Characterizations and Adsorption Behaviors of Resorcinol Solution on Activated Carbon Prepared from Coffee and Tea Residues by Chemical Activation

คุณลักษณะและพฤติกรรมการดูดซับสารละลายรีซอร์ซีนอลของคาร์บอนกัมมันต์ที่เตรียมจากกากกาแฟและกากชา โดยการกระตุ้นทางเคมี

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ABSTRACT

This research studied on using coffee and tea residues as a raw material for preparation of activated carbon (AC). It was divided into two main steps: 1) the carbonization at temperatures 500 °C, for 90 minutes for producing charcoal and 2) activation by heat and chemical with phosphoric acid (H_3PO_4) at 700 °C. It was found that the activated carbon prepared from coffee and tea residues (AC-CR and AC-TR) had characterizations (physical and chemical properties) according to Thai Industrial Standard (TISI) 900-2004 on powder activated carbon (PAC), iodine number ≥600 mg/g and apparent density 0.2-0.75 g/cm^3. When adsorption behaviors was studied on the optimum conditions for adsorption of resorcinol solution of both AC such as adsorption time, adsorbent dose, pH, and initial concentration by batch experiment, the results showed the optimal conditions for adsorption time at 90 minutes, adsorbent dose 0.05 g, pH 6-7 and initial concentration of 200 mg/L resorcinol solution. The study on adsorption isotherm models accordance with the Freundlich model to be good and appropriate for explaining the nature of adsorption with correlation coefficient (R^2) 1.0000 for the AC-CR and AC-TR, while the Langmuir model showed poorly consistent as (R^2) 0.9054 and 0.9433. In addition, the kinetic models showed that the corresponding correlation coefficients values for the pseudo-second order kinetic model were greater than 0.8376 for the AC-CR and 0.9167 for AC-TR. Therefore, the findings indicate the applicability of the pseudo-second order kinetic model to describe the adsorption process on the both adsorbents. Accordingly, it is concluded that this study could be effective and practical for utilizing in hair coloring wastewater treatment.

KEYWORDS: Characterizations, Adsorption Behaviors, Activated Carbon, Resorcinol, Coffee and Tea Residues

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อใช้ประโยชน์จากกากกาแฟและกากชา มาเป็นวัตถุดิบในการเตรียมคาร์บอนกัมมันต์ ใน 2 ขั้นตอนหลัก คือ การคาร์บอไนเซชันให้เป็นถ่านที่อุณหภูมิ 500 องศาเซลเซียส เวลา 90 นาที และการกระตุ้นทางความร้อนและเคมีด้วยกรดฟอสฟอริกที่อุณหภูมิ 700 องศาเซลเซียส คาร์บอนกัมมันต์ที่เตรียมจากกากกาแฟและกากชามีคุณลักษณะอยู่ในเกณฑ์กำหนดตามมาตรฐาน มอก. 900-2547 เรื่อง ถ่านกัมมันต์ชนิดผง กล่าวคือ มีค่าไอโอดีนนัมเบอร์ ไม่น้อยกว่า 600 มิลลิกรัมต่อกรัม และมีค่าความหนาแน่นปรากฏ 0.2 ถึง 0.75 กรัมต่อลูกบาศก์เซนติเมตร เมื่อศึกษาพฤติกรรมการดูดซับสารละลายรีซอร์ซินอลของคาร์บอนกัมมันต์ทั้งสองชนิด โดยวิธีแบบแบทซ์ เพื่อหาสภาวะที่เหมาะสมใน การดูดซับ ได้แก่ เวลาที่ดูดซับ, น้ำหนักของวัสดุดูดซับ, ค่าความเป็นกรด-ด่าง, ความเข้มข้นเริ่มต้น, อุณหภูมิและเวลาในการดูดซับ พบว่า สภาวะที่เหมาะสมในการดูดซับคือ ระยะเวลา 90 นาที น้ำหนักวัสดุดูดซับ 0.05 กรัม ค่าความเป็นกรด-ด่าง 6-7 และความเข้มข้นเริ่มต้น 200 มิลลิกรัมต่อลิตร จากการศึกษาไอโซเทอมของการดูดซับรีซอร์ซินอลบนพื้นผิวของคาร์บอนกัมมันต์ พบว่า สอดคล้องกับสมการแบบฟรอยลิชท์ โดยสมการเส้นตรงไอโซเทอมแบบฟรอยลิชท์มีความเป็นเส้นตรง มีค่าสัมประสิทธิ์สหสัมพันธ์เท่ากับ 1.0000 สำหรับคาร์บอนกัมมันต์ที่เตรียมจากกากกาแฟและกากชา ในขณะที่สมการเส้นตรงไอโซเทอมแบบแลงเมียร์ มีค่าสัมประสิทธิ์สหสัมพันธ์ เท่ากับ 0.9054 และ 0.9433 นอกจากนี้แบบจำลองจลนศาสตร์การดูดซับ พบว่า ข้อมูลทางจลนศาสตร์สอดคล้องกับแบบจำลองปฏิกิริยาอันดับสองเสมือน มีค่าสัมประสิทธิ์สหสัมพันธ์ เท่ากับ 0.8376 และ 0.9167 ตามลำดับ ซึ่งมีความเป็นเส้นตรงมากกว่าแบบจำลองปฏิกิริยาอันดับหนึ่งเสมือน ดังนั้น จึงใช้อธิบายกลไกการดูดซับซึ่งเป็นการถ่ายโอนมวลสารระหว่างสารถูก

ดูดซับและวัสดุดูดซับทั้งสองชนิดได้ วิธีการดูดซับนี้ จึงสามารถนำไปใช้ในระบบกำจัดน้ำทิ้งในสีย้อมผมได้อย่างมีประสิทธิภาพ

คำสำคัญ: คุณลักษณะ พฤติกรรมการดูดซับ คาร์บอนกัมมันต์ รีซอร์ซีนอล กากกาแฟและกากชา

Introduction

The coffee and tea are the most popular drinks in the world and tend to gain popularity in the future. The coffee and tea are one of the products that are important to international agricultural trade and economic crop of many developing countries for a long time (Export-Import Bank of Thailand, 2015). In addition, tea is a healthy drink that has been consistently popular in Thai peoples and foreigners which increasing consumption and development of consumption patterns from buying to drinking or containers in can, UHT, etc. The popular in Thailand for drinking fresh coffee and tea of Thai people has also increased dramatically. From the above, the coffee and tea residues from the beverage industry and coffee shop which has not been utilized, but is often dumped into a large amount of waste and has an impact on the environment cause of organic substances in wastes cannot treatment before. So, the state to pay transportation costs to be by landfills (Tangmankongwora-koon, & Preedasuriyachai, 2013).

Therefore, the researchers introduced this concept on using coffee and tea residues as a raw material for preparation of AC. It has the ability to adsorption various substances and can store various molecules in the interior surface. So, the AC was widely used adsorbent (Phothitontimongkol, 2017). Moreover, the price is main reason for the widespread use of its especially the choice of using raw materials to produce the AC from natural materials that are cheap and environmentally friendly which is a good objective in the current chemical materials by focusing on biomass and wastes that are large, cheap and sustainable (Mopoung, 2015). The according to a research study related to the production and utilization of AC prepared from tea and coffee waste by chemical activation, for example Prachpreecha, Prachpreecha, and Vongchavalitkul (2018) prepared AC-TR by used chemical activation with potassium hydroxide (KOH) for use in the treatment of wastewater from the cafeteria. The results found that the AC-TR had the highest iodine number 769.36 mg/g and has a density of 0.63 g/cm^3 which has characteristics following with TISI standards 900-2004. After that, the study efficiency of AC-TR for treatment of wastewater from the canteen in the wastewater treatment system. It was found that the efficiency of reducing the amount of oil and fat was the best 81.30%, followed by the value BOD was 73.85% and the number of suspended solids was 65.03%, respectively. In addition, Boudrahem, Soualah, and Aissani-Benissad (2011) studied the production of AC-CR by using a chemical activation with zinc chloride ($ZnCl_2$) to be used to adsorption Pb (II) in solution. The study indicated that the concentration of $ZnCl_2$ at 75% was appropriate concentration used to prepare AC. This has a surface area of approximately 890 m^2/g and a total pore volume of 0.772 cm^3/g. Then the prepared charcoal was tested for adsorption Pb (II), it was shown that the concentration of Pb (II) 10 mg/L which receives the highest adsorption value of 63 mg/g. It can be seen that chemical activation is an important step in the production of AC such as $ZnCl_2$, H_3PO_4 and KOH but the elimination and reactivation of the stimulants from the production process is quite complicated. From the studies of Wu and Zhang (2012) found that the problem of efficiency in low recovery and corrosion problems of zinc in cabon activated by $ZnCl_2$ in AC production. Therefore, the uses of H_3PO_4 have been widely used due to many porous structures and have the functional groups containing phosphorus on the activated carbon surface (Yang, Liu, Xu, Li, Zhang, & Hao, 2011)

In this research, the researcher used of coffee and tea residue which is a lot of waste and cheaper to produce the AC according to TISI 900-2004 on PAC (iodine number ≥600 mg/g and density 0.2-0.75 g/cm^3). To study characterizations and adsorption behaviors of resorcinol solution on both AC. The resorcinol was a toxin that comes from the wastewater from the salon in the process of dying and curling. This substance is not naturally biodegradable which may cause polluted water and cancer as well (Thanomsith, Mahachai, & Chanthai, 2009). It is often abandoned without treatment. Therefore, should be another alternative that can bring coffee and tea residue to produce as AC for removal resorcinol solution and used worthless junk to benefit also.

Purpose

The purposes of the study are specified as follows:

1) To preparation and characterization of AC-CR and AC-TR, analyze of the physical properties and chemical composition of AC with TISI 900-2004 standards on PAC

2) To study the optimal conditions for adsorption of resorcinol solution with the AC-CR and AC-TR such as adsorption time (t), the weight of adsorbent (m), pH, initial concentration (C_0), temperature and time of adsorption

3) To study the adsorption isotherm and kinetics adsorption of resorcinol solution onto AC-CR and AC-TR

Benefit of Research

The expected benefits of this research as can be prepared the AC-CR and AC-TR are characterizations following with TISI 900-2004 standards on PAC and to explain the adsorption behaviors for kinetic adsorption and understanding of adsorption isotherms of resorcinol solution onto both AC. Therefore, the research results can be applied to the removal of resorcinol in hair coloring wastewater for the future research.

Research Process

Materials and methods

1) Materials

The coffee and tea residues from brewed beverage stores, Resorcinol ($C_6H_6O_6$), Analytical grade, Sieves 100 mesh, Hot air oven (Beschickung Loading model 100-800), Electric Muffle Furnace (Model LEF-1035), Incubator Shaker (Model KS 4000 I control; IKA), Scanning Electron Microscope (SEM) (Model AURIGA; Carl Zeiss), UV-VIS Spectrophotometer (Model 752)

2) Methods

2.1) Preparation of the AC-CR and AC-TR has two main steps as follows:

(1) Carbonization

Washed thoroughly coffee and tea residues with deionized water, adjust to pH 7, dried to remove moisture in the hot air oven at 110°C for 8 hours. Then, brought about 150 g of coffee and tea residues that had been dried into a ceramic packaging (150 cm^3) for burning in the electric muffle furnace until reaching the desired temperature at 400, 500, 600 and 700°C, respectively and leaving them at that temperature about 1 hour. (Prachpreecha & Prachpreecha, 2017). After that, it was tested to find the iodine number according to the standard method of ASTM D 4607-94 (American Society for Testing Materials, 2006) and selected charcoal of the highest iodine number because iodine number indicates the adsorption capacity of the adsorbate molecules. Moreover, the adsorption of iodine number is directly related to the surface area and small pore volume (Olorundare, Krause, Okonkwo, & Mamba, 2012). After that, test for a optimal time for carbonization such as 30, 60, 90, 120, 150 and 180 minutes.

(2) Activation

The thermal and chemical activation by selected of the charcoal carbonization and the iodine number that were highest to grind and sieve following to the TISI 900-2004 standard on PAC, can pass through the sieve 150 μm, ≥99 (%w/w) (Thai

Industrial Standard Institute, 2004), then dropped with charcoal carbonized, with H_3PO_4 50% in ratio 1:0, 1:1, 1:2, 1:3 and 1: 4 (Charcoal: H_3PO_4) to achieve saturation. Washed thoroughly and dried at 110°C and weighed 150 g of samples packaged in a ceramic bowl again and closed. Brought charcoal to activate in the electric muffle furnace to 600, 700, 800 and 900°C by increasing the temperature at a rate of 10°C/minute until the desired temperature is reached (Jeungsaman & Assawassaengrat, 2016). Put it at this temperature for about 1 hour and then left to cool down. The products were washed with 5% hydrochloric acid (HCl) followed by distilled water many times until getting to pH 6.5-7.0, baked in the electric muffle furnace at 110°C for 8 hours and analyzed for porosity and surface area with SEM.

2.2) Proximate analysis

The both AC were tested for iodine number according to ASTM D 4607-94 (American Society for Testing and Materials, 2006) and analysis for characterization of the AC-CR and AC-TR by using proximate analysis, such as content of moisture (ASTM D 3173-95), volatile (ASTM D 5832-98), ash (ASTM D 2866-11) and Fixed carbon(ASTMD 3172) with ASTM standard method (American Society for Testing and Materials, 2012) in accordance with TISI900-2004 standard on PAC.

2.3) Study the optimum resorcinol solution adsorption conditions

Preparation stock solution of resorcinol (1,000 mg/100 ml), weight 0.1 g resorcinol dissolved with distilled water, adjust the volume to 100 ml. Then, put the bottles in the refrigerator at 4°C for 60 days (Thanomsith et al., 2009). Then, weight 150 g of both AC and move moisture in the hot air oven at 110°C for 8 hours for study on adsorption of resorcinol solution in a batch adsorption experiments at room temperature, which each batch experiments repeated three times. This can be shown in each experiment as follows:

(1) Effect of adsorption time

Weighed 0.05 g of the AC-CR and AC-TR in flask 125 ml and pipette 30 ml of resorcinol solution with initial concentrations of 200 mg/L, pH 6.5-7. The adsorption times were 15, 30, 60, 90 and 360 minutes 3, 5, 7, 9 and 10 days, respectively. The flasks were placed in a shaking incubator at room temperature and shaken at 150 rpm for 5 minutes. After that, the suspension was filtered and measured using a UV-VIS spectrophotometer which was used to determine resorcinol concentration. The percentage of adsorption resorcinol solution with different adsorption time was calculated by equations (1):

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

Where; C_0 and C_t (mg/L) are the concentrations of resorcinol solution at initial equilibrium and at the time (*t*), respectively.

(2) Effect of adsorbent dose

In a batch adsorption experiments were performed in a set of 125 ml weighed 0.01 g of both adsorbents put 30 ml of resorcinol solution with initial concentrations of 200 mg/L, pH 6.5-7. The flasks were placed in a shaking incubator at room temperature and shaken at 150 rpm for 90 minutes. Then, the suspension was filtered and the final concentration of resorcinol in solution was measured using a UV-VIS spectrophotometer. The same experiment was performed but changed the weight of both AC to 0.02, 0.03, 0.05, 0.10 and 0.15g, respectively. The removal percentage (R%) of resorcinol solution by the adsorbents was calculated by the same following equations (1).

(3) Effect of pH value

Weighed 0.05 g of the AC-CR and AC-TR, put 30 ml of resorcinol solution with initial concentrations of 200 mg/L. An effect of pH was studied in the pH at 2, 4, 6, 7, 10 and 12 to investigate the adsorption efficiency of AC from both produce under 90 minutes. The flasks were placed in a shaking incubator at room temperature and shaken at 150 rpm for 90 minutes and then the suspension was filtered. The final concentration of resorcinol in solution was measured using a UV-VIS spectrophotometer which was used to determine resorcinol concentration. The removal percentage of resorcinol with different pH ranges was calculated by the same equations (1).

(4) Effect of initial concentration

Weighed 0.05 g of both AC in a flask and put 30 ml of resorcinol solution with range concentrations of 75 - 250 mg/L, pH 6.5-7 to investigate the adsorption efficiency of both AC produces under 90 minutes. The flasks were placed in a shaking incubator at room temperature, shaken at 150 rpm for 90 minutes and then the suspension was filtered. The last concentration of resorcinol in solution was measured using a UV-VIS spectrophotometer which was used to determine resorcinol concentration. The values of adsorbed resorcinol with different concentrations were calculated with isotherms.

(5) Effect of temperature and adsorption time

Weighed 0.05g of the adsorbents, put 30 ml of resorcinol solution in the flasks with initial concentrations of 200 mg/L, pH 6.5-7. The flasks were placed in a shaking Incubator at room temperature and 30°C and shaken at 150 rpm for 30, 60, 90 and 150 minutes. After that, the suspension was filtered and the final concentration of resorcinol in solution was measured using a UV-VIS spectrophotometer which was used to determine resorcinol concentration.

2.4) The study of adsorption isotherm

Weighed 0.05 g of the both adsorbents in resorcinol solution at 75, 100, 125, 150, 175, 200, 225 and 250 mg/L, 30 ml. The flasks were placed in a shaking incubator at 30°C and shaken at 150 rpm for 90 minutes. Next, the suspension was filtered and the last concentration of resorcinol in solution was measured using a UV-VIS spectrophotometer at 635 nm which was used to determine resorcinol concentration (Reddy, Sivaramakrishna, & Reddy, 2012).

2.5) The study of the kinetics models

Prepare a batch of mixtures of the AC-CR and AC-TR and resorcinol solution at 75, 100, 125, 150, 175, 200, 225 and 250 mg/L, 30 ml, pH 6.5-7, containing 0.05 g of the AC in flask 125 ml. The flasks were placed in a shaking incubator at 30°C and shaken at 150 rpm for 30-150 minutes. After that, the suspension was filtered and the final concentration of resorcinol in solution was measured using a UV-VIS spectrophotometer which was used to determine resorcinol concentration.

Result and Discussion

The result and discussion showed that:

1) The optimum conditions for preparing the AC-CR and AC-TR and proximate analysis

The optimum temperature and time of carbonization found that the temperature of carbonization at 500°C for 90 minutes. The charcoal from coffee and tea residues (C-CR and C-TR) have the highest iodine number 367.19 mg/g and 301.21 mg/g, respectively. The iodine number decreases when temperature increases cause of the weight of coffee and tea residues to decrease at the begin of the period in the volatile matter has decayed. After that, the weight has less change (Jeungsaman & Assawasaengrat, 2016). The carbonization process is important step in which to heat the biomass until the very small porosity structure. The number of volatile decreases between heating to the charcoal product, which solid with a high carbon content (Omri & Benzina, 2012).

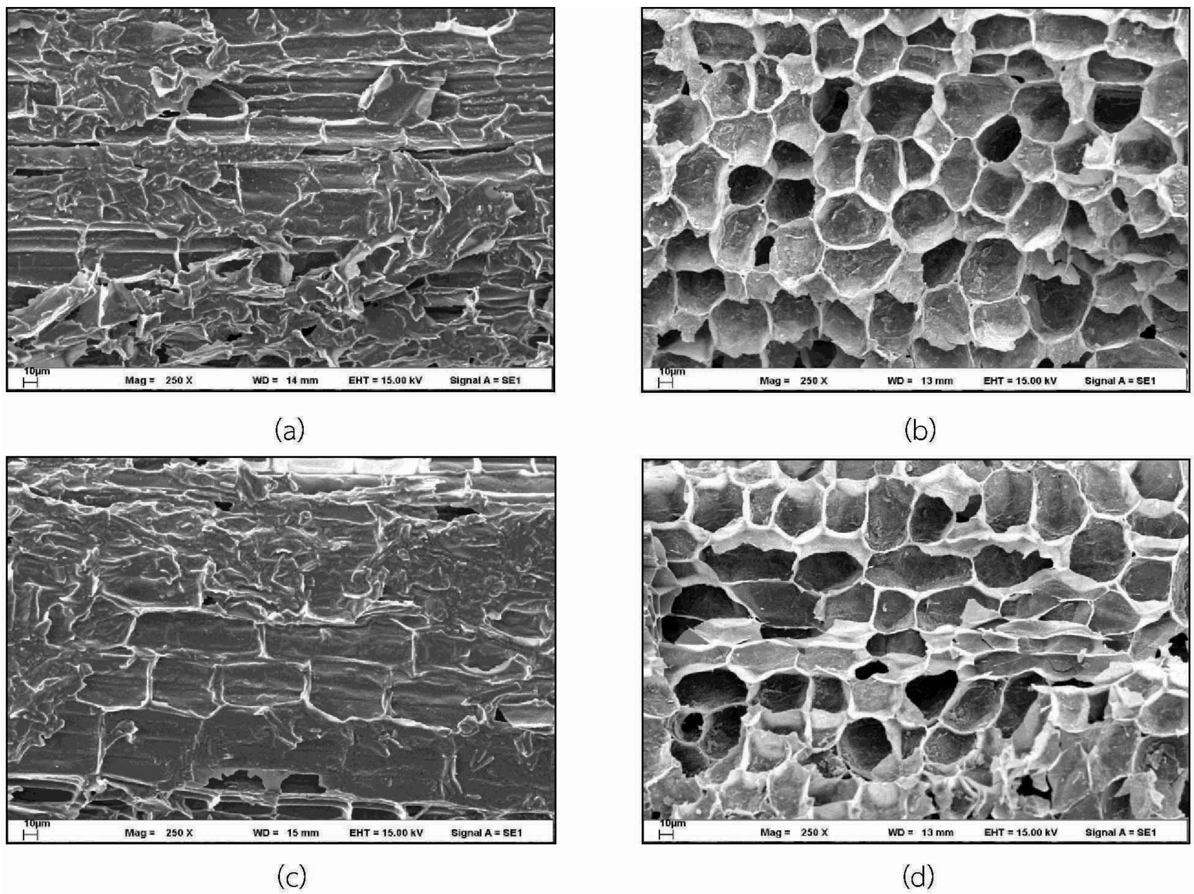


Figure 1 Pore and surface area from SEM (a) C-CR (b) AC-CR (c) C-TR and (d) AC-TR
Source: Microscopic Center (2018)

In addition, the optimum temperature and chemical ratio for thermal and chemical activation shown that iodine number will increase as a result of the porosity structure of the charcoal in a state that chemical activation with H_3PO_4 in the ratios of charcoal: H_3PO_4 as 1: 2 at 700°C. The AC-CR and AC-TR with high iodine number 867.16 mg/g and 770.01 mg/g, the density as 0.47 g/cm^3 and 0.63 g/cm^3, respectively. The both AC are in accordance with the TISI 900-2004 standard on PAC (Thai Industrial Standard Institute, 2004) shown in Table 1. The charcoal obtained from the carbonization process has a very low initial porosity structure and is not good to adsorb. Therefore, the need to increase the porosity structure with activation (Mopoung, Sirikulkajorn, Dummun, & Luethanom, 2012) shown that as Figure 1.

Table 1 Physical properties analysis and chemical composition of the AC-CR and AC-TR

Industrial standard[a]	AC	Iodine number (mg/g)	apparent density (g/cm^3)	Moisture (%)	Component (%w/w)		
					Total Ash	Volatile Matter	Fixed Carbon
Iodine number ≥ 600 (mg/g)	AC-CR	867.16	0.47	2.01	2.65	21.68	89.14
Apparent density 0.2-0.75 (g/cm^3)	AC-TR	770.01	0.63	2.33	3.54	17.67	82.92

Note: [a]TISI 900-2004 standard on PAC (TISI, 2004)

The proximate analysis found that the AC-CR had content of moisture 2.01%, total ash 2.65%, volatile matter 21.68% and fixed carbon 89.14% while the AC-TR had content of moisture 2.33%, ash 3.54%, volatile matter 17.67% and stable carbon 82.92% shown in Table 1. The properties of AC an important factor of adsorbent and indicate the quality of AC for application for various purposes (Li, Sun, Li, & Keener, 2012).

2) Study the optimal resorcinol solution adsorption conditions

(1) Adsorption time

The study for the effect of adsorption time of resorcinol solution by using 0.05 g of AC-CR and AC-TR in 200 mg/L of resorcinol solution, 30 ml and constant adsorption at room temperature. In the study of adsorption efficiency for 5 minutes to 10 days found that the efficiency of AC-CR and AC-TR in adsorption of resorcinol solution since 5 minutes and high adsorption efficiency at 90 minutes as 98.35% and 98.15%, respectively. The results showed as Figure 2(a). This rapid adsorption of resorcinol solution in the first phase because the surface area of the adsorbent is large and when saturated adsorption area the adsorption capacity will increase slowly and steadily (Mopoung, 2015).

(2) Amount of adsorbent

The effect of weight AC-CR and AC-TR for adsorption efficiency of resorcinol solution found that 0.05 g of the both adsorbents had the highest removal percentages as98.89±0.13 and 97.12±0.04, respectively. The results were consistent with Thanomsith, Mahachai, and Chanthai (2009) found that the removal of the resorcinol solution by using rice husk ash showed removal percentage as high as 98.86 as well. When the amount of AC-CR and AC-TR increased from 0.01-0.15 g in 200 mg/L of resorcinol solution, 30 ml, at the same time of 90 minutes and constant adsorption rate at room temperature. So, the adsorbents increases, the surface area of the adsorbent area also increases. However, as the content of AC increased but the adsorption efficiency was relatively stable (Prachpreecha, Prachpreecha, & Vongchavalitkul, 2018). The results showed that Figure 2 (b). In this study, AC-CR and AC-TR were selected to 0.05 g in the next experiment.

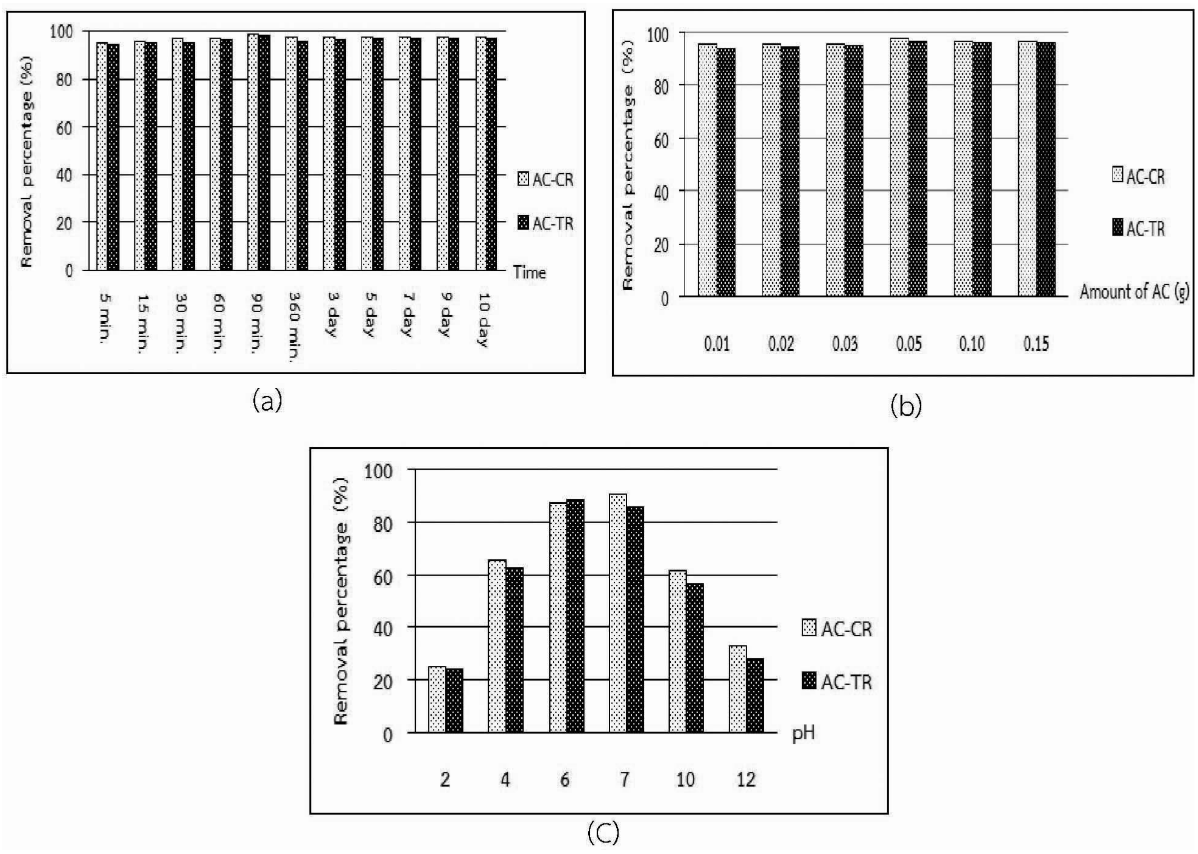


Figure 2 Resorcinol solution removal efficiency versus (a) adsorption time for the AC (b) amount of adsorbent for the AC and (c) pH values

(3) pH value

The effect of pH was studied in the pH range of 2-12 to investigate the adsorption efficiency of AC from both produces under 90 minutes and 0.05 g adsorbent dose. The concentrations of solution containing resorcinol used were 200 mg/L, 30 ml. The rate of constant adsorption at room temperature found that removal percentage of AC-CR highest at pH 7 as 90.76±0.08 and AC-TR was highest at pH 6 as 88.73±0.03 shown in Figure 2 (c). The results were consistent with the research report indicating that the using too low or high pH will cause the function groups on the surface of the AC to change and resulting in reduced absorption (Ritthichai, & Muncharoen, 2014).

(4) Initial concentration

The studied in concentrations of the solution containing resorcinol used were the range of 75-250 mg/L, 30 ml and 0.05 g adsorbent dose of AC-CR and AC-TR. The rate of constant adsorption at room temperature showed that the AC-CR and AC-TR had increased adsorption capacity when the concentration of resorcinol increases (Mopong, & Nogklai, 2008; Hesas, Arimi-Niya, Wan Daud, & Sahu, 2013). The results were Figure 3.

(5) Temperature and adsorption time

The effects of temperature and time on adsorption were studied in the concentrations of 200 mg/L, 30 ml and 0.05 g dose both of AC. The rate of constant adsorption at room temperature and 30°C, the time adsorption efficiency for 30-150 minutes. The results found that at room temperature, AC-CR and AC-TR be able to adsorb the resorcinol solution good well at 90 minutes with removal percentage as 89.86±0.01 and 84.56±0.07 shown in Figure

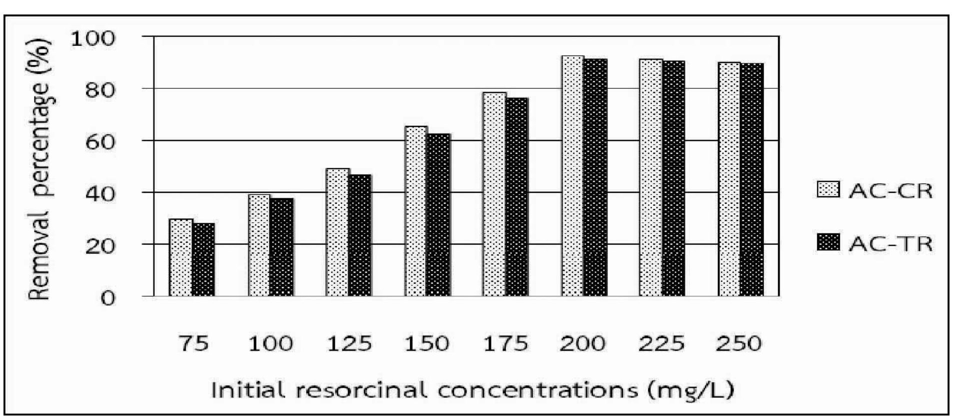
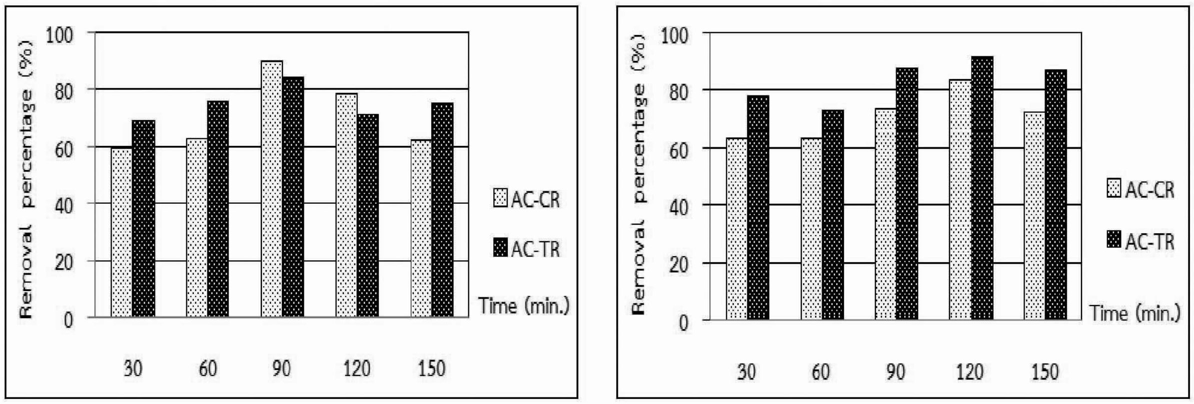


Figure 3 The concentrations of solution containing resorcinol



(a) (b)

Figure 4 The adsorption efficiency of AC-CR and AC-TR (a) at room temperature and (b) at 30°C

4 (a). In addition, at 30°C the both AC can be removal the resorcinol solution good same as at 120 minutes, present removal percentage as 83.87±0.01 and 89.65±0.09, respectively. The result shown that Figure 4 (b).

3) Adsorption isotherms

(1) Langmuir model

Langmuir isotherm equation assumes that the adsorbent molecules will adsorb on the surface in the exact position of the adsorbent. Each molecule of the adsorbent is adsorbed on a monolayer. Which surface of the adsorbent has the homogeneous sites. Linear Langmuir isotherm model can be expressed as equation (2): (Budinova, et al., 2006).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} = \frac{C_e}{q_m} \quad (2)$$

Where q_e (mg/g) are equilibrium adsorption of the resorcinol solution by AC-CR and AC-TR, C_e (mg/L) are the equilibrium concentrations of the resorcinol solution, q_m (mg/g) are the maximum adsorption capacity and K_L (L/mg) are the Langmuir adsorption constant (Lugo-Lugo, Hernandez-Lopez, Barrear-Diaz, Urena Nunez, & Bilyeu, 2009).

The determination of equilibrium adsorption of the resorcinol solution by both adsorbents 0.05 g in the concentrations of resorcinol solution at 75, 100, 125, 150, 175, 200, 225 and 250 mg /L. Then, calculated the equilibrium adsorption of the resorcinol solution (q_e) (mg/g) (Reddy et al., 2012) as equation (3):

$$q_e = \frac{(C_0-C_e)\,V}{W} \quad (3)$$

Where C_o and C_e (mg/L) are the initial and equilibrium concentrations of the resorcinol solution, respectively. The Langmuir plot of C_e/q_e and C_e at 75, 100, 125, 150, 175, 200, 225 and 250 mg/L that shown in Figure 5.

The results calculated from the plot are given in Table 2. The Langmuir adsorption capacity varies 0.0309 mg/g for AC-CR and 0.0332 mg/g for AC-TR over the range of initial resorcinol concentration studied. The Langmuir isotherm showed that the experimental data as (R^2 = 0.9054 and 0.9433).

(2) Freundlich model

The Freundlich isotherm equation assumes that the adsorption that the surface of the sorbent is heterogeneous. The adsorption on the surface of the adsorbent is a multilayer. This isotherm can be described as follows equation (4):

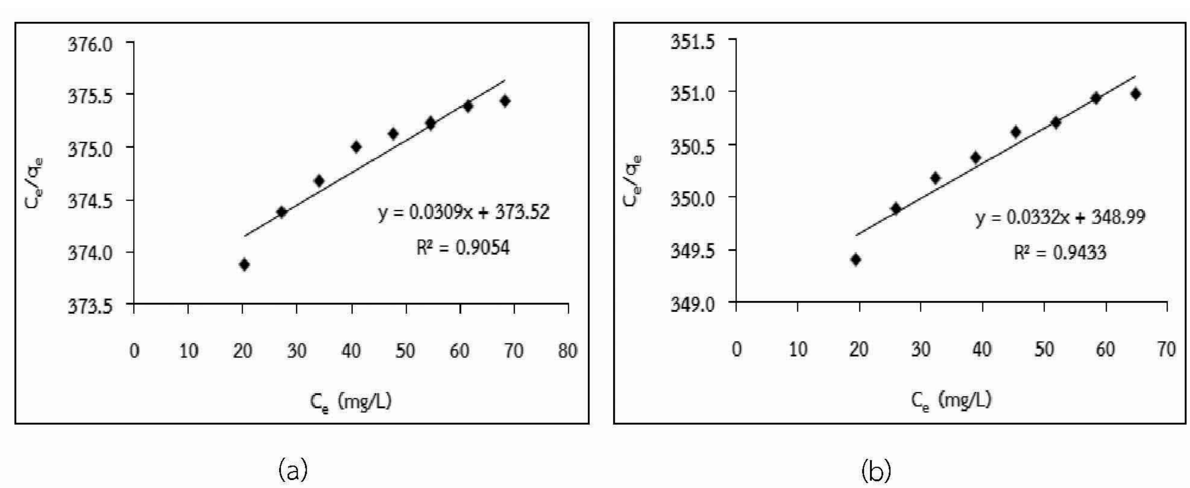


Figure 5 Langmuir isotherm of resorcinol solution by AC (a) AC-CR and (b) AC-TR

Table 2 Parameters obtained for the Langmuir and Freundlich equation

AC	Langmuir equation			Freundlich equation		
	q_m (mg/g)	K_L (L/mg)	R^2	$log\ K_F$ (L/mg)	$1/n$	R^2
AC-CR	0.0309	373.52	0.9054	2.5683	0.9966	1.0000
AC-TR	0.0332	348.99	0.9433	2.5386	0.9963	1.0000

$$\ln q_e = \log k_f + \frac{1}{n}\log C_e \qquad (4)$$

Where k_f (mg/g) $(L/g)^{1/n}$ and n are the physical constants of the Freundlich adsorption isotherm. The k_f and n are indicators of the adsorption capacity and adsorption intensity, respectively (Ajmal, Rao, Ahmad, & Ahmad, 2000).

The Freundlich constants were obtained from a plot of log q_e and log C_e at 75, 100, 125, 150, 175, 200, 225 and 250 mg/L which shown in Figure 6. The results calculated from the plot are given in Table 2. The Freundlich constant (K_f) 2.5683 (L/mg) for AC-CR and 2.5386 (L/mg) for AC-TR. On increasing the initial resorcinol concentration from 75 to 250 (mg/L), the adsorption capacity increases (R^2=1.0000) also.

The value of describes the adsorption isotherms found that less than 1.0000, show that the amount of surface on adsorbent is limited to adsorb and the adsorption will be the Langmuir or Freudian model depend on the correlation coefficient of q_e and C_e (Avelar, Bianchi, Gonçalves, & Mota, 2010).

Adsorption of resorcinol solution on the surface of AC-CR and AC-TR depends on porosity structures and chemical properties. In this study found that adsorption of resorcinol solution have conformable with Freundlich rather than Langmuir models. The experiment shows that adsorption of resorcinol solution is physical adsorption; the surface of AC is not homogeneous. Therefore, the adsorption on multilayer surface of AC (Avelar et al., 2010).

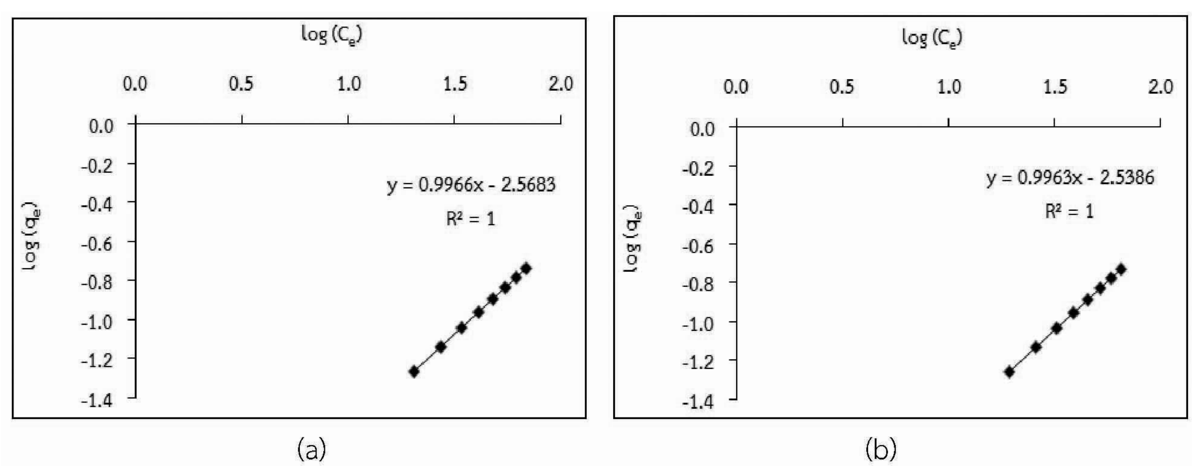


Figure 6 Freundlich isotherm of resorcinol solution by AC (a) AC-CR and (b) AC-TR

4) The kinetics adsorption

The kinetics adsorption help to know the adsorption mechanism, the transfer mass of material between the adsorbed substance and adsorbent material. Therefore, the model for describe the adsorption mechanism are pseudo-first order and pseudo-second order. Both models are based on the assumption that the adsorption is pseudo chemical reaction and adsorption rate depends on the position of reaction of the adsorbent material.

(1) Pseudo first order kinetic model

The pseudo first order rate expression is generally expressed as equation (5):

$$log\,(q_{e,\,exp} - q_t) = log\, q_{e,\,m} - \frac{k_1 t}{2.303} \quad (5)$$

Where q_e (mg/g) is equilibrium adsorption of the resorcinol solution, q_t (mg/g) is adsorption of the resorcinol solution at any time, k_1 (minute) is rate constant of pseudo first order, t (minute) is adsorption time. The slopes of the plots of log (q_e - q_t) versus t, as shown in Figure 7 (a) and 8 (a). The correlation coefficients for pseudo-first order model changed in the range of 0.5585-0.9218 and 0.6998-0.8835 for AC-CR and AC-TR, respectively. Besides, the experimental q_e values, $q_{e,exp}$ did not agree with the calculated values, $q_{e,cal}$ obtained from the linear plots. It suggested that the kinetics of AC from both produces adsorption of resorcinol did not follow the pseudo-first order kinetic model and hence did was not a diffusion-controlled phenomena. The experiment and calculated are summarized in Table 3 and 4.

(2) Pseudo second order kinetic model

The pseudo second order rate expression is generally expressed as equation (6):

$$\frac{dq_t}{dt} = k_2 (q_{e,exp} - q_t)^2 \quad (6)$$

Linear equation of pseudo-second order as follows equation (7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where q_e (mg/g) is equilibrium adsorption of the resorcinol solution, q_t (mg/g) is adsorption of the resorcinol solution at any time, k_2 (minute) is rate constant of pseudo second order, t (minute) is adsorption time. The slopes of the plots of versus t, as shown in Figure 7(b) and 8 (b).

The results of the initial concentrations of resorcinol solution obtained with the pseudo-first order and pseudo-second order found that the results are consistent with pseudo-second order as Table

Table 3 Kinetic parameters for the adsorption of resorcinol solution by AC-CR at various initial concentrations

Initial concentration (mg/L)	q_e(exp) (mg/g)	Pseudo-first-order			Pseudo-second-order		
		q_e(cal) (mg/g)	k_1	R^2	q_e(cal) (mg/g)	k_2	R^2
75	0.055	0.031	0.0020	0.5585	0.031	23.898	0.8515
100	0.073	0.070	0.0030	0.7500	0.070	14.406	0.9999
125	0.091	0.064	0.0062	0.8983	0.064	8.6111	0.8691
150	0.109	0.109	0.0047	0.9218	0.085	10.339	0.9915
175	0.127	0.075	0.0029	0.7500	0.075	8.5444	0.8367
200	0.145	0.080	0.0014	0.7500	0.080	9.6618	0.9517
225	0.164	0.086	0.0006	0.7500	0.086	10.339	0.9915
250	0.182	0.093	0.0002	0.7500	0.093	10.188	0.9984

Table 4 Kinetic parameters for the adsorption of Resorcinol solution by AC-TR at various initial concentrations

Initial concentration (mg/L)	q_e(exp) (mg/g)	Pseudo-first-order			Pseudo-second-order		
		q_e(cal) (mg/g)	k_1	R^2	q_e(cal) (mg/g)	k_2	R^2
75	0.056	0.029	0.0002	0.7500	0.029	38.874	0.9998
100	0.074	0.068	0.0047	0.6998	0.068	13.582	0.9994
125	0.093	0.047	0.0003	0.7953	0.048	19.779	0.9994
150	0.111	0.086	0.0005	0.8835	0.087	11.203	0.9998
175	0.130	0.076	0.0021	0.7500	0.077	9.4145	0.9167
200	0.148	0.082	0.0014	0.7500	0.082	9.4882	0.9544
225	0.167	0.087	0.0006	0.7500	0.087	10.234	0.9917
250	0.185	0.094	0.0003	0.7500	0.094	9.9379	0.9977

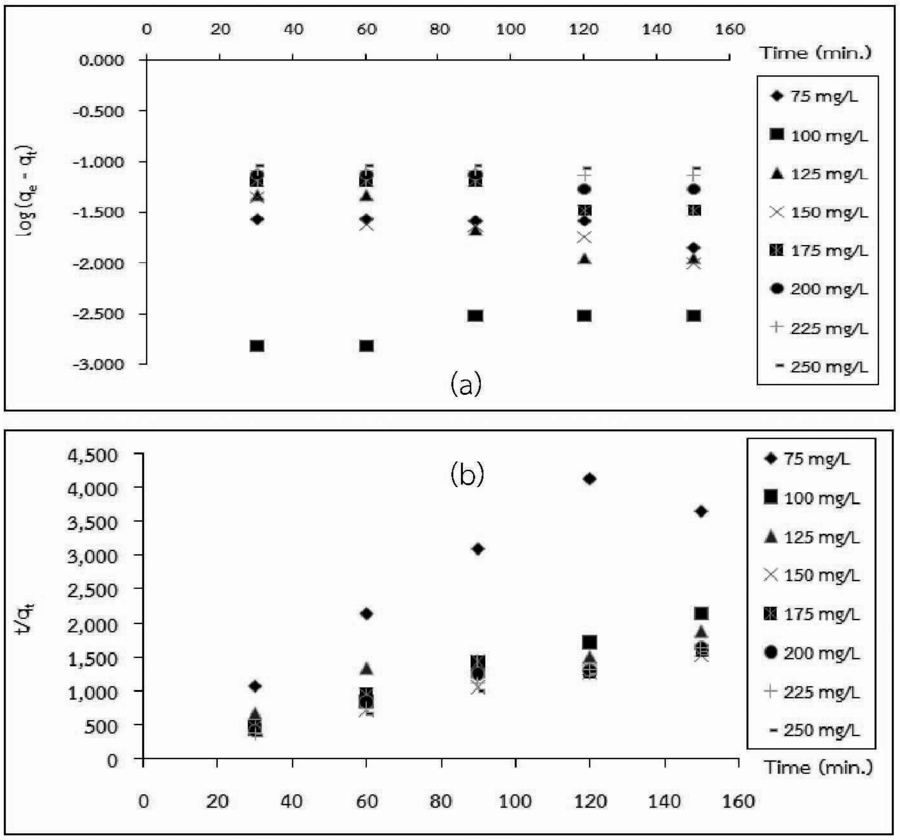


Figure 7 The kinetics plots for the adsorption of AC-CR onto resorcinol solution at different initial concentrations (a) Pseudo-first-order and (b) Pseudo-second-order

3 and 4, the corresponding R^2 values for the pseudo-second order kinetic model were greater than 0.8367 for AC-CR and 0.9167 for AC-TR. The both adsorbents have been used to electron together between both AC with resorcinol solution. Therefore, indicating the applicability of the pseudo-second order kinetic model to describe the adsorption process of both adsorbents. From the above discussion, pseudo-second order adsorption mechanism is predominant, meaning that chemical sorption takes part in the adsorption process. Once the sorptive sites are exhausted, the uptake rate is controlled by the rate of intra particle diffusion (Chaturvedi, Seth, & Misra, 2006).

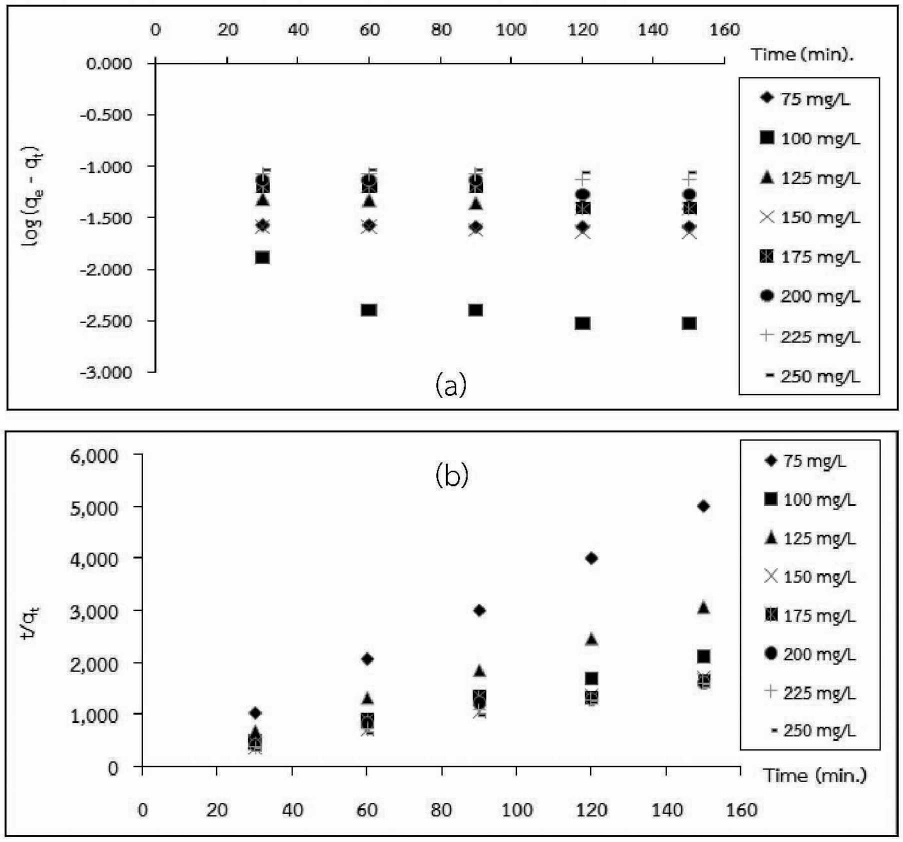


Figure 8 The kinetics plots for the adsorption of AC-TR onto resorcinol solution at different initial concentrations (a) Pseudo-first-order and (b) Pseudo-second-order

Conclusion

In conclusion, the characterizations and adsorption behaviors of resorcinol solution onto both AC can be concluded include: First, the optimum conditions for prepared AC-CR and AC-TR temperature at 500°C for 90 minutes were suitable condition for carbonization to charcoal and the heat and chemical activation with 1: 2 ratios of charcoal: H_3P0_4 at 700°C had Iodine number not less than 600 mg/g and the density 0.2 to 0.75 g/cm^3, which has characteristics in the standard compared with TISI 900-2004 standard on PAC. The optimal conditions for adsorption of resorcinol solution with both AC were adsorption time at 90 minutes, adsorbent dose 0.05 g, pH 6-7 and initial concentration of 200mg/L resorcinol solution. After that, the study of adsorption isotherm models showed that the Freundlich model is more appropriate to explain the nature of adsorption with the same as (R^2= 1.0000). for both absorbents while the Langmuir model shows poorly fit as (R^2 = 0.9054 for AC-CR and R^2 = 0.9433 for AC-TR). Finally, the kinetic models found that the corresponding coefficient R-square (R^2) for the pseudo-second-order kinetic model was greater than 0.8376 for AC-CR and 0.9167 for AC-TR, indicating the applicability of the pseudo-second-order kinetic model to describe the adsorption process of both.

Therefore, the coffee and tea residues have sufficient properties to produces AC and a new alternative considered a product of biomass materials. It also reduces the amount of coffee and tea residue that is waste in the community. From the results of the efficiency for the adsorption of resorcinol solution, it can be further applied in the removal of toxic substances from wastewater.

Suggestions and Recommendations

According to the study, the useful suggestions for further development and improvement were demonstrated as follows:

1) Recommendation for this study

From the results of the study, AC was prepared from coffee and tea residues worthless junks and it was found that there were good properties in some condition. In this study should be done to study AC what are prepared from other agricultural wastes by carbonization. In addition, should study the reuse of AC adsorbed for determining of the ability of after adsorption of resorcinol solution for the first time and analysis of cost-effectiveness in producing of both adsorbents.

2) Recommendation for further study

There should be a study the adsorption in wastewater from the salon in the process of dying and curling in real condition because it is contaminated of other substances such as the para-phenylenediamine which may cause polluted water and cancer as well.

Acknowledgements

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References

Ajmal, M., Rao, R. A., Ahmad, R., & Ahmad, J. (2000). Adsorption studies on Citrus Recticulate (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater. *Journal of Hazardous Materials*, *79*(1-2), 117-131.

American Society for Testing and Materials. (2006). *Standard test method for determination of iodine number of activated carbon D4607-94.* United States: American Society for Testing and Materials.

American Society for Testing and Materials. (2012). *Standard test method for ash in the analysis sample of coal and coke from coal.* United States: American Society for Testing and Materials.

Avelar, F. F., Bianchi, M. L., Gonçalves, M., & Mota, E. G. (2010). The use of piassava fibers (*Attalea funifera*) in the preparation of activated carbon. *Bioresource Technology*, *101*(12), 4639-4645.

Boudrahem, F., Soualah, A., & Aissani-Benissad, F. (2011). Pb(II) and Cd(II) removal from aqueous solutions using activated carbon developed from coffee residue activated with phosphoric acid and zinc chloride. *Journal of Chemical & Engineering Data, 56*(5), 1946-1955.

Budinova, T., Ekinci, E., Yardim, F., Grima, A., Bjornobom, E., Minkova, V., & Goranova, M. (2006). Characterization and application of activated carbon produced by H_3PO_4 and water vapor activation. *Fuel Processing Technology*, *87*, 899-905.

Chaturvedi, P. K., Seth, C. S., & Misra, V. (2006). Sorption kinetics and leach ability of heavy metal from the contaminated soil amended with immobilizing agent (humus soil and hydroxyapatite). *Chemosphere, 64*(7), 1109-1114.

Export-Import Bank of Thailand. (2015). Major change trends in the world coffee market. Retrieved January 5, 2019, from http//www.exim.go. th/doc/newsCenter/45822.pdf

Hesas, R. H., Arimi-Niya, A., Wan Daud, W. M. A., & Sahu, J. N. (2013). Preparation and characterization of activated carbon from apple waste by microwave-assisted phosphoric acid activation: Application in methylene blue adsorption. *Bio Resource, 8*(2), 2950-2966.

Jeungsaman, T., & Assawasaengrat, P. (2016). Synthesis activated carbon from coffee residue by using microwave radiation. *Ladkrabang Engineering Journal, 33*(1), 36-41.

Li, L., Sun, Z., Li, H., & Keener, T. C. (2012). Effect of activated carbon surface properties on the adsorption of volatile organic compounds. *Journal of the Air & Waste Management Association, 62*(10), 1196-1202.

Lugo-Lugo, V., Hernandez-Lopez, S., Barrear-Diaz, C., Urena Nunez, F., & Bilyeu, B. (2009). A comparative study of natural, formaldehyde-treated and copolymer-grafted orange peel for Pb(II) adsorption under batch and continuous mode. *Journal of Hazardous Materials, 161*(2-3), 1255-1264.

Microscopic Center. (2018). *Scanning electron microscope (SEM)*. Faculty of Science; Burapha University.

Moopoung, S. (2015). *Activated Carbon* (1st ed.). Phitsanulok: Naresuan University Publishing House.

Mopoung, S., & Nogklai, W. (2008). Chemical and surface properties of longan seed activated charcoal. *International Journal of Physical Sciences, 3*(10), 234-239.

Mopoung, S., Sirikulkajorn, A., Dummun, D., & Luethanom, P. (2012). Nanocarbonfibril in rice flour charcoal. *International Journal of Physical Sciences, 7*(2), 214-221.

Olorundare, O. F., Krause, R. W. M., Okonkwo, J. O., & Mamba, B. B. (2012). Potential application of activated carbon from maize tassel for the removal of heavy metals in waste. *Physics and Chemistry of the Earth, 50-52*, 104-110.

Omri, A., & Benzina, M. (2012). Removal of manganese(II) ions from aqueous solutions by adsorption on activated carbon derived a new precursor: Ziziphus spina-christi seed. *Alexandria Engineering Journal, 51*(4), 343-350.

Phothitontimongkol, T. (2017). Activated carbon from agricultural residues by chemical activation for the application of pollutant removal in water. *Journal of Research Unit on Science, Technology and Environment for Learning, 8*(1), 196-214.

Prachpreecah, O., & Prachpreecha, T. (2017). A study on kinetic adsorption of methyl orange dye by activated carbon prepared from banana waste. *Journal of Industrial Technology, Ubon Ratchathani Rajabhat University, 7*(1), 179-196.

Prachpreecha, O., Prachpreecha, T., & Vongchavalitkul, S. (2018). Study on characteristic of activated carbon prepared from tea residue and utilization of wastewater treatment. *Phranakhon Rajabhat Research Journal (Science and Technology), 13*(2), 146-166.

Reddy, M. C. S., Sivaramakrishna, L., & Reddy, A. V. (2012). The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium. *Journal of Hazardous Materials, 203- 204*(2012), 118-127.

Ritthichai, A., & Muncharoen, S. (2014). Dye removal of textile wastewaters using crab shell activated carbon. *Burapha Science Journal, 19*(1), 131-140.

Tangmankongworakoon, N., & Preedasuriyachai P. (2013). A study on how to utilize coffee residue and tea residue for the production of briquettes. *Journal of Srinakharinwirot University (Science and Technologies), 7*(13), 15-26.

Thai Industrial Standard Institute (TISI). (2004). *Thai Industrial Standard: Activated Carbon (900-2547)*. Bankok: Thai Industrial Standard Institute.

Thanomsith, K., Mahachai, R., & Chanthai, S. (2009). Removal of resorcinol and para-phenylenediamine in hair coloring wastewater using rice husk ashs. *Sakon Nakhon Rajabhat University Journal, 1*(2), 129-142.

Wu, Q. F., & Zhang, F. S. (2012). A clean process for activator recovery during activated carbon production from waste biomass. *Fuel (Guildford), 94*, 426-432.

Yang, R., Liu, G., Xu, X., Li, M., Zhang, J., & Hao, X. (2011). Surface texture, chemistry and adsorption properties of acid blue 9 of hemp (Cannabis sativa L.) bast-based activated carbon fibers prepared by phosphoric acid activation. *Biomass & Bioenergy, 35*(1), 437-445.