

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon**Bakhtiar K. Hamad****Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon****Bakhtiar K. Hamad**

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bkh119@gmail.com**Received: 2 January 2018****Accepted: 17 April 2018****Abstract**

Apricot Shell Activated Carbon (ASAC) was examined for removal of residual chlorine in aqueous solution through the adsorption process. The effects of solution pH, agitation time, and initial concentrations were estimated. The results showed that the adsorption increased as the contact time increased and the initial concentration decreased, while the high adsorption was at pH=2. Langmuir, Freundlich and Temkin isotherm models were used for studying the adsorption equilibrium data. Adsorption data were fitted better with Freundlich isotherm, with a maximum monolayer adsorption capacity (q_{max}) of 285.71 mg/g for Langmuir isotherm. The pseudo-first-order and pseudo-second-order equations were used for explaining the adsorption kinetics. The results were found to follow the pseudo-second-order model with correlation coefficients (R^2) equal to 0.999. ASAC was shown to be a good adsorbent for removing residual chlorine from aqueous solutions at 25°C.

Keywords: Apricot shell activated carbon, potassium hydroxide, residual chlorine, isotherm adsorption, kinetic adsorption

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

إزالة الكلور المتبقي في الماء عن طريق الامتزاز باستخدام الكربون المنشط المحضر من قشرة نوى

المشمش

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الخلاصة

تم فحص الكربون المنشط المحضر من قشرة نوى المشمش لإزالة الكلور المتبقي في محلول مائي من خلال عملية الامتزاز. تم تقدير تأثيرات درجة الحموضة المحلول، وقت التحريض، والتركيزات الأولية. وأظهرت النتائج أن الامتزاز ازداد مع زيادة وقت الاتصال وانخفض مع زياده التركيز الاولى للمحلول، في حين كان الامتزاز العالي عند الرقم الهيدروجيني = 2. استخدمت نماذج لانكماير و فريوندليتش و تمكين إيزوثرم لدراسة بيانات توازن الامتزاز. تم تركيب بيانات الامتزاز بشكل أفضل مع إيزوثرم فريوندليتش و أقصى أحادية الطبقة الامتزاز بسعة (q_{max}) تصل 285.71 ملغم / غم لإيزوثرم لانكماير. تم استخدام المعادلات الكاذبة من الدرجة الأولى و الكاذبة من الدرجة الثانية لشرح حركية الامتزاز. من النتائج الحاصلة تتبع النموذج الثاني شبه الكاذبة مع معاملات الارتباط (R^2) تساوي 0.999. وأظهرت الممتزة قدرة عالية لإزالة الكلور المتبقي من المحاليل المائية في 25 درجة مئوية.

كلمات مفتاحية: الكربون المنشط المحضر من قشرة نوى المشمش، هيدروكسيد البوتاسيوم، الكلور المتبقي، إيزوثرم الامتزاز، حركية الامتزاز.

Introduction

Chlorine has a wide use because of its capability to kill organisms and microorganisms at moderately low concentrations. The chlorine destroys the cell walls of microorganisms in that way preventing waterborne diseases. There are various health anxieties concerning residual chlorine in water. This is because chlorine has a tendency to inactivate enzymes and not naturally needed by the body as a halogen [1].

The chlorine compounds such as chlorine dioxide, sodium hypochlorite, and calcium hypochlorite are used for disinfection in wastewater treatment facilities [2]. Chlorine tends to

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

penetrate cells and act on cellular substances which is a powerful oxidizing agent killing different microorganisms. Free residual chlorine concentration in clean water should be between 1.5 and 2.0 mg L⁻¹ [3].

Activated carbons prepared from different agricultural by-products are good and superior for removing chlorine residual which is generating unpleasant odour and taste in tap water. Adsorption rate and capacity are significant and must be considered in an activated carbon for wastewater treatment [4]. The high surface area and pore volume of the activated carbon determine the performance and characteristics of activated carbon [5]. In Iraq, a huge amount of apricot shell will throw and causing pollution to Environment annually. The aim of this study is to prepare activated carbon from Apricot shell and investigate adsorption isotherms and kinetics for adsorbing of chlorine from water using apricot shell activated carbon.

Materials and Methods

Stock solutions were prepared by dissolving 1 g each of sodium hypochlorite (SHC) in 1 L of distilled water. A set of solutions were prepared by diluting the stock solution to the desired concentrations. The range of concentrations of SHC prepared from their respective stock solutions varied between 25 and 100 mg/L.

Characterization of Activated Carbon

For preparation of activated carbon from precursors, apricot shells were collected from local markets in Erbil, Iraq. The apricot shells were washed with distilled water and dried overnight in an oven at 100°C. The raw material was cut into small pieces between 1.5 – 2.0 mm. forty grams of raw material was impregnated in 5 % chemical agent (KOH) at 1: 3 ratio (w/v) and heated in a water bath at 75 - 80°C for 24h. After washing the raw material with distilled water, and then dried in an oven. The sample was then placed in the furnace and the process of carbonization was conducted under nitrogen gas at a flow rate of 150 cm³/ min under a heating rate to 500°C for 2 h. The yield was washed with distilled water and then dried in an oven at 100°C.

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

Adsorption Studies

The apricot shell activated carbon (ASAC) was studied for removing residual chlorine from aqueous solutions under different experimental conditions. About 1 g of the activated carbon was added into 250 mL conical flasks containing 100 mL of different concentrations of residual chlorine. Each sample was shaken with magnetic stirring bar at 25°C for 15 h.

The mixtures were then separated by filtration. The total chlorine content in the solution was determined using UV-Vis spectrophotometer at a wavelength of 292 nm. The amount of adsorption at equilibrium, q_e (mg/g) was calculated through the follow equation [6]:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_0 and C_e (mg/g) are the initial and equilibrium concentrations of residual chlorine, respectively, V (L) is the volume of the solution, and W (g) is the mass of dry adsorbent used. Kinetic studies were carried out using initial concentrations of residual chlorine between 25 and 100 mg/L at 25°C. The amount of adsorption at time t , q_t (mg/g), was calculated using the following equation [7]:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

Where C_t is the adsorbate concentration at any time t (mg/L).

The percentage removal of chlorine was calculated using the following equation [8]:

$$\text{Removal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

Effect of pH on Adsorption

The pH of the initial volume of the solution was adjusted by adding a few drops of dilute 0.1 N HCl or 0.1 N NaOH, and the adsorbent dose was 1 g. The adsorption of chlorine onto activated carbon was studied over a pH range of 2.0-12.0 at 25°C by changing the initial pH of 50 mg/L of chlorine fixed for 5 h.

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

Results and Discussion

1. SEM and Iodine Test

To describe the morphology of the adsorbent surface scanning electron microscopy was used. Figure 1 shows the surfaces of the apricot shell activated carbon activated by KOH solution. Several developed pores can be seen in Figure 1, the expansion of pores is due to the effect of the KOH. The expansion of pore sizes is important for increasing the surface area of the activated carbon [9].

For assessing the surface area of activated carbon, the adsorption of iodine solution was utilized. This test was used according to American Society for Testing and Materials Standard [10]. Iodine test shows the iodine number of ASAC equal to 983 mg/g.

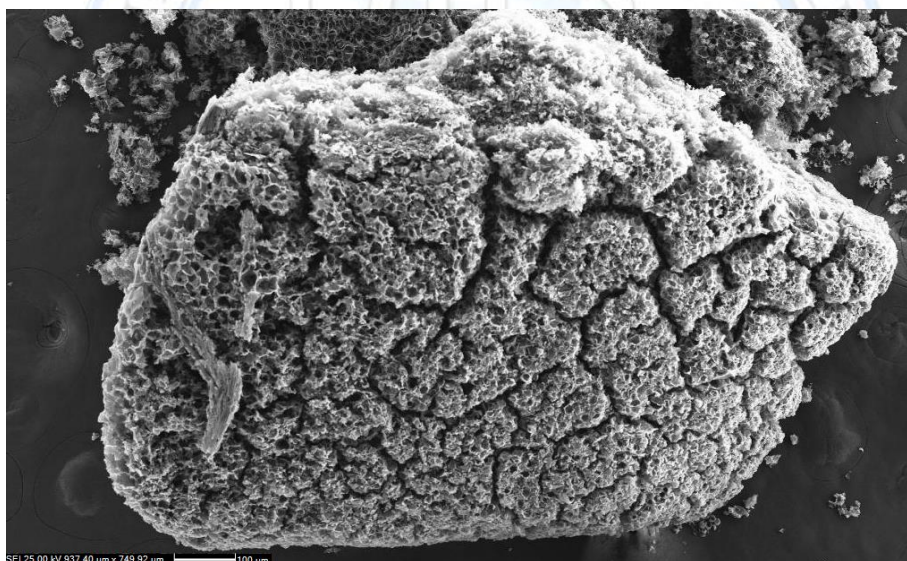


Figure1: SEM micrographs of the Apricot shell activated carbon after carbonization at 500°C

2. Effect of pH

Figure 2 shows the effects of pH on the removal of residual chlorine using ASAC as an adsorbent. The ratio of hypochlorous acid over hypochlorite ion will be affected by pH of the aqueous medium. Thus, the ratio of hypochlorous acid per hypochlorite ion in water will decrease with increasing of pH of solution [11]. The removal of residual chlorine in aqueous

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

solutions decreases with the increasing pH because the pH initially effects the degree of ionization of the sodium hypochlorite ion. Hypochlorous acid are proton donors which, at definite pH, become anions [12]. When the pH is greater than the pK_a of hypochlorite, the negative charge of the hypochlorite ion increases and the adsorption decreases due to the repulsive force between the negative group on the activated carbon surface and the hypochlorite ion [13].

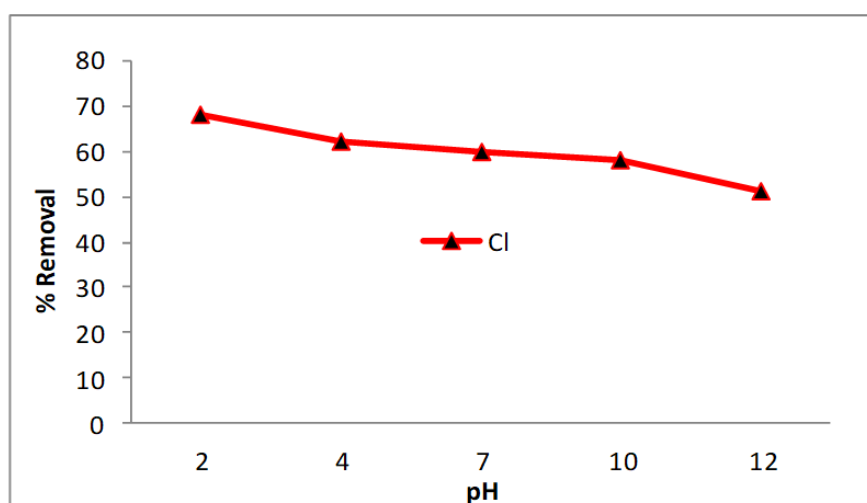


Figure 2: Effect of the different pH on the removal of residual chlorine onto ASAC

3. Effects of Contact Time and Initial Concentration on Chlorine Adsorption

Figure 3 shows the impregnation curves increase gradually in the initial stages, due to many readily available sites. Finally, the curves reach an equilibrium state, demonstrating that a large number of pore surface sites are initially saturated by residual chlorine adsorption [12]. This may be attributed to the decreasing of the available number of pore surface sites with increasing contact times for adsorption. Furthermore, a presence repulsive force between the chlorine ions on the solid and the bulk phase decreased adsorption of chlorine on the apricot shell activated carbon surface [14]. Table 2 demonstrates that increasing the initial concentrations of chlorine from 25 to 100 mg/L results in increasing the equilibrium adsorption capacity (q_e) from 22.99 to 89.34 mg/g and the contact time necessary for residual chlorine solutions with initial concentrations to attain equilibrium was 5 h.

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

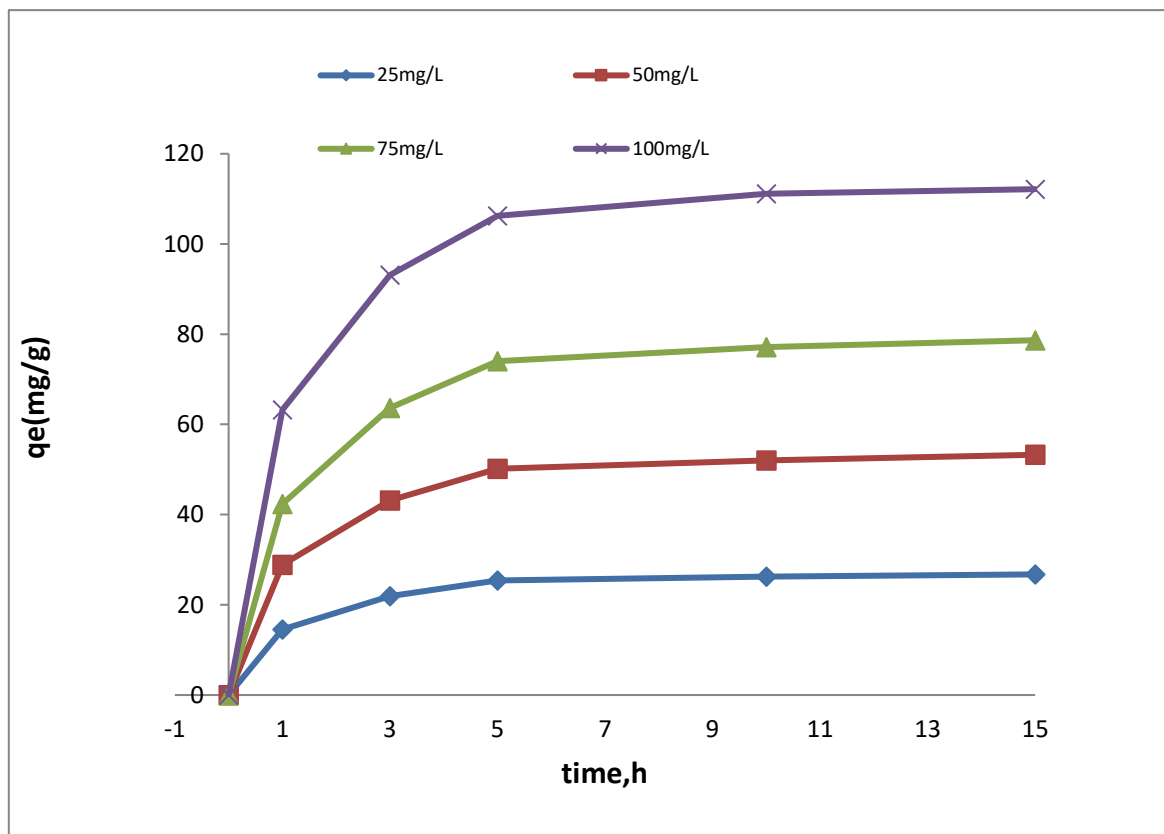


Figure 3: Effect of contact time on the adsorption of residual chlorine onto ASAC for different concentration at 25°C.

4. Effect of Solution Temperature on Chlorine Adsorption

Figure 4. demonstrates the effect of temperature on the residual chlorine adsorption capacity that was studied onto ASAC at different isotherm temperatures of 25, 30, 35°C using 25 mg/L initial chlorine concentration. The equilibrium uptake of chlorine by ASAC was affected by temperature. Generally, it was shown that the removal of residual chlorine onto ASAC decreased slightly with increased temperatures. The decrease in adsorption with the increase of temperature possibly is expected due to the weakening of adsorptive forces between the active sites on the surface of activated carbon and adsorbate molecules and as well as between the close molecules of the adsorbed phase [15, 16].

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

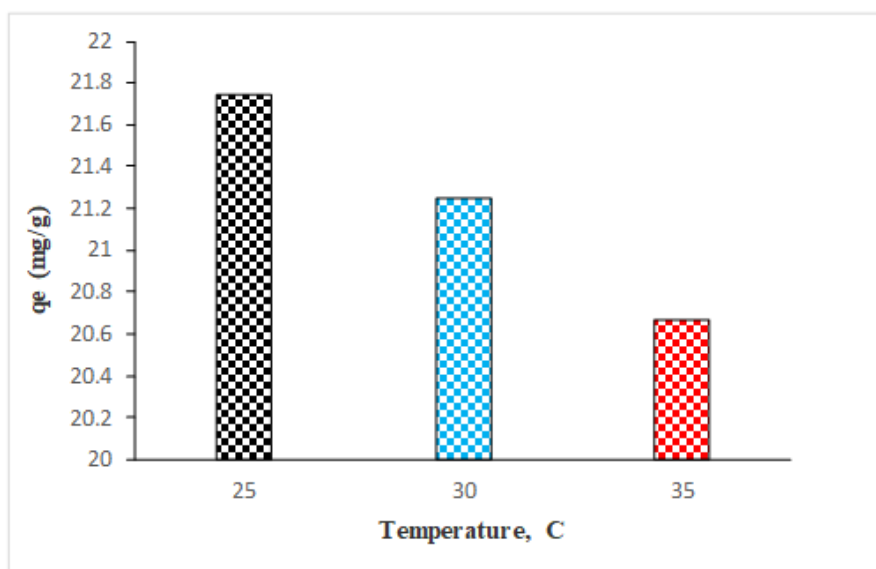


Figure 4: Effect of different temperatures on the adsorption capacity of residual chlorine (25 mg/L) onto ASAC

5. Adsorption Isotherm

Three models were used to study the interpolation and limited extrapolation of the adsorption equilibrium data [17]. The Langmuir sorption isotherm can be calculated in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (4)$$

Where C_e and q_e are the equilibrium concentrations of residual chlorine in the liquid and adsorbed phases (in mg/L and mg/g), respectively, and b and $q_{\max}$ are Langmuir constants, which are related to the energy sorption and maximum adsorption capacity, respectively, and can be calculated from the slope of the linear plot of C_e / q_e versus C_e .

The Langmuir isotherm model accepts a uniform adsorption pattern on the surface and no movement occurs on the plane of the surface and is well-founded for monolayer adsorption on a surface concerning a limited number of identical sites [14]. Fig. 5 shows a linear relationship plot of C_e / q_e versus C_e using the experimental data attained and the values of b

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

and $q_{\max}$ calculated. The apricot shell activated carbon showed a large adsorption capacity for chlorine, which is equal to 285.71 mg/g and the energy of sorption is equal to 0.07, while the commercial activated carbon showed lower adsorption capacity of residual chlorine solution which was equal to 1.75 mg/g [1]. The coefficient of correlation (R^2) for the adsorption of residual chlorine is equal to 0.964.

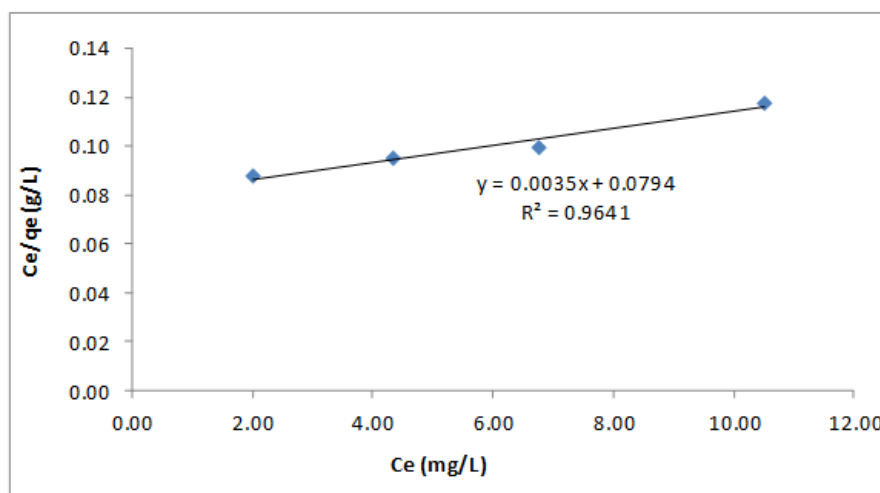


Figure 5: Langmuir isotherm for residual chlorine adsorption onto ASAC at 25°C

The Freundlich isotherm equation can be written as a linear expression as it is illustrated in the following equation [18].

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (5)$$

where n and k_f are the Freundlich constants can be calculated from the slope and intercept of the linear plot of $\ln q_e$ versus $\ln C_e$ which related to the intensity and sorption capacity, respectively.

Table 1 shows the Freundlich constants calculated from Fig. 6. The coefficient of correlation (R^2) for the adsorption of residual chlorine is equal to 0.994. The coefficient, k_f , which represents the adsorption capacity, is 13.7, and the n value for intensity is 0.83 while the coefficient, k_f , for residual chlorine adsorption onto commercial activated carbon was equal to 2.24 [1]. These values indicate that the system conditions are favourable for the adsorption of chlorine.

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

The Temkin isotherm equation is written as follows [12]:

$$q_e = \left(\frac{RT}{b}\right) \ln(A) + \left(\frac{RT}{b}\right) \ln C_e \quad (6)$$

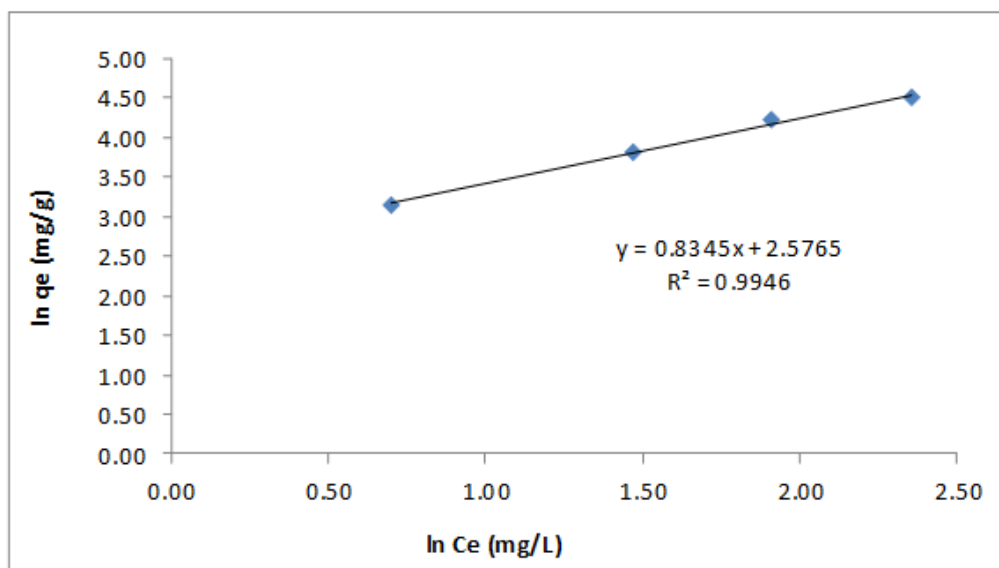


Figure 6: Freundlich isotherm for residual chlorine adsorption onto ASAC at 25 °C

The Temkin model characterizes the uniform distribution as well as considers a maximum binding energy for adsorption. Furthermore, due to the effects of indirect adsorbate/adsorbent interactions the heat of adsorption decreases linearly with the coverage of all the molecules in the layer of adsorption [14].

Where $RT/b = B$. Therefore, a plot of q_e versus $\ln C_e$ enables the determination of constants A and B . Depend on Fig. 7, the values A and B for chlorine adsorption are equal to 0.42 and 51.72 as listed in Table 1, respectively, demonstrating a good adsorbate/adsorbent interaction for chlorine molecular on ASAC. The correlation coefficient (R^2) of the Temkin isotherm adsorption of chlorine was equal to 0.929.

Table 1: Isotherm parameters constants for residual chlorine adsorption onto ASAC at 25°C

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
$q_{\max}(\text{mg/g})$	b	R^2	k_f	n	R^2	B	$A(\text{L/g})$	R^2
285.71	0.07	0.964	13.7	0.83	0.994	51.72	0.42	0.929

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

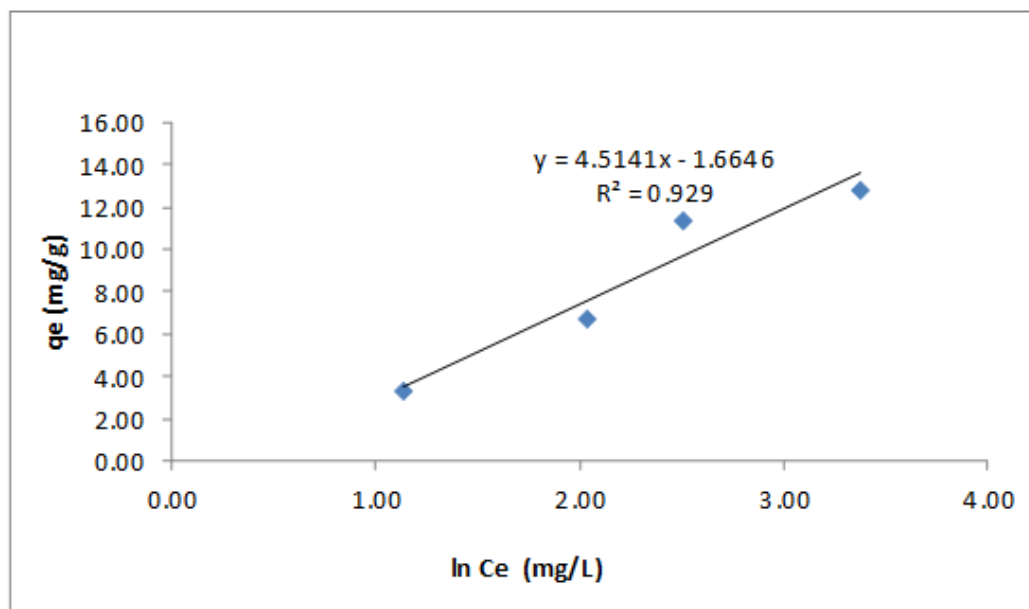


Figure 7: Temkin isotherm for residual chlorine adsorption onto ASAC at 25°C

6. Kinetic Modelling

Pseudo-first order and pseudo-second order sorption equations were used to examine the sorption kinetic data of chlorine calculated on activated carbon. Lagergren's first-order model and rate constants were treated for the adsorption of residual chlorine on ASAC which can be written as [17]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

Where q_t (mg/g) is the amount of sorption at time t (min), k_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption, and q_e (mg/g) is the amount of sorption at the adsorption equilibrium. Fig. 8 show the first-order-rate constant, k_1 , which can be attained from the plot of $\log (q_e - q_t)$ versus time, t . The sorption rate constant, k_1 , can be calculated by plotting $\log (q_e - q_t)$ versus t .

The values of correlation coefficients (R^2) of the second-order kinetic model were not high for all chlorine concentrations. Additionally, the results from Table 2 have revealed that there is a big variance between calculated and experimental q_e values indicating that the model is not suitable to describe the adsorption process [19].

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

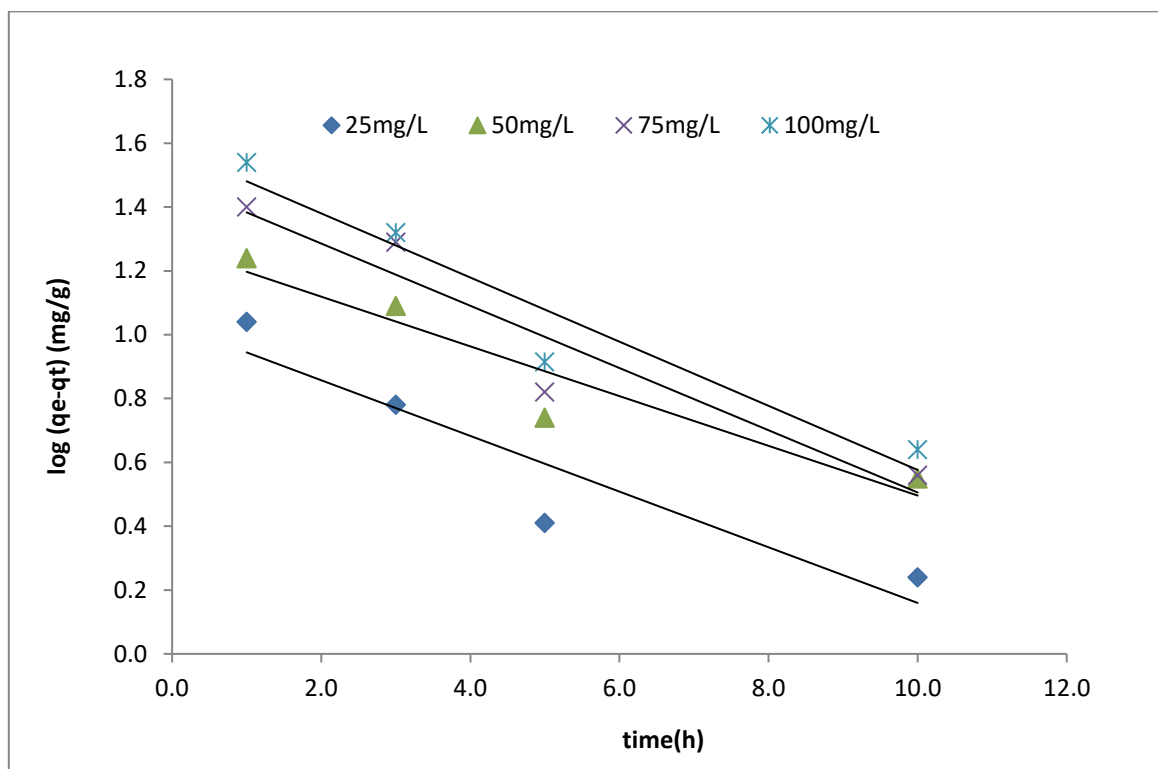


Figure 8: Pseudo-first order kinetic for residual chlorine adsorption onto ASAC at 25°C

The pseudo-second order equation can be written as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Where k_2 (g/mg h) is the rate constant. The values of k_2 and q_e can be calculated from the slope and intercept of plotting t/q_t versus t . The second-order rate constants, k_2 (g/mg h) were calculated from the slopes of the corresponding linear plots of t/q_t versus time, t (Fig. 9). Generally, the values in Table 2 of the rate constant decreased with the increase in residual chlorine concentration and the correlation coefficients were equal 0.999 for all concentrations of chlorine. This demonstrates a good relationship between the variables. Correspondingly, there is a slight deviation between the calculated and experimental q_e values representing a good agreement between the variables, which shows that the kinetics follows pseudo-second-order kinetics [20, 21].

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

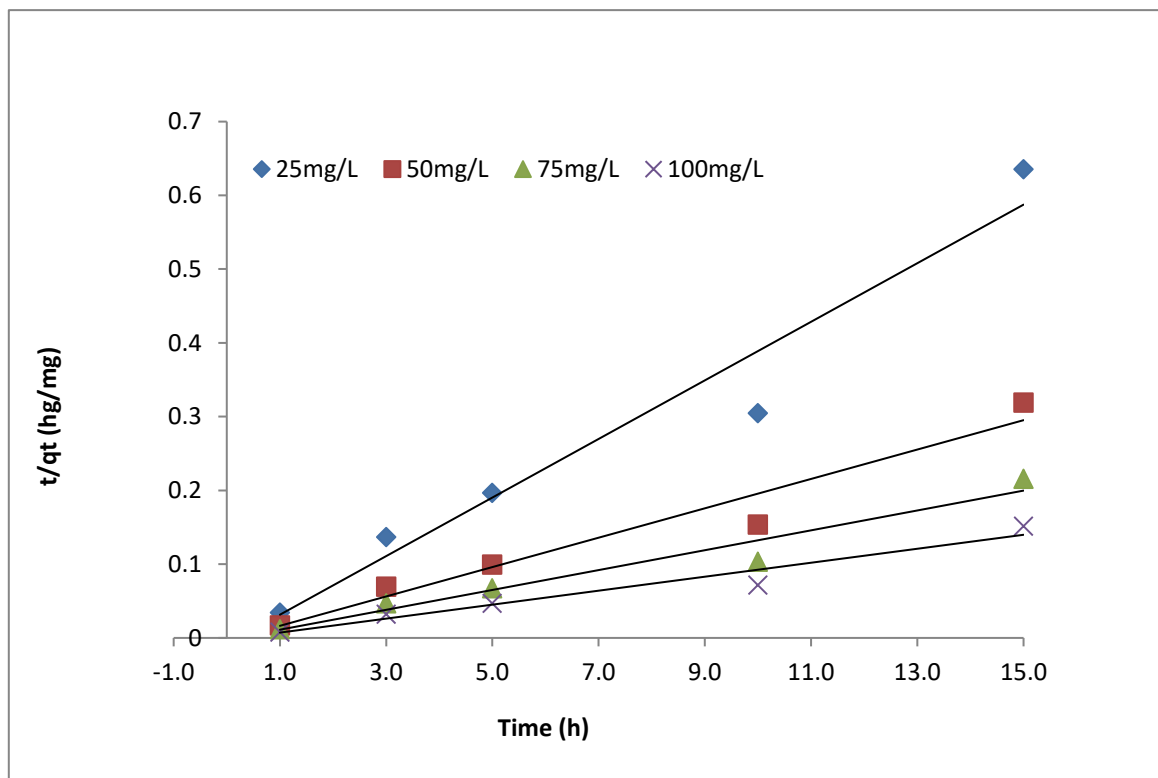


Figure 9: Pseudo-second order kinetic for residual chlorine adsorption onto ASAC at 25 °C

Table 2: The pseudo-first order and second order rate constants at different initial concentration of residual chlorine adsorption onto ASAC at 25 °C

C_o (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		$q_{e,cal}$ (mg/g)	k_1 (1/h)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg h)	R^2
25	22.99	13.64	0.086	0.871	23.75	0.042	0.999
50	45.67	27.92	0.077	0.905	46.05	0.021	0.999
75	68.23	40.11	0.097	0.907	68.87	0.014	0.999
100	89.34	61.39	0.102	0.926	91.16	0.010	0.999

The activated carbon from babassu and coconut shell showed lower than % 40 adsorption in Jaguaribe's et al (2005) study while this work showed more than 91.34 % adsorption of residual chlorine onto ASAC.

Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

Conclusion

Depending on the results, we can conclude that the high surface area of ASAC can be successfully used as an activated carbon for the removal of residual chlorine from aqueous solutions. Adsorption was studied through different parameters, such as the initial pH and initial concentration of residual chlorine. The highest removal of residual chlorine was demonstrated at low pH. The removal efficiency increased with the decreasing of residual chlorine concentrations and solution temperatures.

The Freundlich adsorption isotherm was the best model for representing the adsorption for adsorbate removal. Adsorption kinetics were conventional to follow a Pseudo-second-order model with good correlations for residual chlorine.

In conclusion, ASAC is capable of adsorbing 91.34 % of the residual chlorine in aqueous solutions at the adsorption equilibrium.

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Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

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Removal of Residual Chlorine from Water by Adsorption Using Apricot Shell Activated Carbon

Bakhtiar K. Hamad

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