with concentrations of 30, 50, 70, 90, 110, 130, and 150 ppm at the optimal interaction time through the stirring method [18]. The measurement of the absorbance of the solution was carried out using a UV-Vis spectrophotometer ($\lambda_{max} = 515$ nm) based on the calibration curve obtained previously. The adsorption capacity ($q_e$) is determined using the following equation [19]:

$$q_e = \frac{(C_0 - C_e)V}{W},$$

where $C_0$ and $C_e$ each is the initial concentration and equilibrium of Co(II) (mg/L), V is the volume of the solution Co(II) (Litre), and W is the mass of ACWHL (g).
3. Results and discussion

3.1. Adsorption kinetics

The kinetic adsorption of Co(II) ion by ACWHL was obtained through the Arrhenius zero-order reaction equation, Arrhenius first-order, Arrhenius second-order [20], and pseudo second-order [17] at various contact times from 20 to 150 minutes.

Arrhenius zero-order kinetic model:

\[ [C]_t = -kt + [C]_0 \]  \hspace{1cm} (2)

Arrhenius first-order kinetic model:

\[ \ln [C]_t = -kt + \ln [C]_0 \]  \hspace{1cm} (3)

Arrhenius second-order kinetic model:

\[ \frac{1}{[C]_t} = -kt + \frac{1}{[C]_0} \]  \hspace{1cm} (4)

where \([C]_0\) and \([C]_t\) is the initial and final concentration of Co(II) solution in molar, \(k\) is the reaction rate constant (m/s), and \(t\) is time (minutes).

Pseudo second-order kinetic model is given as follows:

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t, \]  \hspace{1cm} (5)

where \(k_2\) is the pseudo second-order rate constant of adsorption (g/mg.h). The magnitudes of \(q_e\) and \(k_2\) are determined from the slope and intercept of the plot of \(t/q_t\) versus \(t\). The results of the adsorption kinetics modeling plot for Co(II) ions by ACWHL are presented in figure 1.

**Figure 1.** Adsorption kinetics models of adsorption Co(II) by ACWHL.

Determination of the appropriate adsorption kinetics model can be seen from the value of \(R^2\) which approaches the value of 1 from the adsorption kinetics equation [21]. Based on Figure 1, it can be seen that the modeling of ACWHL on Co(II) adsorption tends to follow pseudo second-order modeling with a value of \(R^2 = 0.3086\).
The effect of interaction time on the adsorption capacity of Co(II) ions is presented in figure 2. Adsorption of Co(II) by ACWHL runs very fast within 60 minutes with a maximum adsorption capacity of 140.725 mg/g. This result is faster than the study of [22] obtaining 150 minutes and 100 minutes equilibrium time for Co(II)-smectite and Co(II)-thiol/smectite systems. The reported study [23] was reported to take 4 hours to balance Co(II)-montmorillonite. Another research before [24] reported a longer time of 72 hours to achieve equilibrium of the Co(II)-vermiculite adsorption system. The results of the study with similar interaction times were obtained in the study [25] regarding the study of cationization of cation Co(II) adsorption with the fastest results in 60 minutes with equilibrium at 120 minutes. The same equilibrium time was also reported by [26] for the Co(II) adsorption system in kaolinite.

The adsorption of Co (II) by ACWHL showed less stable adsorption data, but it can be seen that ACWHL is able to adsorb Co (II) optimally at 60 minutes of interaction time. After 60 minutes of interaction time, the adsorption has decreased, this is estimated because of the desorption. This happens because the longer the contact time, the saturation stage will be achieved, where there will be an aggregation of the colored solution molecules, so it will be difficult to continue to enter the pore structure of activated carbon [27].

![Figure 2. The effect of interaction time on the adsorption capacity of Co(II) by ACWHL.](image)

### 3.2. Adsorption Isotherms

Adsorption isotherm can be used to determine the adsorption mechanism of Co (II) by ACWHL. Bonds created by the adsorbate molecule and the surface of the adsorbent can occur physisorption and chemisorption [28]. In the study of adsorption isotherm, the optimum contact time was used for 60 minutes. Some models of adsorption isotherms used are:

**Langmuir isotherm model** [29]:

\[
\frac{C_e}{q_e} = \frac{1}{K_Lq_m} + \frac{C_e}{q_m},
\]

where \(C_e\) is the balance concentration of the adsorbate (mg/g), \(K_L\) is a Langmuir constant (mg/g), and \(C_0\) is the initial concentration of the adsorbate (mg/g).

**Freundlich isotherm model** [30]:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e,
\]

where \(K_F\) is the adsorption capacity (L/mg) and \(1/n\) is the adsorption intensity. It also shows the relative distribution of energy and heterogeneity of absorbing sites. The Freundlich isotherm applies to the adsorption process that occurs on heterogeneous surfaces.

**Temkin isotherm model** [31]:

\[
q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e.
\]
where \( b \) is the constant Temkin associated with heat absorption (J/mol) and \( K_T \) is the constant Temkin isotherm (L/g). Temkin isotherm takes into account the effects of direct adsorbate interactions or indirect adsorbates on the adsorption process and it can also be assumed that the adsorption heat (\( \Delta H_{ads} \)) of all molecules in the layer decreases linearly as a result of increased surface coverage. Temkin isotherm only applies to various intermediate ion concentrations.

Elovich isotherm model [32]:

\[
\ln \frac{q_e}{C_e} = ln K_E \ q_m - \frac{\varphi_n}{q_m}
\]  

(Eq. 9)

Elovich maximum adsorption capacity and Elovich constant can be calculated from the slope and intercept of the plot of \( \ln \frac{q_e}{C_e} \) versus \( q_e \). The Elovich kinetic model can study the adsorption rate based on absorption capacity on heterogeneous surfaces. The results of the isotherm adsorption modeling plot of Co(II) by ACWHL are presented in figure 3.

In figure 3, it can be seen that the linearity of the four isotherm types in the adsorption has different linearity, namely the value of \( R^2 = 0.005 \) (Langmuir isotherm), \( R^2 = 0.120 \) (Freundlich isotherm), \( R^2 = 0.050 \) (Temkin isotherm) and \( R^2 = 0.664 \) (Elovich isotherm). Determination of the appropriate adsorption isotherm model of Co(II) by ACWHL can be seen by looking at the correlation coefficient \( R^2 \) which approaches the value of 1. From figure 3 it can be seen that the right modeling \( R^2 \) approaches 1 for ACWHL in solution Co(II) is an Elovich isotherm model with an \( R^2 \) value of 0.664. The best determination of adsorption modeling is done by linear regression analysis because this analysis quantifies the adsorbate distribution, analyzes the adsorption system, and verifies the assumption of the consistency of the adsorption isotherm model. Elovich isotherm modeling is based on kinetic principles which assume adsorption will increase exponentially, or in other words, it can be said that multilayer adsorption occurs [32].
4. Conclusions
Based on the results of the research, it can be concluded that ACWHL can be applied in order to adsorp Co(II) by following the pseudo second-order kinetic model with $R^2 = 0.3086$ and the Elovich isotherm with $R^2 = 0.664$ with a maximum adsorption capacity of 140.725 mg/g. Fulfillment of this model can be assumed if the adsorption process of Co(II) on the surface of ACWHL occurs in multilayer.

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References
[1] Esterlita M O and Herlina N 2015 Tek. Kim. USU 4 47
[2] Turmizi M and Syaputra A 2015 J. Tek. Kim. USU 4 42
[3] Yustinah and Hartini 2011 Prosiding Seminar Nasional Teknik Kimia "Kejuangan" p 1
[4] Theasy Y and Yulianti I 2016 Prosiding Pertemuan Ilmiah XXX HFI Jateng & DIY 155
[5] Rachmawaty R, Meriyani M and Priyanto I S 2013 Jur. Tek. Kim. Fak. Tek. Univ. Diponegoro, 2 8–16
[6] Winanto 2013 Teknologi Kayu Bambu dan Serat “Pengolahan Eceng Gondok Sebagai Bahan Baku Kertas Seni” Universitas Brawijaya
[7] Eshtiaghi M N, Yoswathana N, Kuldiloke J and Ebada A G 2012 African J. Biotechnol. 11 4921
[8] Rozaq A and Novanto G 2010 “Pemanfaatan Tanaman Enceng Gondok Sebagai Pupuk Cair” Universitas Pembangunan Nasional "Veteran"
[9] Sangkota V D A and Suid I 2017 6 48
[10] Habib A, Islam N, Islam A and Alam A M S 2007 J. Anal. Environ. Chem 8 21
[11] Horsfall M J, Abia A A and Spiff A I 2003 African J. Biotechnol. 2 360
[12] Mohadi R, Hidayati N, Saputra A and Lesbani A 2013 Cakra Kim. 1 8
[13] Munaf E and Zein R 2010 Enviromental Technology 18 359
[14] Yuliusman 2016 Pros. Semin. Nas. Tek. Kim. “Kejuangan” 1
[15] Anisuzzaman S M, Joseph C G, Daud W M A B W, Krishnaiah D and Yee H S 2015 Int. J. Ind. Chem. 6 9
[16] Shamsuddin M S, Yusoff N R N and Sulaiman M A 2016 Procedia Chem. 19 558
[17] Zhang Y, Pan K and Zhong Q 2013 J. Agric. Food Chem. 61 9230
[18] Musapatika E T, Onyango M S and Aoyi O 2010 Cobalt(II) removal from synthetIC wastewater by adsorption on south african coal fly ash
[19] Omri A and Benzina M 2012 J. la Société Chim. Tunisie 14 175
[20] Sanjaya A S and Agustine D P 2015 Konversi 4 17
[21] Misran E, Panjaitan F and Yanuar F M 2016 Rekayasa Kim. dan Lingkung. 11 92
[22] Guerra D L and Airoldi C 2008 J. Solid State Chem. 181 2507
[23] Bhattacharyya K G and Sen S 2008 Appl. Clay Sci. 41 1
[24] Fonseca M G da, Oliveire M M de, Arakaki L N ., Espinola J G . and Airoldi C 2005 J. Colloid Interface Sci. 285 50
[25] Muhdarina, Mohammad A W and Muchtar A 2010 Reaktor 13 81
[26] Yavuz O, Altunkaynak Y and Guzel F 2003 Water Res. 37 948
[27] Afifah M, Moersidik S S, Priadi C R, Red C and Dye A 2016 "Adsorpsi dan Regenerasi Karbon Aktif Batu Bara dan Tempurung Kelapa terhadap Zat Warna Anionik Congo Red" Universitas Indonesia
[28] Nafi R 2016 J. Farm. Sains dan Prakt. I 28
[29] Dabrowski A 2001 Adv. Colloid Interface Sci. 93 135
[30] Boparai H K, Joseph M and Carroll D M O 2011 J. Hazard. Mater. 186 458
[31] Vijayaraghavan K, Padmesh T V N, Palanivelu K and Velan M 2006 J. Hazard. Mater. 133 304
[32] Ayawei N, Ebelegi A N and Wankasi D 2017 J. Chem. 2017 1–11