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Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon

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Abstract

The adsorption characteristics of 2,4,6-trichlorophenol (TCP) on coconut husk-based activated carbon prepared under optimized conditions were evaluated. Batch adsorption studies were conducted to study the effects of various parameters such as initial concentration, agitation time and solution pH on TCP adsorption. Adsorption capacity was found to increase with increase in initial concentration and agitation time, while acidic pH was more favourable for the adsorption of TCP. Equilibrium data were analyzed by the Langmuir, Freundlich, Temkin and Redlich–Peterson models by using non-linear regression technique. The equilibrium data were best represented by the Langmuir isotherm, yielding maximum monolayer adsorption capacity of 716.10 mg/g at 30 °C. The adsorption kinetics was found to follow the pseudo-second-order kinetic model. The mechanism of the adsorption process was determined from the intraparticle diffusion model. Boyd plot revealed that the adsorption of TCP on the activated carbon was mainly governed by particle diffusion. Coconut husk-based activated carbon was shown to be an efficient adsorbent for removal of TCP from aqueous solutions.

Keywords: Coconut husk activated carbon; 2,4,6-trichlorophenol; Adsorption; Isotherm; Kinetics

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1. Introduction

Cholorophenols are a group of chemicals in which chlorines (between one and five) have been added to phenol. The main pollution sources containing chlorophenols are the wastewaters from pesticide, paint, solvent, pharmaceutics, wood, paper and pulp industries as well as water disinfecting process [1]. Chlorophenols are weak acids, which permeate human skin by in vitro and are readily absorbed by gastro-intestinal tract [2]. 2,4,6-Trichlorophenol (TCP) is a toxic, mutagenic and carcinogenic pollutant. It is found in the emissions from fossil fuel combustion, municipal waste incineration, and chlorination of water containing phenol or certain aromatic acids with hypochlorite or during disinfection of water [3]. TCP has been also reported to cause adverse effects on human nervous system and respiratory problems such as chronic bronchitis, cough and altered pulmonary function [4]. The stable C–Cl bond and the position of chlorine atoms relative to the hydroxyl group are responsible for their toxicity and persistence in the biological environment [5]. Due to its high toxicity, carcinogenic properties, structural stabilization and persistence in the environment, the removal of TCP from the environment is crucial.

From literature, various treatment methods have been applied to remove chlorophenols from aqueous solutions, such as biological treatment using anaerobic granular sludge [1] and dead fungus [6], catalytic wet oxidation [3], adsorption technology using activated clay [4] and activated carbons prepared from various precursors [2,7–10]. Other treatment technologies include air stripping, incineration, ion exchange and solvent extraction. Adsorption on activated carbon is one of the most effective and widely used techniques in treating high strength and low volume of phenolic wastewaters [2,8]. Commercially available activated carbons like F300 granular activated carbon (Calgon Corp., Pittsburgh, PA) are used for the adsorption of chlorophenols [11]. However, the usage of activated carbon has been limited by its high cost due to the use of non-renewable and relatively expensive starting material such as coal, which is a major economic consideration [12]. This has prompted a growing research interest in the production of low cost activated carbons especially for application concerning wastewater treatment.

Recently, focus has been given on the preparation of activated carbons from agricultural by-products such as jackfruit

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peel waste [13], rice husk [14], bagasse pith [15], coir pith [16], palm pith [17], durian shell [18], corn cob [9,19], oil palm fibre [20], bamboo [21] and rubber seed coat [22]. In our previous works, coconut husk has been successfully converted into activated carbons and the preparation conditions have been optimized [23,24]. Not many studies have been reported in literature on the adsorption of TCP using coconut husk-based activated carbon. In the present investigation, coconut husk-based activated carbon prepared under optimized conditions was evaluated for its potential to remove TCP from aqueous solutions. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption characteristics and mechanism of TCP on the prepared activated carbon.

2. Materials and methods

2.1. Activated carbon preparation

The coconut husk used for preparation of activated carbon in this study was obtained locally. The activated carbon preparation procedure was referred to our previous work [24] where the pre-treated coconut husk was loaded in a stainless steel vertical tubular reactor placed in a tube furnace and the carbonization of the precursor was carried out by ramping the temperature from room temperature to 700 °C with heating rate of 10 °C/min and hold for 2 h. Throughout the carbonization process, purified nitrogen (99.995%) was flown through at flow rate of 150 cm^3/min. The optimum preparation conditions obtained in our previous work [24] were applied to prepare the activated carbon from coconut husk, which gave high carbon yield and high TCP uptake. The char produced from the carbonization process was mixed with potassium hydroxide (KOH) pallets with KOH:char impregnation ratio (IR) of 2.91. The dried mixture was then activated under the same condition as carbonization, but to a final temperature of 750 °C. Once the final temperature was reached, the nitrogen gas flow was switched to CO_2 and activation was held for 2.29 h. The activated product was then cooled to room temperature under nitrogen flow and then washed with hot deionized water and 0.1 M hydrochloric acid (HCl) until the pH of the washing solution reached 6–7.

2.2. 2,4,6-Trichlorophenol

2,4,6-Trichlorophenol (TCP) supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as the adsorbate in this study, and was not purified prior to use. TCP has a chemical formula of $C_6H_3Cl_3O$, with molecular weight of 197.46 g/mol. Deionized water supplied by USF ELGA water treatment system was used to prepare all the reagents and solutions.

2.3. Batch adsorption studies

Batch adsorption was performed in a set of 250 ml Erlenmeyer flasks where 100 ml of TCP solutions with various initial concentrations (25–250 mg/l) were placed. 0.1 g of the prepared activated carbon was added to each flask and kept in an isothermal water bath with agitation speed of 120 rpm and 30 °C solution temperature. For equilibrium studies, the experiment was carried out for 24 h to ensure equilibrium was reached. Aqueous samples were taken from the solutions and the concentrations were analyzed. All samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. The concentrations of TCP in the supernatant solutions before and after adsorption were determined using a double beam UV–vis spectrophotometer (Shimadzu UV-1601, Japan) at its maximum wavelength of 296 nm. The TCP uptake at equilibrium, q_e (mg/g), was calculated by Eq. (1).

$$q_{\mathrm{e}} = \frac{(C_0 - C_{\mathrm{e}})V}{W} \tag{1}$$

where C_0 and C_e (mg/l) are the liquid-phase concentrations of TCP at initial and at equilibrium, respectively. V (l) is the volume of the solution and W (g) is the mass of dry adsorbent used.

For batch kinetic studies, the same procedure was followed, but the aqueous samples were taken at preset time intervals. The concentrations of TCP were similarly measured. The TCP uptake at any time, q_t (mg/g), was calculated by Eq. (2).

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

where C_t (mg/l) is the liquid-phase concentration of TCP at any time, t (h).

2.4. Effect of initial concentration and solution pH

To study the effect of initial concentrations on the TCP uptake, the initial concentrations were varied from 25 to 250 mg/l. The initial pH of the solutions was original without any pH adjustment whereas the adsorbent dosage, agitation speed and solution temperature were remained constant. The effect of solution pH on the TCP removal was studied by varying the pH from 2 to 12, where the pH was adjusted by adding either 0.01N HCl or 0.01N NaOH. The initial concentration used was 100 mg/l, whereas other parameters like adsorbent dosage, agitation speed and solution temperature were remained constant. The TCP percent removal was calculated as:

$$\text{Romoval}\,(\%) = \frac{(C_0 - C_{\mathrm{e}})}{C_0} \times 100 \tag{3}$$

2.5. Chemical characteristics of activated carbon

The surface chemistry characterization of the prepared activated carbon was performed with pH drift method. This test was conducted to determine the pH of the point of zero charge, pH_{pzc} of the prepared activated carbon. pH_{pzc} is the pH when the charge on the activated carbon surface is zero. For this purpose, 50 ml of 0.01N NaCl solutions were prepared and added into a series of Erlenmeyer flasks. Then, their pH values were adjusted in range between 2 and 12 using 0.01N HCl solution and 0.01N NaOH. The initial pH of the solutions were measured with pH meter and noted as $\text{pH}_{\text{initial}}$. After constant value of $\text{pH}_{\text{initial}}$ had been reached, 0.15 g of the activated carbon sample was added into each Erlenmeyer flask. The solution pH was measured after

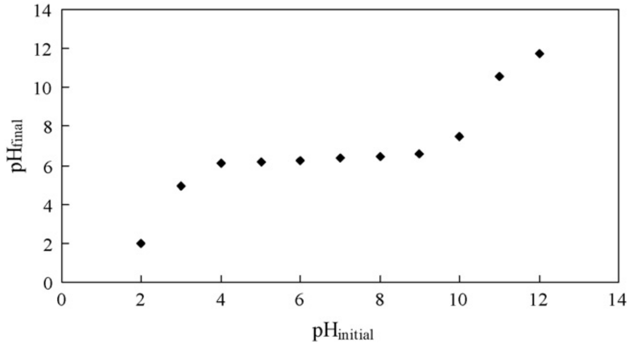

Fig. 1. pH$_{pzc}$ determination using pH drift method.

48 h and noted as pH$_{final}$, then plotted against pH$_{initial}$. pH$_{pzc}$ of the activated carbon sample is the point when pH$_{initial}$ = pH$_{final}$.

The functional groups available on the surface of the prepared activated carbons before and after TCP adsorption were detected by KBr technique using a Fourier Transform Infrared (FTIR) spectroscope (FTIR-2000, PerkinElmer). The spectra were recorded from 4000 to 400 cm^{-1}.

3. Results and discussion

3.1. Chemical characteristics of activated carbon

Fig. 1 illustrates the plot obtained from the pH drift method. From the graph, the pH$_{pzc}$ value obtained for the prepared activated carbon was around 6, indicating that the surface of the activated carbon was more on the acidic group. This was in agreement with the work carried out by Hamdaoui and Naffrechoux [25], which reported that the surface of commercial granular activated carbon was as well showing acidic characteristic.

The FTIR spectrums obtained revealed that there were various functional groups detected on the prepared activated carbon. The broad band at 3434.99 and 3431.44 cm^{-1}, respectively, found in the spectrum of the activated carbon before and after TCP adsorption, can be assigned to O–H stretching vibration of hydroxyl functional groups including hydrogen bonding. This shows that the O–H group was not affected by the TCP adsorbed on the activated carbon. This functional group has also been detected on the surface activated carbons prepared from palm shell [26] as well as commercial granular activated carbons [7]. Other peaks detected on the activated carbon before TCP adsorption were located at 1384.48, 1138.20, 1017.53, 767.32, 651.54 and 607.23 cm^{-1}, respectively, assigned to C–H stretching in alkanes/alkyl groups, C–N stretching, C–O–C stretching, C–H out-of-plane bending in benzene derivatives, O–H stretching and C–O–H twist. C–H out-of-plane bending in benzene derivatives was commonly found on the surface of various activated carbons [26,27]. However, after TCP adsorption, all these functional groups disappeared and a new peak was detected at 1196.01 cm^{-1}, which might be due to the overlapping of C–O–C stretching, C–O stretching and O–H bending modes of alcoholic, phenolic and carboxylic groups [7].

3.2. Effect of agitation time and TCP initial concentration on adsorption equilibrium

The experiments were carried out with activated carbon dosage of 0.1 g/100 ml solution and 30 °C solution temperature. The natural solution pH was used without any adjustment. Fig. 2 shows the effects of agitation time and TCP initial concentration on the removal of TCP by the prepared activated carbon. The plots show that the adsorption of TCP increases with an increase in agitation time and attains equilibrium earlier for solutions with lower initial concentrations. The adsorption curves are single smooth and continuous leading to saturation. The results revealed that the TCP adsorption was fast at the initial stages of the contact period, and thereafter it became slower near the equilibrium. This phenomenon was due to the fact that a large number of vacant surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Similar trend was observed in the adsorption of TCP on activated clay and coconut shell-based activated carbon [2,4]. The equilibrium time of 15–90 min was needed for solutions of 25–150 mg/l initial concentrations. However, for higher initial concentrations of 200 and 250 mg/l, longer time was required for the system to reach equilibrium, which was 135 and 360 min, respectively. Radhika and Palanivelu [2] found that the equilibrium time for the adsorption of TCP by coconut shell-based commercial grade activated carbon was 60–210 min for TCP initial concentration of 10–100 mg/l. Denizli et al. [6] reported that for initial concentration of 500 mg/l, adsorption amount of TCP was very high at the beginning of adsorption, and saturation level was gradually reached within 4 h. Hameed [4] found that the equilibrium time needed for adsorption of TCP on activated clay was almost 30 min for initial concentration below 150 mg/l, and more than 60 min was required for higher concentration. This shows that the adsorption performance of the activated carbon prepared in this study was comparable with the works done by previous researchers.

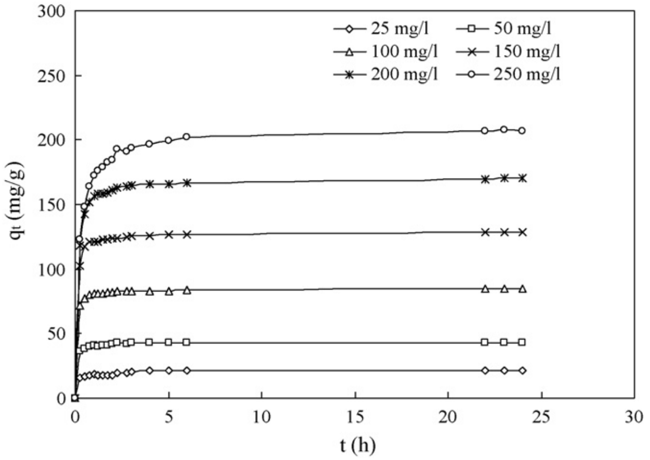

Fig. 2. Effect of agitation time on adsorption of TCP at various initial concentrations at 30 °C.

TCP was adsorbed fast due to high affinity of the interacting groups on the surface of the activated carbon. The high adsorption rate at the beginning of adsorption was due to the adsorption of TCP by the exterior surface of the adsorbent. When saturation was reached at the exterior surface, the TCP entered into the pores of adsorbent and were adsorbed by the interior surface of the particles [4,6]. Adsorption rate might vary as it depends on several parameters such as stirring rate, structural properties of adsorbent, adsorbent dosage and adsorbate properties.

For all initial concentrations (25–250 mg/l), the amount of TCP adsorbed by the activated carbon increases with time and, at some point in time, it reaches a constant value beyond which no more TCP is further removed from the solution. At this point, the amount of the TCP desorbing from the activated carbon is in a state of dynamic equilibrium with the amount of the TCP being adsorbed on the activated carbon. The amount of TCP adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. In this study, the adsorption capacity at equilibrium, q_e, increased from 21.53 to 202.27 mg/g with an increase in initial concentration from 25 to 250 mg/l. When the initial concentration increased, the mass transfer driving force became larger, hence resulting in higher TCP adsorption.

3.3. Effect of solution pH on TCP adsorption

Fig. 3 shows the effect of solution pH on the removal of TCP by the prepared activated carbon, together with the error bars representing the deviation errors for the replicates data. As can be seen from this plot, the TCP percent removal was found to decrease with increase in solution pH and the readings obtained from the replicates for each solution pH were quite consistent, giving deviation errors which were relatively small.

In this study, the highest TCP removal was achieved at pH 2, with TCP removal as high as 92.93%, at TCP initial concentration of 100 mg/l. This was due to the chemical characteristics of the activated carbon with acidic pH_{pzc}, which was around 6. At a solution pH lower than the pH_{pzc}, the total surface charge would be on average positive, whereas at a higher solution pH, it would be negative. The TCP uptake was the highest at lower pH where the pH was below the pK_a of TCP. This was because at acidic pH, the TCP was undissociated and the dispersion interactions predominated [25]. The unionized species of halogenated organic compounds were high, which did not favour any repulsion between the activated carbon surface and the molecular species of TCP, thereby increased the electrostatic attractions between the TCP molecules and the adsorption sites. However, at basic pH, the 2,4,6-TCP uptake was lower due to the electrostatic repulsions between the negative surface charge and the chlorophenolate anions and between chlorophenolate–chlorophenolate anions in solution [25]. Besides, there might be competition between the OH^- ions and the ionic species of TCP. Similar trends were reported in the adsorption of TCP on coconut shell-based activated carbon [2] and activated clay [4] as well as adsorption of 4-chlorophenol and 2,4-dichlorophenol on anaerobic granular sludge [1].

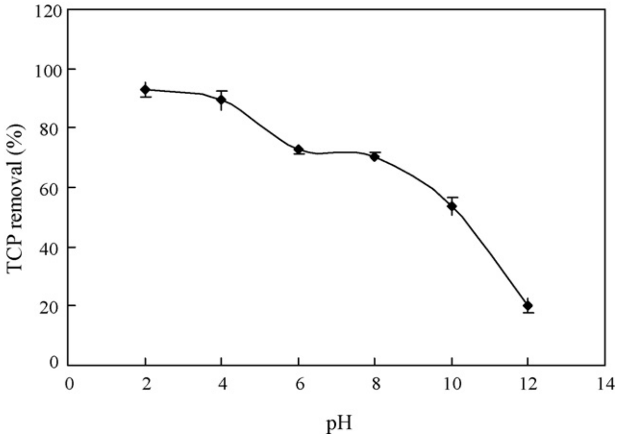

Fig. 3. Effect of solution pH on TCP removal by coconut husk-based activated carbon (TCP initial concentration = 100 mg/l, temperature = 30 °C).

3.4. Adsorption isotherms

In order to optimize the design of an adsorption system, it is important to establish the most appropriate correlation for the equilibrium curves. In this study, four adsorption isotherms namely the Langmuir, Freundlich, Temkin and Redlich–Peterson (R–P) isotherms in their non-linear forms were applied to the equilibrium data of adsorption of TCP on coconut husk-based activated carbon.

The Langmuir equation is valid for monolayer sorption on a surface with a finite number of identical sites and is expressed as [28]:

$$q_e = \frac{QK_LC_e}{1 + K_LC_e} \tag{4}$$

where Q (mg/g) is the maximum amount of the adsorbate per unit weight of the adsorbent to form a complete monolayer on the surface whereas K_L(l/mg) is Langmuir constant related to the affinity of the binding sites.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called separation factor or equilibrium parameter, R_L, defined by Weber and Chakkravorti [29] as:

$$R_L = \frac{1}{1 + K_LC_0}. \tag{5}$$

The parameter R_L indicates the shape of isotherm as follows:

Value of R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Fig. 4 represents the calculated R_L values versus the initial concentration of TCP at 30 °C. All the R_L values were between 0 and 1, indicating that the adsorption of TCP on the prepared activated carbon was favourable at the conditions being studied. However, as the initial concentration increased from 25 to

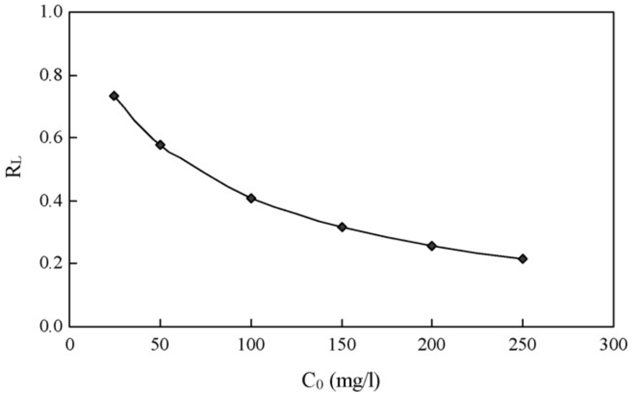

Fig. 4. Effect of TCP initial concentration on separation factor R_L.

250 mg/l, the R_L values decreased from 0.734 to 0.216. This indicated that adsorption was more favourable at higher concentration.

Freundlich model is an empirical equation based on sorption on a heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation [30]. The isotherm is expressed as:

$$q_e = K_F {C_e}^{1/n} \tag{6}$$

where K_F (mg/g (l/mg)$^{1/n}$) and n are Freundlich constants related to sorption capacity and sorption intensity of the adsorbent. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon for a unit equilibrium concentration. A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [31].

Temkin isotherm [32] contains a factor that explicitly takes into account the adsorbent–adsorbate interactions. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent–adsorbate interactions. The adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Temkin isotherm is expressed as:

$$q_e = (RT/b_T)\ln(AC_e) \tag{7}$$

where $RT/b_T = B$ (J/mol), which is the Temkin constant related to heat of sorption whereas A (l/g) is the equilibrium binding constant corresponding to the maximum binding energy. R (8.314 J/mol K) is the universal gas constant and T (K) is the absolute solution temperature.

The Redlich–Peterson (R–P) equation [33] is widely used as a compromise between Langmuir and Freundlich systems. This model has three parameters and incorporates the advantageous significance of both models. R–P model can be represented as follows:

$$q_e = \frac{K_{RP} C_e}{1 + (\alpha C_e)^\beta} \tag{8}$$

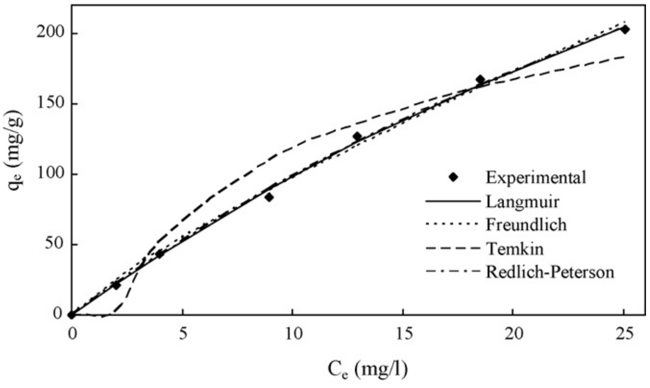

Fig. 5. Equilibrium adsorption isotherms of TCP on coconut husk-based activated carbon at 30 °C fitted to Langmuir, Freundlich, Temkin and Redlich–Peterson models.

where K_{RP} (l/g) and α (l/mg)$^\beta$ are Redlich–Peterson isotherm constants whereas β is the exponent which lies between 0 and 1. R–P model has two limiting cases, when $\beta = 1$, the Langmuir equation results whereas when $\beta = 0$, R–P equation transforms to Henry's law equation.

The four non-linear equations of Eq. (4) and Eqs. (6)–(8) were solved using MATLAB® software. The isotherms of TCP on the prepared activated carbon predicted from all the four models were plotted in Fig. 5. All the correlation coefficient, R^2 values and the constants obtained for the models are summarized in Table 1. The Langmuir model yielded the best fit with the highest R^2 value of 0.997, thus the Langmuir isotherm was the most suitable equation to describe the adsorption equilibrium of TCP on the activated carbon prepared from coconut husk. As can be seen from Fig. 5, the q_e values predicted from the Langmuir model agreed well with the experimental values. The suitability of the Langmuir isotherm to fit the data was confirmed by the exponent value of R–P model, β, which was equal to 1, resulted to the original Langmuir equation. The $1/n$ value from Freundlich model, which was below 1, also indicated a normal Langmuir isotherm.

Table 1
Langmuir, Freundlich, Temkin and Redlich–Peterson isotherm model constants and correlation coefficients for adsorption of TCP on prepared activated carbon at 30 °C

Isotherms	Parameters
Langmuir	$Q = 716.10$ mg/g $K_L = 0.016$ l/mg $R^2 = 0.997$
Freundlich	$K_F = 14.20$ mg/g (l/mg)$^{1/n}$ $1/n = 0.83$ $R^2 = 0.994$
Temkin	$A = 0.52$ l/g $B = 71.12$ J/mol $R^2 = 0.936$
Redlich–Peterson	$K_{RP} = 11.42$ l/g $\alpha = 0.016$ (l/mg)$^\beta$ $\beta = 1$ $R^2 = 0.997$

Table 2
Comparison of maximum monolayer adsorption capacity of various chlorophenols on different adsorbents

Adsorbent	Adsorbate	Maximum monolayer adsorption capacity, Q (mg/g)	Ref.
Coconut husk-based activated carbon	2,4,6-Trichlorophenol	716.10	This work
Activated clay	2,4,6-Trichlorophenol	123.46	[4]
Coconut shell-based commercial grade activated carbon	2,4,6-Trichlorophenol	112.35	[2]
Coconut shell-based commercial grade activated carbon	Parachlorophenol	134.10	[2]
Anaerobic granular sludge	4-Chlorophenol	6.32	[1]
Palm pith carbon	2,4-Dichlorophenol	19.16	[17]
Coir pith carbon	2,4-Dichlorophenol	19.12	[35]
Rice straw-based carbon	3-Chlorophenol	14.20	[10]

Conformation of the experimental data into the Langmuir isotherm equation indicated the homogeneous nature of coconut husk-based activated carbon surface, i.e., each TCP molecule/activated carbon adsorption had equal adsorption activation energy. The results also demonstrated the formation of monolayer coverage of TCP molecule at the outer surface of the coconut husk-based activated carbon. Similar phenomenon was observed in the adsorption of 3-chlorophenol on rice straw-based carbon [10], 4-chlorophenol on anaerobic granular sludge [1] and 2,4-dichlorophenol on corncob-based activated carbon [9]. However, some researchers found that the Freundlich model gave a better fit than the Langmuir model on the adsorption of chlorophenols using different adsorbents [2,4,34]. This might be influenced by the characteristics of the adsorbents used as well as the original nature of the adsorbates. Table 2 lists the comparison of the maximum monolayer adsorption capacity of various types of chlorophenols on different adsorbents. The activated carbon prepared in this work had a relatively large adsorption capacity of 716.10 mg/g, as compared to some previous works found in the literature.

3.5. *Adsorption kinetic studies*

The kinetic of adsorption describes the rate of TCP uptake on the activated carbon, which controls the equilibrium time. The kinetic parameters are helpful for the prediction of adsorption rate, which gives important information for designing and modeling the processes. The kinetic of the adsorption data were analyzed using three different kinetic models: the pseudo-first-order, pseudo-second-order and Elovich equations.

3.5.1. *Pseudo-first-order kinetic model*

The pseudo-first-order kinetic model has been widely used to predict sorption kinetics. The model given by Langergren and Svenska [36] is defined as:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1(q_\mathrm{e} - q) \tag{9}$$

Integrating Eq. (9) with respect to boundary conditions $q = 0$ at $t = 0$ and $q = q_\mathrm{e}$ at $t = t$, Eq. (9) becomes

$$\ln(q_\mathrm{e} - q_t) = \ln q_\mathrm{e} - k_1 t \tag{10}$$

where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (h), respectively, and k_1 (h^{-1}) is the adsorption rate constant. The plot of $\ln(q_\mathrm{e} - q_t)$ versus t (figure not shown) gave the slope of k_1 and intercept of $\ln q_\mathrm{e}$. The values of k_1 and correlation coefficient R^2 obtained for the plots are given in Table 3. The R^2 values were relatively small, which varied from 0.512 to 0.870 for TCP initial concentration of 25–250 mg/l. Besides, the experimental q_e values did not agree with the calculated values obtained from the linear plots. This shows that the adsorption of TCP on the activated carbon is not a first-order reaction.

3.5.2. *Pseudo-second-order kinetic model*

The pseudo-second-order equation [37] based on equilibrium adsorption is expressed as:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2(q_\mathrm{e} - q)^2 \tag{11}$$

Table 3
Pseudo-first-order model, pseudo-second-order model and Elovich equation constants and correlation coefficients for adsorption of TCP on prepared activated carbon at 30 °C

Initial TCP concentration (mg/l)	$q_\mathrm{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Elovich equation			
		$q_\mathrm{e,cal}$ (mg/g)	k_1 (h^{-1})	R^2	$q_\mathrm{e,cal}$ (mg/g)	k_2 (g/mg h)	R^2	$q_\mathrm{e,cal}$ (mg/g)	a	b	R^2
25	21.53	8.80	0.62	0.512	18.38	1.56	0.9996	18.32	3.11×10^7	0.98	0.828
50	42.96	13.96	1.39	0.768	42.55	0.46	0.9997	41.88	3.25×10^7	0.41	0.969
100	83.45	23.82	1.74	0.797	84.03	0.28	0.9999	83.18	1.06×10^8	0.21	0.909
150	126.46	36.38	1.52	0.732	126.46	0.16	0.9998	125.97	5.65×10^6	0.11	0.799
200	166.82	71.65	1.49	0.843	169.49	0.07	0.9998	165.65	4.84×10^4	0.05	0.902
250	202.27	113.61	1.06	0.870	200.00	0.03	0.9999	188.31	8.76×10^3	0.03	0.975

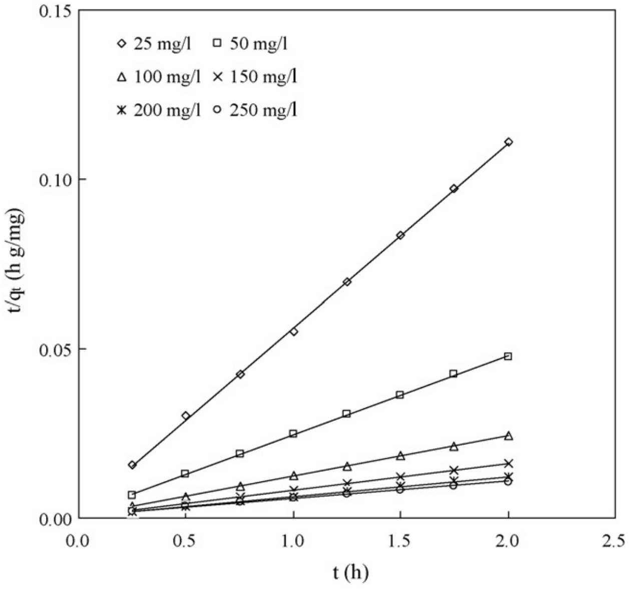

Fig. 6. Pseudo-second-order kinetics for adsorption of TCP on prepared activated carbon at 30 °C.

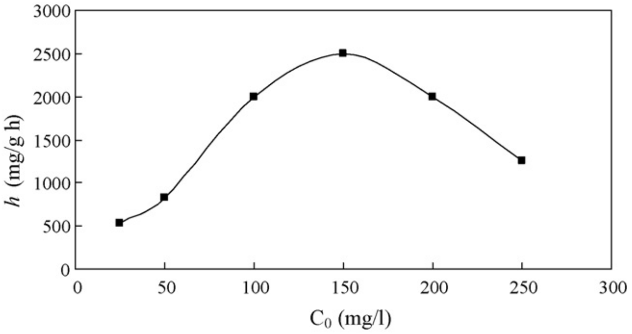

Fig. 7. Initial sorption rate versus initial concentration for adsorption of TCP on prepared activated carbon at 30 °C.

Separating the variables in Eq. (11) gives

$$\frac{dq}{(q_e - q)^2} = k_2\,dt \tag{12}$$

Integrating Eq. (12) with respect to boundary conditions $q = 0$ at $t = 0$ and $q = q_e$ at $t = t$,

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{13}$$

where k_2 (g/mg h) is the rate constant of second-order adsorption. The linear plot of t/q_t versus t gave $1/q_e$ as the slope and $1/k_2 q_e^2$ as the intercept. This procedure is more likely to predict the behavior over the whole range of adsorption. The linear plot of t/q_t versus t, as shown in Fig. 6, shows a good agreement between the experimental and the calculated q_e values (Table 3). Besides, the correlation coefficient values for the second-order kinetic model were almost equal to unity for all TCP concentrations, indicating the applicability of the second-order kinetic model to describe the adsorption process of TCP on the prepared activated carbon.

The second-order rate constants were used to calculate the initial sorption rate given by:

$$h = k_2 q_e^2 \tag{14}$$

The calculated h values are plotted against TCP initial concentration, as shown in Fig. 7. The initial sorption rate, h, was found to increase with initial concentration, however, the value started to decrease when the initial concentration was higher than 150 mg/l. The possible reason might be that too high solute concentrations would slow down the adsorption process, as for all initial concentrations, the same amount of adsorbent was used, which might not be enough for the TCP molecules to adsorb fast on the activated carbon when the initial concentration was too high. The h value could also be influenced by the characteristics of the adsorbent and adsorbate. Kavitha and Namasivayam [16] reported that for adsorption of methylene blue on coir pith carbon, the h value increased when the dye initial concentration increased from 10 to 20 mg/l, however, the h value started to decrease when the dye initial concentration was higher than 20 mg/l.

3.5.3. *Elovich equation*

Elovich equation is one of the most useful models for describing activated chemisorption. After arrangement and simplification, Elovich equation can be expressed as follows [38]:

$$q_t = \left(\frac{1}{b}\right)\ln(ab) + \left(\frac{1}{b}\right)\ln t \tag{15}$$

where a and b are the constants for this model obtained from the slope and intercept of the linear plot of q_t versus $\ln t$ (Fig. 8). The R^2 values obtained from Elovich equation was in the range of 0.799–0.975 for TCP initial concentration of 25–250 mg/l (Table 3). The q_e values calculated from Elovich equation agreed quite well with the experimental values.

3.5.4. *Validity of kinetic model*

The applicability of the kinetic model to describe the adsorption process was further validated by the normalized standard

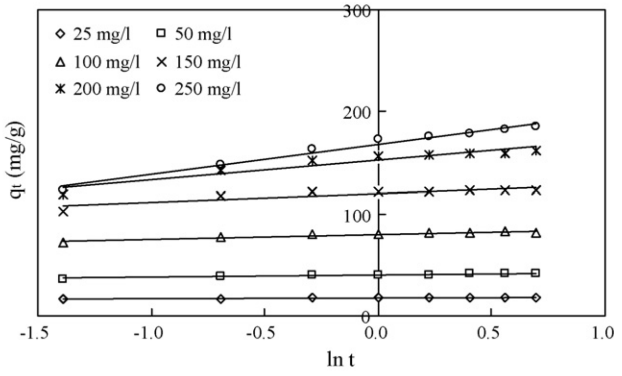

Fig. 8. Plot of Elovich equation for adsorption of TCP on prepared activated carbon at 30 °C.

deviation, Δq_e (%), which is defined as:

$$\Delta q_e(\%) = 100\sqrt{\frac{\sum[(q_{e,\exp} - q_{e,\mathrm{cal}})/q_{e,\exp}]^2}{(N-1)}} \tag{16}$$

where N is the number of data points, $q_{e,\exp}$ and $q_{e,\mathrm{cal}}$ (mg/g) are the experimental and calculated equilibrium adsorption capacity value, respectively.

The Δq_e obtained for the pseudo-first-order kinetic model was 68.42%, which was relatively high as compared to the Δq_e values of 6.62% and 7.44% obtained for the pseudo-second-order kinetic model and Elovich equation, respectively. Based on the highest R^2 values that approached unity and the lowest Δq_e value, the pseudo-second-order model was the most suitable equation to describe the adsorption kinetics of TCP on the prepared activated carbon. This suggested that the overall rate of the adsorption process was controlled by chemisorption which involved valency forces through sharing or exchange of electrons between the sorbent and sorbate [39]. Similar phenomena have been observed in the adsorption of TCP on activated clay [4] and coconut shell-based activated carbon [2] as well as adsorption of 2-chlorophenol on coir pith carbon [11].

3.6. Adsorption mechanism

As the above kinetic models were not able to identify the diffusion mechanism, intraparticle diffusion model based on the theory proposed by Weber and Morris [40] was tested. It is an empirically found functional relationship, common to the most adsorption processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t. According to this theory:

$$q_t = k_{\mathrm{p}i}t^{1/2} + C_i \tag{17}$$

where $k_{\mathrm{p}i}$ (mg/g h$^{1/2}$), the rate parameter of stage i, is obtained from the slope of the straight line of q_t versus $t^{1/2}$ (Fig. 9). C_i, the intercept of stage i, gives an idea about the thickness of boundary layer, i.e., the larger the intercept, the greater the boundary layer effect [16]. If intraparticle diffusion occurs, then q_t versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved.

For intraparticle diffusion plots, the first, sharper region is the instantaneous adsorption or external surface adsorption. The second region is the gradual adsorption stage where intraparticle diffusion is the rate limiting. In some cases, the third region exists, which is the final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in the solutions [34]. Referring to Fig. 9, for all initial concentrations, the first stage was completed within the first 15 min and the second stage of intraparticle diffusion control was then attained. The third stage only occurred for higher TCP initial concentration of 150, 200 and 250 mg/l. The different stages of rates of adsorption observed indicated that the adsorption rate was initially faster and then slowed down when the time increased.

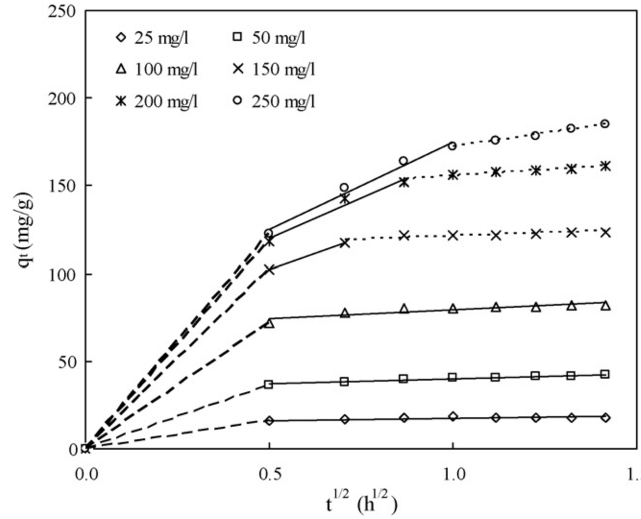

Fig. 9. Plot of intraparticle diffusion model for adsorption of TCP on prepared activated carbon at 30 °C.

As can be seen from Fig. 9, the linear lines of the second and third stages did not pass through the origin and this deviation from the origin or near saturation might be due to the difference in the mass transfer rate in the initial and final stages of adsorption [41]. It shows that intraparticle diffusion was not the only rate limiting mechanism in the adsorption process. The values of $k_{\mathrm{p}i}$, C_i and correlation coefficient R^2 obtained for the plots are given in Table 4.

Kinetic data as obtained by the batch method has been treated by the expressions given by Boyd et al. [42], which is in accordance with the observations of Reichenberg [43]. The three sequential steps in the adsorption are:

Table 4
Intraparticle diffusion model constants and correlation coefficients for adsorption of TCP on prepared activated carbon at 30 °C

Initial TCP concentration (mg/l)	Intraparticle diffusion model						
	$k_{\mathrm{p}1}$ (mg/g h$^{1/2}$)	$k_{\mathrm{p}2}$ (mg/g h$^{1/2}$)	C_2	$(R_2)^2$	$k_{\mathrm{p}3}$ (mg/g h$^{1/2}$)	C_3	$(R_3)^2$
25	32.14	2.16	15.35	0.738	–	–	–
50	73.15	5.34	34.59	0.920	–	–	–
100	143.54	9.98	69.45	0.811	–	–	–
150	204.69	73.49	65.60	1.000	7.21	113.73	0.833
200	237.10	100.03	74.98	0.984	15.02	140.41	0.923
250	245.72	93.24	73.33	0.974	30.40	141.78	0.997

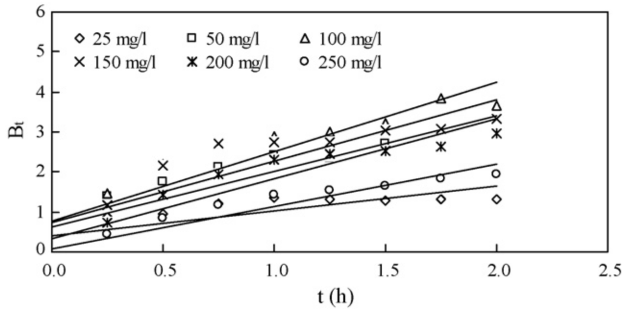

Fig. 10. Boyd plot for adsorption of TCP on prepared activated carbon at 30 °C.

(i) Film diffusion, where adsorbate ions travel towards the external surface of the adsorbent.
(ii) Particle diffusion, where adsorbate ions travel within the pores of the adsorbent excluding a small amount of adsorption that occurs on the exterior surface of the adsorbent.
(iii) Adsorption of the adsorbate ions on the interior surface of the adsorbent.

The third step is considered to be very fast and thus it cannot be treated as rate limiting step. If external transport > internal transport, rate is governed by particle diffusion. If external transport < internal transport, rate is governed by film diffusion and if external transport ≈ internal transport, the transport of adsorbate ions to the boundary may not be possible at a significant rate; thus, formation of a liquid film surrounding the adsorbent particles takes place through the proper concentration gradient [44].

In order to predict the actual slow step involved in the adsorption process, the kinetic data were further analyzed using the Boyd model given by:

$$F = 1 - (6/\pi^2)\exp(-B_t) \tag{18}$$

and

$$F = \frac{q_t}{q_0} \tag{19}$$

where q_0 (mg/g) is the amount of TCP adsorbed at infinite time and q_t (mg/g) is the amount of TCP adsorbed at any time t (h). F represents the fraction of solute adsorbed at any time t and B_t is a mathematical function of F.

Substituting Eq. (19) in Eq. (18), Eq. (18) simplifies to:

$$B_t = -0.4977 - \ln(1 - F) \tag{20}$$

The calculated B_t values were plotted against time t (h), as shown in Fig. 10. The linear lines for all TCP initial concentrations did no pass through the origin and the points were scattered. This indicated that the adsorption of TCP on the prepared activated carbon was mainly governed by external mass transport where particle diffusion was the rate limiting step [45].

4. Conclusions

The present investigation showed that coconut husk-based activated carbon was a promising low-cost adsorbent to be used in the removal of TCP from aqueous solutions over a wide range of concentrations. Adsorption of TCP was found to increase with increase in agitation time and initial concentration while acidic pH was more favourable for the adsorption of TCP. Equilibrium data were fitted to non-linear models of Langmuir, Freundlich, Temkin and Redlich–Peterson, and the equilibrium data were best described by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 716.10 mg/g at 30 °C. R_L values were found to decrease with increase in TCP initial concentration. Kinetic data were tested using the pseudo-first-order, pseudo-second-order kinetic models and Elovich equation. The kinetics of the adsorption process was found to follow the pseudo-second-order kinetic model, suggesting that the adsorption process was controlled by chemisorption. Intraparticle diffusion model was applied to identify the adsorption mechanism. From Boyd plot, it was found that the adsorption of TCP on the prepared activated carbon was mainly governed by particle diffusion. FTIR analysis was conducted on the prepared activated carbon before and after TCP adsorption to study the surface chemistry of the activated carbon. The adsorption potential of the coconut husk-based activated carbon was comparable to commercial activated carbon and some other adsorbents reported in earlier studies.

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