

One Pot Synthesis of Carboxylated Activated Carbon for Water Purification: A Kinetic Study

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Abstract

Modification of a carboxylated activated carbon was obtained by simple one pot heat treatment method. This carboxylated activated carbon was confirmed by its physical and chemical structure. The efficiency of this carboxylated activated carbon was evaluated for adsorption of Cu(II) and Pb(II) based on their kinetic parameters to understand their adsorption mechanism. The pseudo-second-order model was the best fitted to describe the adsorption behavior of Cu(II) and Pb(II) indicating that chemisorption process took place during the adsorption. The adsorption capacity of Cu(II) and Pb(II) of carboxylated activated carbon was higher, which was 0.726 and 1.312 mg g⁻¹, respectively for CAC and 1.093 and 1.160 mg g⁻¹, respectively for PAC, compared to pristine AC, which was 0.314 and 0.365 mg g⁻¹, respectively.

Keywords: Carboxylate activated carbon; One pot synthesis; Adsorption; Kinetic study*

1.Introduction

Water is indispensable and crucial element in our lives. The escalation of industrialization and high density of population cause great concern on clean water availability. The untreated wastewater discharged from industrial activities can be potentially harmful because of organic and inorganic substances contained in it, namely heavy metals. Limitation trace of heavy metal is regulated because of its threat. For example, excess of copper (Cu) induce gastrointestinal damage and disorders, while having risk to cardiovascular is one of the effects for being exposure to lead (Pb) [1]. One of the effective and efficient techniques known for treating polluted aqueous environment is adsorption among other various physical and chemical process such as chemical precipitation, ion exchange and etc. Adsorption is considered as the most widely applied technique for water treatments owing to its efficiency, process simplicity and less cost [2]. Carbon materials is one of the most utilized adsorbents for aqueous or gaseous pollutant uptake due to its attractive properties, such as extensive surface area, large porosity and wide spectrum of functional group attach to the surface [3-6]. In order to enhance its performance, the modification have been applied to its surface which can alter the presence of functional groups, which are reliant on preparation, doping and functionalization. The functionalization of carbon materials is generated by physical (carbonization of a precursor and gasification) and chemical activation (reaction of a precursor with a chemical reagent) resulting modification on carbon materials backbone, like oxygen and nitrogen moieties [7]. It is also known that the extent of oxidation shows different oxygenated functional groups formed depends on conditions and oxidizing agents applied. For example, oxidation with nitric acid introduces large amounts of carboxylic groups, along with phenol and carbonyl groups, while oxygen oxidation creates mainly phenol and carbonyl groups. However, the use of acid for oxidation may lead to extensive damage to carbon material with drastic changes in structural characteristics [8]. The chemical treatment for manipulating the functional groups existing on carbon surface usually done in several steps, which create wastewater for neutralization [9]. In this study, one pot synthesis was applied. One pot synthesis is used to describe the strategy to improve the efficiency of chemical reaction that are carried out in a single vessel or reactor [10]. This method is beneficial because no waste was produced, no addition of chemicals as reagents or solvents, simple and economical. Our previous results revealed that the certain functional groups of oxygenated groups like carboxyl, hydroxyl and lactone could be generated via one pot synthesis under air oxidation treatment [11]. In this work, we report the kinetic study of Cu(II) and Pb(II) adsorption from water by comparing the performance capacity of carbon materials contained different carboxyl functional group. The adsorption kinetics of modified activated carbon are studied based on pseudo-first-order and pseudo-second-order kinetic models and the adsorption properties of carboxylated activated carbon are studied based on Langmuir-Freundlich isotherm models.

1. Experimental

2.1. Materials

All chemicals used in the present study were of analytical grade purchased from Merck and were used without further treatment. Stock metal solutions of 1 g L^{-1} were prepared by dissolving in distilled water according to appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$. The stock solution of each nitrate salt was diluted to get the desired initial metal ion concentration (C_0). Cu(II) and Pb(II) standard solutions used to obtain the calibration curves for Atomic Absorption Spectrometry (AAS) was prepared from different diluted metal concentrations.

2.2. Preparation of Adsorbent

Chemical and one pot synthesis activated carbon, here after is known as CAC and PAC, respectively, were used to perform adsorption for Cu(II) and Pb(II) removal. Chemical activated carbon (CAC) was prepared from 2.0 g of AC which then mixed with 20 mL of HNO₃ for 3h at 90 °C. The mixture was filtered and washed to neutralize the pH using distilled water and further dried at 110 °C overnight. One-pot synthesis activated carbon (PAC) was prepared by placing 4.0 g carbon which distributed evenly into petri dish and heated under air flow in calcination apparatus. The calcination temperature was 425 °C with temperature rate at 10 °C/min and kept the temperature for 3 h.

2.3. Adsorption Experiments

A Pb(NO₃)₂ and Cu(NO₃)₂ 10 ppm pollutant solutions were prepared for heavy metal pollutant. Adsorption efficiency for the heavy metals was performed by contacting 0.1 g of carbon sample with 20 mL of heavy metal pollutant solutions. Samples were collected at interval times and filtered using filter paper, then analyzed using Atomic Absorption Spectroscopy (AAS).

2.4 . Analytical Methods

The amount of metal ion adsorbed onto CAC and PAC at any time (q_t) was calculated from:

$$q_t = \frac{V(C_0 - C_t)}{W} \quad (1)$$

at equilibrium $q_t = q_e$ and $C_t = C_e$, thus the amount of adsorbed metal ion (q_e) was calculated from:

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (2)$$

where C_0 , C_t and C_e are initial concentration, concentration at any time and equilibrium concentration of metal ion in solution (mg L⁻¹), respectively, V is the volume of the solution (L) and W is the mass of AC (g).

2. Results and discussion

3.1. Comparative Studies on Adsorption Capacity of Cu(II) and Pb(II) on AC

The effectiveness of surface modified AC toward removal of Cu(II) and Pb(II) was compared according its removal capacity as shown in Figure 1. The adsorption pattern of Cu(II) and Pb(II) removal showed that for the first 30 min the adsorption went fast until it reached equilibrium at about 120 min. This is because the heavy metal needs time to encounter the boundary layer effect, then diffuse to the surface of AC before going through the porous structure of the adsorbent [12]. The adsorption of heavy metal using CAC was the highest for both Cu(II) and Pb(II), whilst PAC showed moderate adsorption activity compared to pristine AC. The adsorption capacities for Cu(II) were 0.314, 0.726 and 1.312 mg g⁻¹ for AC, CAC and PAC, respectively. Adsorption capacities for Pb(II) were 0.365, 1.093 and 1.160 mg g⁻¹. This phenomena is related to the functional groups owe by each of activated carbon. The surface of CAC contained 3.38 mmol g⁻¹ of total acidic functional group compared to PAC with 2.64 mmol g⁻¹ while pristine AC has the lowest, only 0.35 mmol g⁻¹ [11]. The acidic functional groups are essential for heavy metal adsorption due to chelating attribute of metal cations to form complexes when exchanges site with hydrogen ion attached as in whole carboxylic group [13]. This finding is in accordance with some studies that suggested the increased of some heavy metal uptake from aqueous solution in the presence of weakly acidic functional groups like carboxylic, lactonic, phenolic and carbonic [14-16]. These results indicated that surface modified AC, namely CAC and PAC offered great adsorption capacity compared to pristine AC.

3.2. Adsorption Kinetics

The adsorption kinetics depends on the adsorbate-adsorbent interaction and the condition of the system. Two important evaluation elements for the operating unit of the adsorption process are the reaction mechanism and the reaction rate. The absorption rate of solutes will determine the time needed to complete the adsorption reaction and can be calculated through kinetic analysis [17]. Various methods have been carried out in order to express the general formula in describing the process of adsorption kinetics on the surface of a solid for the adsorption system of a solution, including the kinetics of pseudo-first-order and pseudo-second-order.

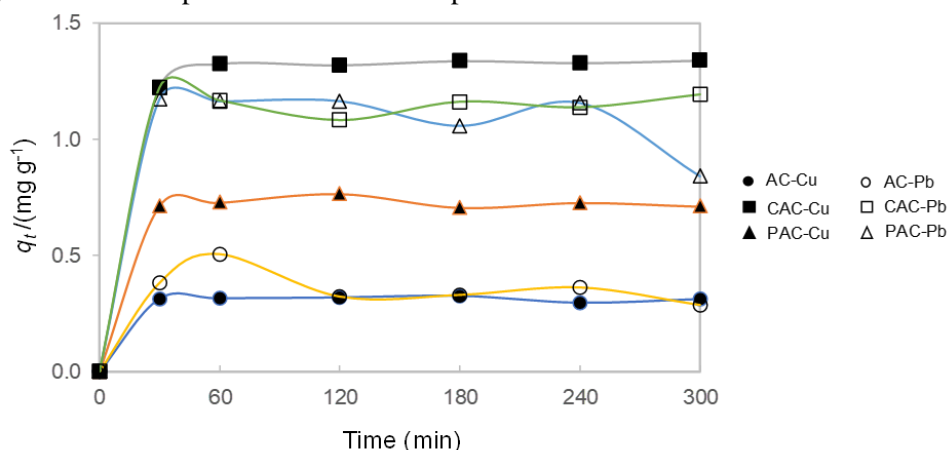


Figure 1. Adsorption capacity of modified AC on the removal of Cu(II) and Pb(II) ions

The absorption kinetics of pseudo-first-order reaction generally has the following equation [18, 19].

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (3)$$

In this equation, q_e and q_t represent the amount of metal absorbed by the adsorbent (mg g^{-1}) at equilibrium and time (min) respectively; and K_1 is the rate constant of pseudo-first-order ($1/t$). The integration equation (1) under certain conditions for $t = 0$ and $q = 0$ is obtained as follows.

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (4)$$

The values of K_1 and q_e are calculated from the slope and intercept in the plot of the log graph ($q_e - q_t$) toward t . The value of R^2 determines the level of linearity of pseudo-first-order reaction graph. If the value of R^2 is close to 1, the adsorption kinetics follows the pseudo-first-order reaction.

The absorption kinetics of pseudo-second-order reaction is based on the adsorption capacity equilibrium with the following equation [18].

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad (5)$$

K_2 is the absorption rate of pseudo-second-order ($\text{g mg}^{-1} \text{ min}^{-1}$). In the integration of equation (3) under certain conditions for $t = 0$ and $q = 0$, the following equation is obtained.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (6)$$

The values of K_2 and q_e are calculated from the slope and intercept of the plot of the graph t/q_t toward t . The value of R^2 determines the level of linearity of pseudo-second-order graph. If the value of R^2 is close to 1, the adsorption kinetics follows the pseudo-second-order. The modified activated carbon adsorption kinetics for heavy metal Pb(II) and Cu(II) absorption was determined at various concentrations of 10 mg L^{-1} for 1 hour and taken at intervals of 10 minutes. The results are as follows. Table 1 shows that the adsorption kinetics with a linear regression value of R^2 which is close to 1 occurs in the pseudo-second-order with the value of R^2 is above 0.98 for all three AC towards the

absorption of heavy metal Cu(II) and Pb(II) of 10 mg L⁻¹. The calculated value of q_e that are quite same with the value of q_e from the experimental result indicated that the modified activated carbon for the absorption of heavy metal Cu(II) and Pb(II) of 10 mg L⁻¹ follows the absorption kinetics of the pseudo-second-order. There is a difference in the values of q_e between AC, CAC and PAC implying the effect of functional groups on modified activated carbon to the heavy metal Cu(II) and Pb(II) adsorption because the value of q_e indicate the amount of metal adsorbed at equilibrium. The rate of absorption of pseudo-second-order on AC is 0.389 mg g⁻¹ min⁻¹, CAC is 1.016 and PAC is 0.330 mg g⁻¹ min⁻¹ for Cu(II), while for Pb(II) the adsorption rate of pseudo-second-order on AC, CAC and PAC are 0.126, 0.824 and 1.331 mg g⁻¹ min⁻¹.

Table 1: Adsorption Kinetic Parameters for Cu(II) and Pb(II) onto different AC (T: 298 K, t: 300 min, [Pb(II) = Cu(II)]₀: 10 mg L⁻¹, V: 0.02 L, mAC: 0.1 g L⁻¹)

Pseudo-first-order kinetic model								
Adsorbent	Cu(II)				Pb(II)			
	q_e , exp (mg g ⁻¹)	q_e , cal (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e , exp (mg g ⁻¹)	q_e , cal (mg g ⁻¹)	k_1 (min ⁻¹)	R^2
AC	0.353	28.774	0.001	0.075	0.350	26.996	0.003	0.098
CAC	0.759	5.120	0.003	0.019	1.287	107.448	0.008	0.161
PAC	1.341	10.955	0.015	0.712	1.248	20.488	0.003	0.085

Pseudo-second-order kinetic model								
Adsorbent	Cu(II)				Pb(II)			
	q_e , exp (mg g ⁻¹)	q_e , cal (mg g ⁻¹)	k_2 (g mg ⁻¹ min)	R^2	q_e , exp (mg g ⁻¹)	q_e , cal (mg g ⁻¹)	k_2 (g mg ⁻¹ min)	R^2
AC	0.353	0.336	0.389	0.988	0.350	0.355	0.126	0.983
CAC	0.726	0.716	1.016	0.999	1.287	1.273	0.824	0.999
PAC	1.341	1.348	0.330	0.999	1.248	1.197	1.331	0.999

2.3. Isotherms for Cu(II) and Pb(II) Sorption onto AC

Langmuir-Freundlich adsorption isotherm is used to determine the adsorption properties that occur at the surface site of the modified activated carbon. Langmuir isotherm shows that adsorption occurs in one layer (monolayer) and illustrates that adsorption occurs chemically on homogeneous surfaces [18, 20] with the following equation.

$$q = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

q_m is the maximum adsorption capacity (mg g⁻¹); q_e is the adsorption capacity at equilibrium (mg g⁻¹); C_e is the concentration of adsorbate at equilibrium (mg L⁻¹); and K_L is a constant associated with the bound affinity at the site (L mg⁻¹) or can be called the constant of Langmuir isotherm. In Langmuir isotherm, there is a separating factor (R_L) to determine the characteristics of the adsorption that occurs. The equation is as follows.

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

C_0 is the initial concentration of adsorbate (mg.L^{-1}). The value of the R_L separator factor provides important information regarding the adsorption characteristics. The values of R_L between 0 and 1 are good adsorption; $R_L > 1$ indicates bad adsorption; $R_L = 1$ indicates that adsorption occurs linearly; and $R_L = 0$ indicates the adsorption process is irreversible [21].

From the linear plot between $1/q_e$ and $1/C_e$ on Langmuir isotherm graph, the value of q_m and the value of K_L determined from the calculation of the intercept and slope values respectively can be obtained. The value of R^2 itself determines the linearity level of Langmuir isotherm graph. If the value of R^2 is close to 1 in Langmuir isotherm, the adsorption that occurs follows Langmuir isotherm adsorption. Freundlich isotherm shows that adsorption occurs in several layers (multilayer) and illustrates that adsorption occurs physically on heterogeneous surfaces [18, 20] with the following equation.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (9)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

K_F is a multilayer indicator of adsorption capacity (L.mg^{-1}) and $1/n$ represents adsorption intensity and shows the relative energy distribution and heterogeneity of the adsorbent site. From the linear plot between $\log q_e$ and $\log C_e$ on Freundlich isotherm chart, the value of K_F and the value of $1/n$ determined from the calculation of the intercept and slope values respectively can be obtained. The value of R^2 itself determines the linearity level of Freundlich isotherm graph. If the value of R^2 is close to 1 in Freundlich isotherm, the adsorption that occurs follows Freundlich isotherm adsorption.

The following are the results of adsorption isotherms within 3 hours at room temperature. The values of Langmuir and Freundlich constant for different carbon samples are shown in Table 2.

Table 2: Langmuir and Freundlich isotherm constant of different AC for Cu(II) and Pb(II) removal in aqueous solution

Adsorption Isotherm of Pb(II)							
Activated carbon	Langmuir Isoterm				Freundlich Isoterm		
	R^2	q_m (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_F (L mg^{-1})	$1/n$
AC	0.8159	0.8125	0.0090	0.8876	0.5199	104.9301	0.9559
CAC	0.9987	1000	0.0002	0.9976	0.9948	5.7253	0.9927
PAC	0.9942	23.3645	0.0063	0.9194	0.9852	6.4298	0.9254

Adsorption Isotherm of Cu(II)							
Activated carbon	Langmuir Isoterm				Freundlich Isoterm		
	R^2	q_m (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_F (L mg^{-1})	$1/n$
AC	0.9326	1.2338	0.0281	0.7175	0.7697	20.3329	0.6937
CAC	0.8937	0.2899	0.0766	0.4825	0.8421	32.2107	1.1649
PAC	0.9869	6.8540	0.0418	0.6309	0.9724	3.3520	0.8177

Table 2 shows the adsorption properties of Pb(II) are well described by the linear form of Langmuir isotherm with R^2 for AC, CAC and PAC are 0.8159, 0.9987 and 0.9942, respectively. In contrast to the results on Freundlich isotherm which lacks a good linear form, especially in AC with R^2 of 0.5199 compared to the R^2 of CAC of 0.9948 and PAC of

0.9852. The value of R_L based on Langmuir isotherm at AC value of 0.8876 and CAC and PAC values were 0.9976 and 0.9852, which demonstrate a good adsorption process because it is in the range of R_L between 0 and 1, while the value of $1/n$ (adsorption intensity) based on Freundlich isotherm for all AC were at range 0.9254 to 0.9927 which means a good adsorption process because of the value of $1/n < 1$ [21]. In line with adsorption properties of Pb(II), the adsorption properties for Cu(II) are well described by the linear form of Langmuir isotherm with R^2 for AC, CAC and PAC were about 0.9326, 0.8937 and 0.9869. Followed by the value of R_L which pointing to a good adsorption process because it is in the range of R_L between 0 and 1, while the value of $1/n$ (adsorption intensity) based on Freundlich isotherm also in agreement with the value of $1/n < 1$ displaying a good adsorption process. It can be concluded that the CAC adsorption properties tend to be chemisorption, whereas in PAC which is activated by air oxidation in one-pot system has adsorption properties that can be both adsorption and physisorption. The maximum adsorption capacity in the value of q_m based on Langmuir isotherm increases from only 0.8125 mg g⁻¹ at AC to 1000 mg g⁻¹ at CAC. This indicates the effect of functional groups on the absorption of heavy metal. The isotherm adsorption of pure AC, CAC and PAC for the heavy metal pollutants follows Langmuir isotherm model as presented in Table 2. Isotherm Langmuir is based on the assumption that a maximum limiting uptake exists, corresponding to a saturated monolayer of adsorbate molecules at the adsorbent surface [22]. As shown on the Table 2, due to higher value of R^2 of Langmuir isotherm, the adsorption of heavy metal ion is mostly based on the formation of monolayer on its outer surface [18, 23, 24]. Meanwhile, isotherm Freundlich assumed that adsorption occurs on a heterogeneous surface through a multilayer adsorption mechanism [22]. Those indicate that the absorption of ion Pb(II) was not only to the homogeneous surface (macropore and mesopore) but also to the heterogeneous surface (micropore). Even though the value of R^2 of Freundlich is smaller than Langmuir, it is still contributes to the absorption mechanism of heavy metal to the AC. Mechanisms of metal ions onto the adsorbent are complex. However, according to literature, physical adsorption, chemical interaction, electrostatic attraction and sorption-precipitation are among the dominant mechanism. The modified activated carbon, CAC and PAC, the chemical interaction are the most obvious mechanisms between carbon and metal ions. This is relevant with the result of adsorption of Cu(II) and Pb(II) where both CAC and PAC which possess high surface functional groups show high adsorption capacity compared to pristine AC. It is important to note that the adsorption capacity of carboxylated AC synthesized from one-pot air oxidation is comparable with that synthesized from chemical oxidation. Thus, these results suggested that the adsorption of heavy metals on activated carbon depends mainly on the properties of activated carbon.

3. Conclusion

The difference in the number of functional groups influences the adsorption process on the heavy metals Pb(II) and Cu(II). Surface modified AC obtained from one-pot air oxidation showed high adsorption capacity which is comparable with that synthesized with chemical oxidizing agent, compared to pristine AC. The adsorption kinetics study of Cu(II) and Pb(II) removal is best in accordance with the pseudo-second-order model. This indicates that the adsorption may be controlled by chemisorption. In addition, adsorption isotherm shows that removal of Cu(II) and Pb(II) follows Langmuir isotherm model which suggests that adsorption occurs on the outer surface of the adsorbent. In addition, PAC has adsorption properties which can be both chemisorption and physisorption.

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