Immobilisation of tannic acid onto activated carbon from durian peels to improve Cu (II) ion removal

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Abstract

We present the synthesis of tannic acid immobilized activated carbon from durian peels (TA-AC) offering a low-cost adsorption material for removal of Cu (II) ions. To achieve this synthesis, we use pyrolysis at 300 ºC for 5 hours, followed by adding H_2SO_4 as an activating agent. The commercially available TA is then added to modify the adsorption properties in order to produce TA-AC. We investigated removal of Cu (II) from synthetic wastewater in order to evaluate the adsorption properties of TA-AC; where activated carbon from durian peels (D-AC) and TA-AC were analyzed using FTIR and the concentration of Cu-(II) in solution was determined using FAAS. Effects of factors are presented including contact time, temperature and adsorbent dosage, allowing us to calculate chemical kinetics and thermodynamics. Cu (II) removal using TA-AC is 5-10% more effective than D-AC, with an equilibrium contact time of 60 minutes. We implemented two simplified kinetic models; pseudo-first order and pseudo- second order equations where the Cu (II) adsorption follows the pseudo-second order equations (R^2 = 0.9786). Comparing between Langmuir and Freundlich isotherms, the Freundlich equations offer a more accurate model for describing Cu (II) adsorption on TA-AC (R^2 = 0.9907). Our thermodynamic investigation showed that adsorption of Cu (II) is endothermic owing to a positive enthalpy.

Keywords: activated carbon, adsorption isotherm, thermodynamics, kinetic

1. Introduction

Heavy metal contamination from industrial water sources is one of Thailand's environmental issues. Particularly, it was reported that copper metal is a crucial element in the manufacture of electrical equipment. When copper is contaminated in water and the body consumes more than 16 to 23 milligrams of copper per day, the body will suffer negative effects such nausea, diarrhea, stomach pain, and abnormal cardiac function [14]. According to recent studies, several researchers have looked at different methods for removing heavy metals, including co-precipitation (Al-Qodah et al., 2017), ion exchange, and biosorption [3], etc. These methods have significant production costs. Another good approach for getting rid of heavy metals is the absorption technique, which is also a cheap and efficient way to do it [4]. It has been found that activated carbon is one of a porous material which is an excellent adsorbent to remove metal ions.

Activated carbon, also known as activated charcoal, is a solid material with high surface area due to high-degree of pore size and surface reactivity. The raw material used for synthesizing the activated carbon are wood, lignite, peat shells, coconut and so on [7]. There are two ways for the preparation of the activated carbon: carbonization and activation [2,8]. The carbonization method is to reduce volatile by-product *via* pyrolysis, while the activation method is to modify the surface of charcoal *via* activating agents. The commonly activation techniques used to activate the charcoal are physical activation or chemical activation. The chemical activation is more crucial than physical one. The most benefits of chemical activation are its low heating temperature, safe-time, high yield, high specific surface area and easy to control [12,16]. According to chemical activation process, acidic and basic species are commonly used as activation agents. The acidic activating agents include H_2SO_4 [9], H_3PO_4 [5], HNO_3 [10], etc. It has been found that H_2SO_4 increased threefold in contrast to the untreated activated carbon [11] and acid-treated activation is more hydrophilic and thermally active. Briefly, it has been denoted that the acidic activating agent is a good one to perform the treating the carbon.

In order to the environmental issues and considering the methods for removing the heavy metals from the environment, the activated carbon is one of a good choice to treat the wastewater sources where it is a simple way to implement and inexpensive. Due to the fact that durian is a fruit that thrives in hot and humid climates. It is a common fruit in some Southeast Asia countries, such as Thailand, Malaysia, Indonesia etc. Due to Thailand's extensive durian cultivation, which results in about 600 kilograms (or more than 58 percent) of peel remaining from each ton of durian, the issue of plant waste of the durian peel from durian fruit consumption causes environmental problems if not discarded in a good manage. It is found that durian contains around 35% of cellulose and 20% of hemicellulose [9]. Taking into account these findings, durian peels are organic materials which are commonly known as carbonized material. In theory, cellulose and hemicellulose are carbon sources for producing the activated carbon.

Due to issues with wastewater containing heavy metals and agricultural waste from durian peel, therefore we designed an experiment to bring agricultural waste to add value by synthesizing the durian peels into activated carbon. To improve the efficiency of activated carbon from durian peel. We decided to immobilize our activated carbon using tannic acid. Tannic acid is an organic molecule composed of several negatively charged hydroxyl groups, which can bond to metal ions [15]. To gain inside into the immobilized activated carbon from durian peels, we will study the chemical kinetic, thermochemical factors and isothermal models for removing the copper ion from synthetic wastewater. The advantage of this work is to use of plant waste as raw materials. Overall, this study is to provide a potential eco-friendly application of the durian peels.

2 Materials and methods

2.1 Preparation of activated carbon from durian peel

Fresh durian peels were provided by local market in Salaya, Phutthamonthon, Nakhon Pathom province, Thailand. The durian peels were cut into small pieces and dried by oven at 100 ºC. Charcoal from durian peels of durian peels was produced by furnacing at 300 ºC for five hours. Next, the charcoal was activated by 3 molar H_2SO_4 for 12 hours. Then, activated carbon from durian peels was washed with deionized water until pH 7. Finally, the activated carbon was soaked in tannic acid solution for 10 hours. The immobilized activated carbon was dried in the oven and stored for further use.

2.2 Characterization

Fourier transform infrared spectrum (FTIR) was performed to analysis the immobilized activated carbon, compared to activated carbon. The spectrum was collected between 500 and 4,000 cm^{-1}.

2.3 Adsorption experiment

The copper (II) concentrations in the wastewater were investigated by using a flame atomic absorption spectrometer (FAAS). A commercial activated carbon (AC), AC prepared from durian peels (D-AC) and tannic acid immobilized activated carbon production from durian peels (TA-AC) were studied. 0.5xxx g of AC, D-AC and TA-AC in 50 mL of copper (II) ion (30 mg/L) were studied at 15, 30, 60, 90, 120 and 180 min to examine the contact time. Using optimum condition, we determined the kinetics, thermodynamics and also model adsorption for all type of activated carbon.

3. Result and Discussion

3.1 Characterization of durian peel activated carbon and tannic acid immobilized on activated carbon

Based on FTIR spectrum, the tannic acid immobilization of durian peel activated carbon showed that peak signal occurred at approximately 2900 cm^{-1} of tannic acid-immobilized activated carbon. While, activated carbon obtained from durian peel, no such peak signal occurred at that wavenumber, indicating that the tannic acid was immobilized on the surface of activated carbon after modification of durian peel (Figure 1).

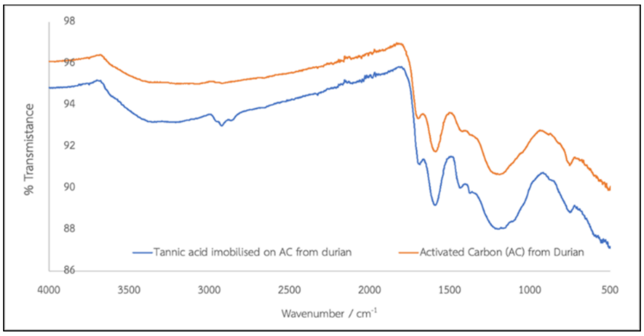


Figure 1: FTIR spectrum of tannic acid immobilized durian activated carbon (blue line) and durian activated carbon (orange line).

3.2 Percentage removal of copper (II)

Compared between the activated carbon obtained from D-AC and TA-AC, it was found that the TA-AC is approximately 5 - 10% more effective than the D-AC (Figure 2). The TA-AC performs better because the hydroxy group of tannic acid fixed on activated carbon binds to copper (II) ions in solution, thus the tannic acid immobilization increases. The active site adsorbed more copper (II) ions, but in a comparative study between activated carbon fixed with tannic acid at a concentration of 30 ppm and fixed with a high concentration of tannic acid. It was found that activated carbon fixed with tannic acid concentration of 30 ppm had a higher efficiency of about 3 - 5 percent when the charcoal was immobilized with more than enough concentration of tannic acid. The more concentration of the tannic acid led to decreasing the adsorption efficiency because of phenols in the tannic acid interacting with themselves using π-π interaction.

3.3 Contact time

Our study shows that contact time of copper (II) ions with activated carbon of commercial AC, D-AC and TA-AC reach to the equilibrium after 60 minutes. It indicates that that if the commercial AC, D-AC and TA-AC are to be used to remove copper (II) ions, these materials must be immersed in the wastewater more than 60 minutes in order to maximize the absorption of copper (II) ions (Figure 3).

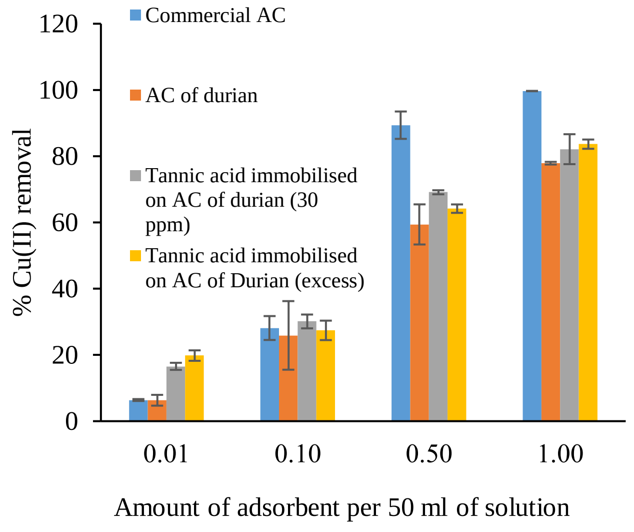


Figure 2: Percent removal of Cu(II) using commercial activated carbon (AC), durian AC, tannic acid immobilized durian AC.

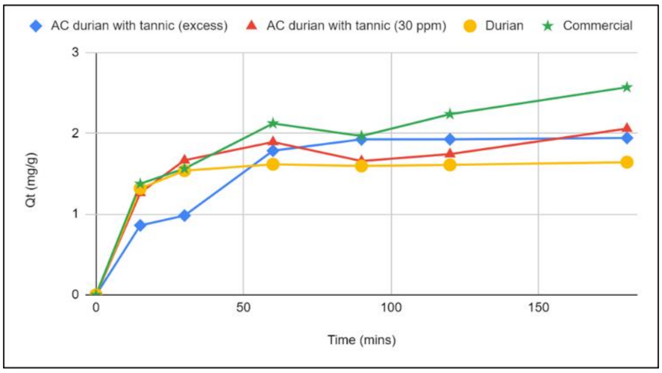


Figure 3: Contact time using commercial AC (green line), D-AC (orange line), TA-AC using 30 ppm tannic acid (red line) and TA-AC using excess tannic acid.

3.4 Kinetic study

A pseudo-order reaction was study to determine the rate of the adsorption [6]. The pseudo-first order is given by:

$$\ln(Q_e - Q_t) = \ln Q_e - kt \qquad (1)$$

Where Q_e is the amount adsorbed at equilibrium (mg/g); Q_t is the amount adsorned at time (mg/g); *k* is kinetic constant and t is time. Whereas, the pseudo-second order is given by:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \qquad (2)$$

The results of the kinetic study of reactions revealed that when plotting a straight line to compare between the pseudo-first order and the pseudo-second order, it was found that, the *R*-square value of the pseudo-second order was closer to one than the pseudo-first order, indicating that the adsorption of copper (II) on the commercial AC is the pseudo-second order reaction. The study of adsorption order using D-AC and TA-AC. The results show that the copper (II) adsorption rankings were also pseudo-second order rather than pseudo-first order (Table 1). The adsorption model of the copper (II) will be discussed later in the results.

Table 1: R-squared (R^2) of the pseudo-first order and pseudo-second order of commercial AC, durian AC, tannic acid immobilized durian AC

Adsorbent	***R*-squared**	
	Pseudo-1st order	**Pseudo-2nd order**
Commercial AC	0.8028	0.9800
D-AC	0.6081	0.9997
TA-AC (30 ppm)	0.5974	0.9786

3.5 Adsorption Isotherm

To describe the adsorption isotherms, two adsorption models were analyzed; the Langmuir and the Freundlich isotherm adsorption model. The Langmuir isotherm proposes a monolayer adsorption, while the Freundlich isotherm equation can be used to determine multilayer adsorption. The Langmuir is presented in Eq.(3) and the Freundlich is shown in Eq.(4) [6];

$$\frac{C_e}{Q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (3)$$

Where C_e is the equilibrium concentration of the copper(II) (mg/g); b is the constant related to energy of adsorption (L mg/g); q_m is the Langmuir monolayer adsorption capacity (mg/g).

$$Q_e = k_f C_e^{1/n} \qquad (4)$$

Where k_f is roughly an indicator of the adsorption capacity; *n* is the constant related to adsorption intensity;

The natural logarithmic form of Eq.(4) is a linear equation of the Freundlich isotherm. This equation is shown as following:

$$\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (5)$$

In order to study Langmuir Isotherm, we plotted between C_e/Q_e and C_e, but for Freundlich Isotherm, we plotted between $\ln Q_e$ and $\ln C_e$.

To study by fitting the Freundlich isotherm equation and the Langmuir isotherm equation, the results showed that the commercial AC (Figure 4a) and b)) and D-AC (Figure 4c) to f)). All adsorbents showed that the R^2 of the Freundlich isotherm model was closer to one than the R^2 of the Langmuir isotherm model thus all adsorption isotherms are multi-layered. The adsorption model experiment was related to the reaction order that the rapid adsorption is the second order reaction resulting from the multilayer adsorption.

In Table 2, the Freundlich isotherm constant is a measure of adsorption efficiency. The value of TA-AC was higher than D-AC. This showed that when tannic acid was immobilized, the removal efficiency of copper (II) ions was increased and was consistent with the results of the above-mentioned heavy metal adsorption percentage experiments.

Table 2. Freundlich isotherm constant (k_f) and adsorption density constant (n) of the Freundlich isotherm model.

Adsorbent	Freundlich isotherm constant	
	k_f	n
Commercial AC	2.180	5.297
D-AC	0.124	0.889
TA-AC (30 ppm)	0.276	1.129

3.6 Thermodynamics

The study of thermodynamic parameters can be used to gain insight into the adsorption behavior associated with temperature. Each country has different water temperatures in water sources. Therefore, the researcher used thermodynamic equations to explain the adsorption of the studied adsorbents. Thermodynamic parameters such as change in enthalpy (ΔH^o) and entropy (ΔS^o) were determined using the following equation (Romero-González et al., 2005):

$$\ln K_C = -\frac{\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R} \qquad (6)$$

Where K_c is the equilibrium constant; T is temperature in Kelvin and R is the gas constant. To obtaine the K_c, we estimated this value using Eq.(7):

$$K_C = \frac{Qe}{Ce} \qquad (7)$$

$$\Delta G^o = -RT \ln K_c \qquad (8)$$

ΔH^o and ΔS^o were obtained from the slope and y-intercept of Eq. (6). Thus, we plotted of $\ln K_c$ versus 1/T to determine these parameters (Figure 3).

In Table 3, it was found that the adsorption of copper (II) ions was positive enthalpy, indicating that the reactions are endothermic processes. Therefore, it was stated that the higher the temperature, the better the adsorption by the commercial AC, D-AC and TA-DC. Moreover, it can be said that if the tannic acid immobilized on activated carbon is to be used at high temperature and the driving force that effectively removes copper (II) ions is temperature.

Table 4 shows the value of ΔG^o at various temperature. The ΔG^o indicate the non-spontaneous process of adsorption. However, the increase of ΔG^o with the increase temperature shows that the adsorption is more favorable processes. This evidence supports the ΔH^o value that the temperature is the driving force for copper (II) adsorption on the TA-AC.

Table 3. Thermodynamic values obtained from the study on the adsorption of copper (II).

Adsorbent	Thermodynamic values	
	ΔS^o / J K^{-1} mol^{-1}	ΔH^o / kJ mol^{-1}
Commercial AC	228.2	68.3
D-AC	25.6	12.5
TA-AC (30 ppm)	24.4	11.1

Table 4. Thermodynamic parameters for studying the adsorption of copper (II) onto TA-AC.

T	Kc	ΔG^o
K		kJ K^{-1} mol^{-1}
298	0.222	3.78
333	0.292	3.40
353	0.472	2.21

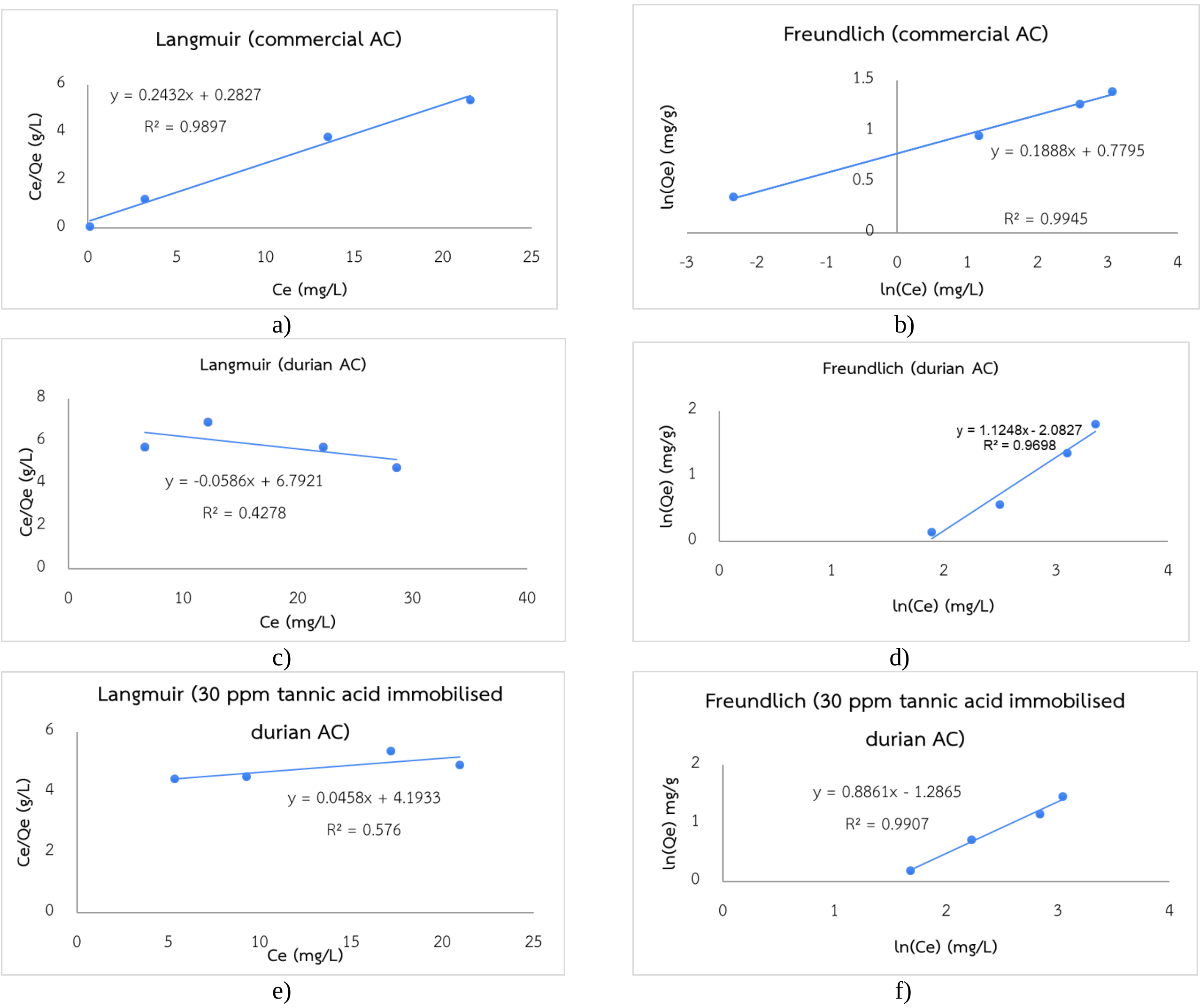
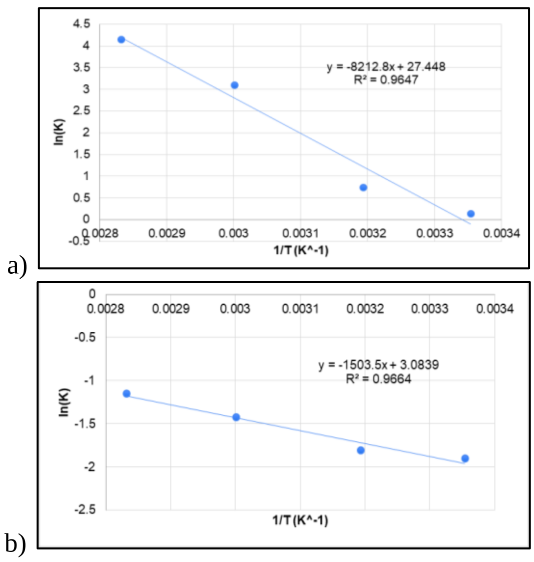


Figure 4: Adsorption model of copper (II) ions on adsorbent a) Langmuir isotherm adsorption using durian peel AC b) Freundlich isotherm adsorption using AC c) Langmuir isotherm adsorption using AC from durian peel immobilized with 30 ppm tannic acid d) Freundlich isotherm adsorption using AC from durian peel immobilized with 30 ppm tannic acid. e) Langmuir isotherm adsorption using commercial AC and f) Freundlich isotherm adsorption using commercial AC



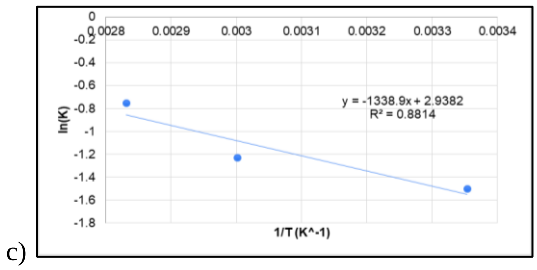


Figure 5: Thermodynamics study of copper (II) ion adsorption by a) commercial AC b) D-AC and c) TA-AC.

4 Conclusion

The tannic acid immobilized on activated carbon was successfully synthesized. It can be used as adsorbent to remove copper (II) from wastewater.

The TA-AC increases the efficiency of absorbing copper (II) ion metal solution about 5-10%, compared to D-AC. The copper (II) approach to equilibrium about 60 minutes. Under optimum condition, the TA-AC has a higher adsorption capacity and good performance for removing the copper (II). In kinetic study, the TA-AC had the pseudo-second order reaction rank, which corresponds to the results of finding the model adsorption which is the Freundlich isotherm. The thermodynamic study shows that the TA-AC has the endothermic adsorption. Overall results indicates that TA-AC can enhance the removal of metal ions in synthetic wastewater. This is to bring value to agricultural waste in the future.

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