



Equilibrium and kinetics study on the adsorption of perfluorooctanoic acid from aqueous solution onto powdered activated carbon

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ABSTRACT

Powdered activated carbon (PAC) was applied to remove perfluorooctanoic acid (PFOA) from the aqueous PFOA solution in this study. Contact time, adsorbent dose and temperature were analyzed as the effect factors in the adsorption reaction. The contact time of maximum PFOA uptake was around 1 h while the sorption removal efficiency increased with the PAC concentrations. And the process of adsorption increased from 303 K to 313 K and then decreased from 313 K to 323 K. Among four applied models, the experimental isotherm data were discovered to follow Langmuir isotherm model more closely. Thermodynamically, adsorption was endothermic because enthalpy, entropy and Gibbs constants were 198.5 kJ/mol, 0.709 kJ/mol/K and negative, respectively, which also indicated that the adsorption process was spontaneous and feasible. From kinetic analysis, the adsorption was suggested to be pseudo-second-order model. The adsorption of PFOA on the PAC was mainly controlled by particle diffusion.

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1. Introduction

Perfluorinated acids and their salts have been widely used in industry as surfactants for over five decades, especially in the fields of polymer synthesis, photolithography, fire retardants, carpet cleaners and paper coatings [1–3]. As the usage of bioaccumulative [4,5] perfluorinated acids is increasing, some of them, typically, perfluorooctanoic acid (C₇F₁₅COOH; PFOA) have recently been detected in environmental waters, animals, and humans [6–10], even in the zooplankton, Arctic cod, and the seal's tissues of Canadian Arctic. These compounds have been considered to be probable human carcinogens, leading to reproductive toxicity and immune toxicity [11–13].

PFOA, the anthropogenic compound is of high stability, thus the mechanism of its natural decomposition processes remains unknown till now. To alleviate the accumulation of this compound in the environment, development of techniques for eliminating it (as waste, especially in wastewaters) under mild conditions is necessary. The application of conventional treatments for removing PFOA from aqueous solution is restricted by technical and/or economical constraints. PFOAs are not amenable to biological treatment due to their outstanding stability against microbial attack [14,15]. The existed research focused on decomposition by chemical approaches involving strict temperature or pressure

conditions such as sonochemical treatment [16], reduction with zero-valent iron in subcritical water [17] and photocatalysis with various catalysts [18–20]. These treatment technologies present some drawbacks and limitations, mainly due to their high-energy demand and/or strict reaction conditions.

Adsorption is a versatile treatment technique practiced widely for wastewater treatment. Activated carbon adsorption has proved to be the most economical treatment option, particularly in treating low concentrations of wastewater. The systems based on activated carbon can remove a wide variety of toxic pollutants with very high removal efficiencies. Recently, adsorption using powdered activated carbon (PAC) has been receiving a considerable attention for the removal of refractory contaminants from wastewater [21]. Adsorption onto a porous surface is influenced by the nature of adsorbent and its substituent groups. The presence and concentration of the surface functional groups play an important role in the adsorption capacity of the adsorbent and the removal mechanism of the adsorbates. Because the PAC provides superior performance and operational flexibility, the use of PAC for removal of recalcitrant organics has increased in recent years [22]. Although published data on the removal of PFC surfactants are lacking, there is some evidence that non-fluorinated alkyl sulfonated compounds can be adsorbed onto activated carbon [23,24]. And researchers have discovered perfluorinated surfactants adsorbed on some natural adsorbents [25–27].

The objective of this study is to evaluate the usage of PAC as a simple adsorbent for the removal of PFOA from aqueous solutions

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Nomenclature

A	equilibrium binding constant corresponding to the maximum binding energy (L/g)
C_0	initial concentrations of the solute solution (mg/L)
C_e	equilibrium concentrations of the solute solution (mg/L)
F_e	the fraction of solute adsorbed at equilibrium
k_1	rate constant of first-order adsorption (min^{-1})
k_2	rate constant of pseudo-second-order model (g/mg/min)
K_F	Freundlich constants ($\text{mg/g (L/mg)}^{1/n}$)
k_i	intraparticle diffusion rate constant ($\text{mg/g/min}^{0.5}$)
K_L	Langmuir constant related to the affinity of the binding sites (L/mg)
K_{RP}	Redlich–Peterson isotherm constants (L/g)
M	the mass of PAC (g)
n	Freundlich constant
Q	the maximum amount of the adsorbate per unit weight of the adsorbent (mg/g)
q_e	solute uptake at equilibrium (mg/g)
q_t	the amount of adsorbed solute on the PAC at time t (mg/g)
R	the universal gas constant (8.314 J/mol K)
T	absolute solution temperature (K)
V	the volume of the solution (L)
ΔG°	Gibbs constant change (kJ/mol)
ΔH°	enthalpy change (kJ/mol)
ΔS°	entropy change (kJ/mol/K)

by batch experiments. The adsorption isotherm, kinetics, thermodynamics, and mechanism involved in the sorption process are also carried out to lay a theoretical foundation for the liquid/solid phase transport of PFOA in environment.

2. Materials and methods

2.1. Chemicals and adsorbent

Perfluorooctanoic acid (PFOA) was purchased from Fluka in the form of white powder. The purity of PFOA is $\geq 90\%$ (T). The commercially available PAC, supplied by Xinhua Activated Carbon Co. Ltd., China, was used as the adsorbent throughout this study. Before the experiment, PAC was sieved to obtain more than 100 mesh size particles using standard test sieves. Prior to the use of the activated carbon, it was washed by Milli-Q water and dried at 105°C for 24 h, then cooled and stored in a desiccator. Some properties of the PAC were shown in Table 1. Surface area was obtained from N_2 adsorption isotherms at -196°C , which was measured in a quantachrome autosorb system. Samples were outgassed at 300°C for 3 h under a dynamic vacuum of 10^{-6} Torr. Specific surface areas were determined according to the Brunauer Emmet and Teller (BET) method.

Table 1
Properties of the powdered activated carbon (PAC).

Parameters	Value
Particle size (mesh)	≥ 100
Bulk density (g/cm^3)	0.5
Ash content (%)	4.5–5.0
Mechanical strength (%)	90
Specific surface area (m^2/g)	1000

2.2. Batch adsorption studies

Batch adsorption experiments were carried out in series of 250 mL PP Erlenmeyer flasks, containing 100 mL PFOA solution. The PAC was added into these flasks and shaken at 120 rpm for 2 h in a thermostat controlled shaker at a pre-set temperature.

For estimating the optimal amount of adsorbent per unit mass of adsorbate, PFOA solution was contacted with different amount of adsorbents till equilibrium was reached. The effect of adsorbent dose was studied by injection of different doses into 100 mL of 25 mg/L PFOA solution and agitated for equilibrium time. The kinetics of adsorption was determined by analyzing adsorption of PFOA from the aqueous solution at different time intervals. For adsorption isotherms, 0.25 g PAC was suspended in 100 mL of 5–40 mg/L PFOA solution at 313 K. For thermodynamic studies, adsorption of 20 mg/L of PFOA by 0.25 g of PAC was carried out at 293 K and 323 K in the thermostated rotary shaker, respectively. Samples were separated by fast filtration, then diluted 100 times by Milli-Q water, and the concentrations of PFOA at equilibrium (C_e) were determined by LC–MS/MS.

The amount of PFOA adsorbed by the PAC was calculated from the differences between the PFOA quantity added to the PAC and the PFOA content of the supernatant by the following equation:

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

where q_e is the PFOA uptake (mg/g), C_0 and C_e are the initial and final or equilibrium concentrations in the solution (mg/L), respectively, V is the volume of the solution (L) and M is the mass of PAC (g).

2.3. Analytical methods

Analysis of PFOA was performed by a Finnigan Surveyor Plus LC System (HPLC; Thermo Electron, San Jose, CA, USA) consisting of a surveyor autosampler and a surveyor LC Pump. Aliquots of 10 μL of extractions were injected onto a 150 mm \times 2.1 mm Hyperdil Gold C18 column (3- μm pore size, Thermo Hypersil-Keystone, Bellefonte, PA) by the Surveyor auto sampler, and a mobile phase of methanol and 2 mM ammonium acetate aquatic solution was delivered at a flow rate of 250 $\mu\text{L}/\text{min}$ by the Surveyor LC Pump. The percentages of methanol and ammonium acetate aquatic solution were 80% and 20%, respectively. The column and tray temperature were maintained at 30°C and 4°C , respectively, and the total run time was 20 min. The HPLC tubing and internal fluoropolymer parts were identified as the instrumental blanks, therefore, the HPLC tubing made up of polytetrafluoroethylene (PTFE) were replaced with polyetheretherketone (PEEK) tubing and degasser with fluoropolymer coatings was isolated from HPLC. In order to stabilize the retention times of analytes, helium gas was used for degasification of the mobile phase solvents.

For quantitative determination, the HPLC was interfaced to a Finnigan TSQTM quantum accessTM (Thermo Electron, San Jose, CA, USA) triple quadrupole mass spectrometer equipped with electrospray ionization (ESI) source. Electrospray negative ionization was used in the tandem mass spectrometer (MS/MS) ion source. The spray voltage was set at negative 3200 V. Sheath gas pressure, ion sweep gas pressure and auxiliary gas pressure were set at 25 arbitrary units (au), 0 au and 5 au, respectively. Capillary temperature was 320°C . Transitions for all ions were observed using selected reaction monitoring (SRM) mode. The argon gas was used for collision gas and its pressure was optimized to 1.5 mTorr. The collision energy was optimized to 11 eV and 19 eV for transmission of $413 \rightarrow 369$ and $413 \rightarrow 169$, respectively. The limit of detection (LOD) was 1 $\mu\text{g}/\text{L}$.

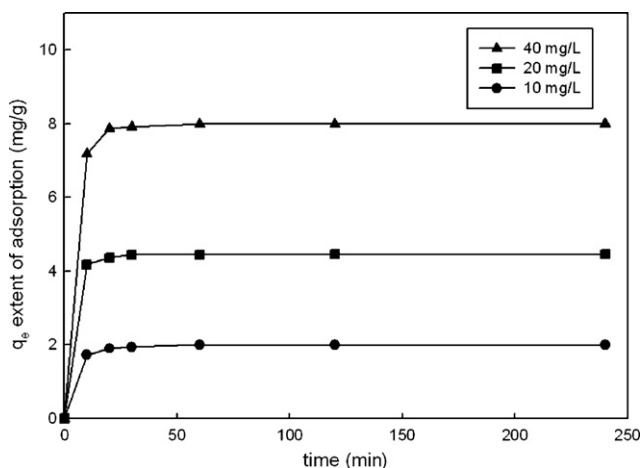


Fig. 1. Effect of various initial PFOA concentrations on the adsorption of PFOA onto PAC (T , 298 K; V , 100 mL; PAC, 0.5 g; agitation rate, 120 rpm).

2.4. Adsorption isotherms

It is important to establish the most appropriate correlation for the equilibrium curves. The most commonly applied isotherms in solid/liquid system are the theoretical equilibrium isotherms, i.e. Langmuir, the Freundlich, the Raedlich and Peterson, and Tempkin. In this study, these four isotherms were applied to the equilibrium data of adsorption of PFOA on powder activated carbon. The linear regression was used to determine the most suitable model among these four isotherms.

2.5. Adsorption kinetics

The kinetic of adsorption describes the rate of PFOA uptake on the powder activated carbon. The kinetic parameters are helpful for the prediction of adsorption rate, which provides important information for modeling the processes. Successful application of the adsorption technique demands development of inexpensive, non-toxic, readily available adsorbents of known kinetic parameters and sorption characteristics. Therefore, kinetic models were used to analyze the adsorption data: the pseudo-first-order, pseudo-second-order and Elovich equations.

3. Results and discussion

3.1. Effect of contact time

Adsorption experiments lasted for over 240 min to find the optimum contact time. The effect of contact time on the removal rate of PFOA by powder activated carbon is shown in Fig. 1. The results indicate that the maximum adsorption takes place during the first hour. In this stage, 90% of the PFOA was adsorbed. This phenomenon was due to surface adsorption and in this stage, the surface is free and reaction proceeds at a fast rate.

3.2. Effect of adsorbent dosage

To study the effect of adsorbent dosage on the kinetics of adsorption, the dosage of adsorbent was varied from 1 g/L to 10.0 g/L, the initial PFOA concentration was maintained at 20 mg/L at the temperature of 298 K. The results are shown in Fig. 2. As expected, the removal efficiency increased with PAC concentration. Indeed, the removal rate increased from 51.1% to 99.9%, as the PAC concentration increased from 0.1 g/L to 10.0 g/L. Such a trend may be due to the availability of more surface area. However, the decrease in PFOA

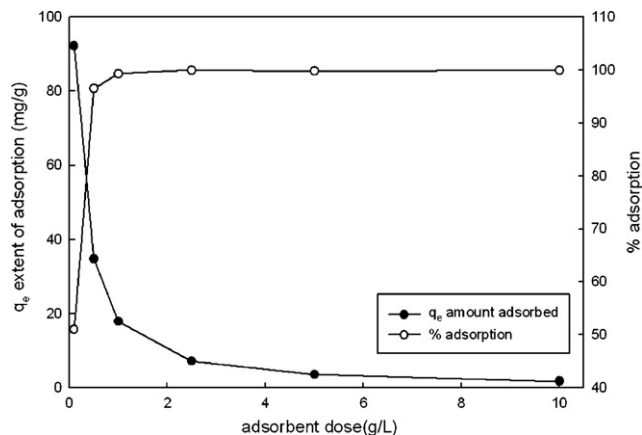


Fig. 2. Effect of PAC dosage on the adsorption of PFOA onto PAC (T , 298 K; pH, 6.1; C_0 , 20 mg/L; V , 100 mL; agitation rate, 120 rpm).

adsorption quantity from 92.2 mg/g to 1.8 mg/g with the increase in the PAC dose can be attributed to the reduction in the available substrate for the adsorbent and consequently effective surface area.

3.3. Effect of temperature

To study the effect of temperature on the kinetics of adsorption, the initial PFOA concentration was varied from 10 to 40 mg/L at three different temperatures, i.e. 303 K, 313 K and 323 K. The results of experiments at different initial concentrations and different temperatures are listed in Fig. 3 and indicate that adsorption increases from 303 K to 313 K and then starts to drop from 313 K to 323 K. This observation can be explained with the help of the following facts, i.e. the diffusion rate of PFOA molecules increases with the temperature, which results in the opening of greater number of active sites for the PAC surface. Thus, the adsorption increases with increasing temperature. The decrease in PFOA uptake with higher adsorption temperature from 313 K to 323 K is mainly due to two effects. One is that the solubility of PFOA increases with temperature, which reduces hydrophobic interactions. The other is the increase in vibrational energy of the adsorbed PFOA molecules at higher temperatures, so that more PFOA molecules have sufficient energy to overcome the attractive force and desorb back into solution [28,29].

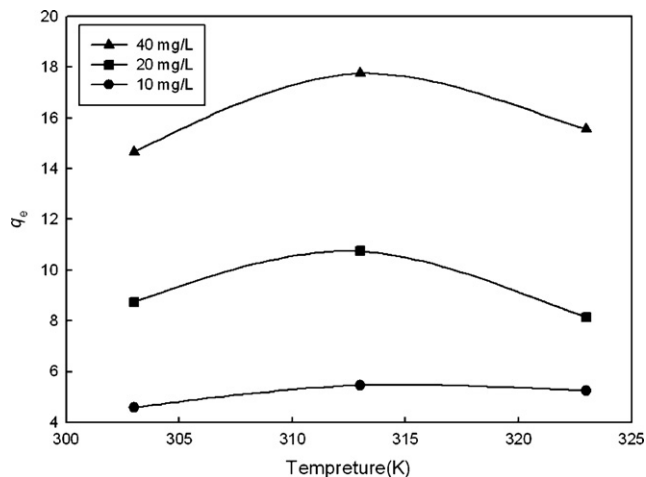


Fig. 3. Effect of temperature on the adsorption of PFOA onto PAC (T , 298 K; V , 100 mL; agitation rate, 120 rpm).

3.4. Adsorption isotherms

In order to optimize an adsorption system, it is important to establish the most appropriate correlation for the equilibrium curves. In this study, four adsorption isotherms named Langmuir, Freundlich, Temkin and Redlich–Peterson (R–P) isotherms in their non-linear forms were applied to the equilibrium data of adsorption of PFOA onto PAC.

The Langmuir equation is valid for monolayer sorption on the surface with a finite number of identical sites and is expressed as [30]:

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

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, K_L (L/mg) is Langmuir constant related to the affinity of the binding sites.

Freundlich model is an empirical equation based on sorption on the heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and the binding strength decreases with the increasing degree of site occupation. The isotherm is expressed as [31]:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F (mg/g (L/mg)^{1/n}) and n are Freundlich constants related to sorption capacity and sorption intensity of the adsorbent, which represent the quantity of PFOA 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 [32].

Temkin isotherm contains a factor that adsorbent–adsorbate interactions are taken into account explicitly [33]. 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. The Temkin isotherm is expressed as:

$$q_e = \left(\frac{RT}{b_T} \right) \ln(AC_e) \quad (4)$$

where $RT/b_T = B$ (J/mol), which is the Temkin constant related to heat of sorption, 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 is widely used as a compromise between Langmuir and Freundlich systems [34]. This model has three parameters and incorporates the advantageous significance of both models. R–P model can be represented as follows:

$$q_e = \frac{K_{RP} C_e}{1 + (\alpha C_e)^\beta} \quad (5)$$

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

All the correlation coefficient, R^2 values and the constants obtained for the models are summarized in Table 2. 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 PFOA on the activated carbon. And this suitability of the Langmuir isotherm to fit the data was confirmed by the value of exponent " β " calculated from Redlich–Peterson plots were found close to 1, which tends this model towards Langmuir model. The $1/n$ value from Freundlich model, which was below 1, also indicated a normal Langmuir isotherm.

Table 2

Isotherm constants for the Langmuir, Freundlich, Temkin and Redlich–Peterson (R–P) isotherm.

Isotherms	Parameters
Langmuir	$Q = 16.502$ mg/g $K_L = 0.606$ L/mg $R^2 = 0.997$
Freundlich	$K_F = 24.238$ mg/g (L/mg) ^{1/n} $1/n = 0.450$ $R^2 = 0.959$
Temkin	$A = 5.066$ L/g $B = 3.341$ J/mol $R^2 = 0.976$
Redlich–Peterson	$K_{RP} = 17.508$ L/g $\alpha = 0.179$ (L/mg) ^{1/β} $\beta = 0.681$ $R^2 = 0.998$

3.5. Thermodynamic parameters

The thermodynamic parameters for the adsorption process, ΔH° and ΔS° , were evaluated by the Van't Hoff equation:

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (6)$$

where ΔH° and ΔS° are the enthalpy (kJ/mol) and entropy (kJ/mol/K) change of adsorption, respectively, R is universal gas constant (8.314 J/mol/K), and T is the absolute temperature (K).

The values of $\log K_c$ were defined as follows [35]:

$$\log K_c = \frac{F_e}{1 - F_e} \quad (7)$$

where F_e is the fraction of PFOA adsorbed at equilibrium.

The value of ΔH° and ΔS° were calculated from the slope and intercept of linear regression of $\log K_c$ versus $1000/T$. The plot shown in Fig. 4 is linear at the range of temperature investigated. And the value of ΔG° was estimated by:

$$\Delta G^\circ = -RT \ln K_c \quad (8)$$

the calculated thermodynamic parameters such as ΔH° , ΔS° and ΔG° are given in Table 3.

At all temperatures, the values of ΔG° are negative, which indicates that PFOA adsorption onto PAC is spontaneous. The more negative values of ΔG° imply a greater driving force to the adsorption process. As the temperature increases from 293 K to 323 K, the

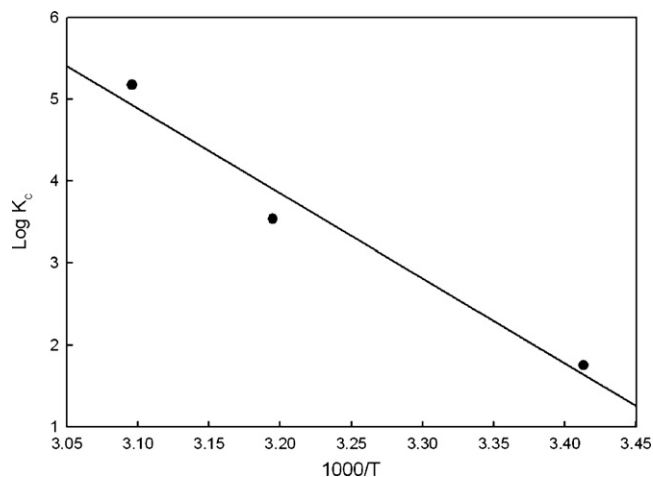


Fig. 4. Plot of $\log K_c$ versus $1000/T$ for the estimation of thermodynamic parameters for the adsorption of PFOA onto PAC.

Table 3
Thermodynamic parameters for the adsorption of PFOA onto PAC.

ΔH° (kJ/mol)	ΔS° (kJ/mol/K)	ΔG° (kJ/mol)		
		293 K	313 K	323 K
198.5	0.709	-15.07	-33.91	-44.15

ΔG° values decrease, indicating less driving force and hence resulting in lesser adsorption capacity at higher temperatures [36]. This result is also corresponding with the conclusion drawn by Fig. 3. The adsorption process is endothermic, which can be justified by the fact that the value of ΔH° is positive. Further, the positive value of the entropy change suggests the increased randomness at the solid–solution interface during the fixation of the PFOA on the active sites of PAC [37]. Since the adsorption process is endothermic, under these conditions the process becomes spontaneous because of the positive entropy change.

3.6. Adsorption kinetics modeling

The kinetic of adsorption describes the rate of PFOA uptaken 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. In order to investigate the controlling mechanism of adsorption processes such as transfer and chemical reaction, three different kinetic models: the pseudo-first-order model; pseudo-second-order model and Elovich equations are applied to model the kinetics of PFOA adsorption onto PAC.

3.6.1. Pseudo-first-order model

The pseudo-first-order equation is

$$\frac{dq}{dt} = k_1(q_e - q) \quad (9)$$

after integrating with the initial conditions, rate expression of Lagergren is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (10)$$

where q_t (mg/g) is the amount of adsorbed PFOA on the PAC at time t , k_1 (min^{-1}) is the rate constant of first-order adsorption, q_e the equilibrium sorption uptake, is extrapolated from the experimental data at time $t = \infty$. A straight line of $\log(q_e - q_t)$ versus t suggests the applicability of this kinetic model. q_e and k_1 were determined from the intercept and slope of the plot, respectively.

3.6.2. Pseudo-second-order model

The pseudo-second-order equation is [38]

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (11)$$

after integrating with the initial conditions, the form can be obtained as:

$$\frac{t}{q} = \frac{1}{(k_2 q_e)^2} + \frac{t}{q_e} \quad (12)$$

Table 4
Comparison of the pseudo-first-order model, pseudo-second-order model and Elovich equations adsorption rate constants and calculated and experimental q_e values for different initial concentrations.

Initial PFOA concentrations (mg/L)	$q_{e, \text{exp}}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model			Elovich equations			
		$q_{e, \text{cal}}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e, \text{cal}}$ (mg/g)	k_2 (g/mg/min)	R^2	$q_{e, \text{cal}}$ (mg/g)	a	b	R^2
5	1.144	0.878	0.126	0.979	1.212	0.348	1.000	1.185	1.525	5.893	0.955
10	2.680	2.300	0.177	0.965	2.802	0.269	0.999	2.745	25.590	3.367	0.909
15	5.672	5.790	0.111	0.998	5.618	0.088	0.997	5.882	0.729	0.699	0.955
20	7.216	8.763	0.261	0.995	7.5553	0.170	0.999	7.715	13.860	0.955	0.789

where k_2 (g/mg/min) is the rate constant of pseudo-second-order model. The plot t/q versus t giving a straight line, pseudo-second-order kinetics applicable and q_e and k_2 were determined from the slope and intercept of the plot, respectively.

3.6.3. Elovich equations

Elovich equation is one of the most useful model for describing activated adsorptions. After arrangement and simplification, Elovich equations can be expressed as below [39]:

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln t \quad (13)$$

In this study, we take the above three equations to simulate the kinetic of the adsorption reaction. The adsorption rate constants were determined at different initial PFOA concentrations by the pseudo-first-order model, pseudo-second-order model and Elovich equations, and the results were listed in Table 4. The value of the correlation coefficient R^2 for the pseudo-second-order model was ≥ 0.997 for all PFOA concentrations, and the adsorption capacities calculated by the model are also close to those determined by experiments. These results indicate that it is feasible for the applicability of the second-order kinetic model to describe the adsorption process of PFOA on the PAC.

3.7. Adsorption mechanisms

It is important to predict the rate-limiting step in an adsorption process to understand the mechanism of the sorption. Generally, for a solid–liquid sorption process, three steps are involved in the adsorption process as following [40]:

1. Film diffusion, which involves the movement of adsorbate molecules from the bulk of the solution towards the external surface of the adsorbent.
2. Particle diffusion, where the adsorbate molecules move in the interior of the adsorbent particles.
3. Sorption of the adsorbate molecules on the interior of the porous adsorbent.

According to Crank [41], the third step being very rapid for adsorption of organic compounds on porous adsorbent, does not represent the rate-limiting step. Therefore, the third step can be negligible. The slowest step determines the rate-controlling parameter in the adsorption process. However, the rate-controlling parameter might be distributed between particle and film diffusion mechanisms. If external transport > internal transport, rate is governed by particle diffusion. If external transport < internal transport, rate is governed by film diffusion. So it is important to distinguish between film diffusion and particle diffusion.

The intraparticle diffusion equation can be described as:

$$q_t = k_i t^{0.5} \quad (14)$$

where k_i is the intraparticle diffusion rate constant ($\text{mg/g}/\text{min}^{0.5}$), the results for the system are shown in Fig. 5. It has been observed that all plots have an initial curved portion and final linear portion.

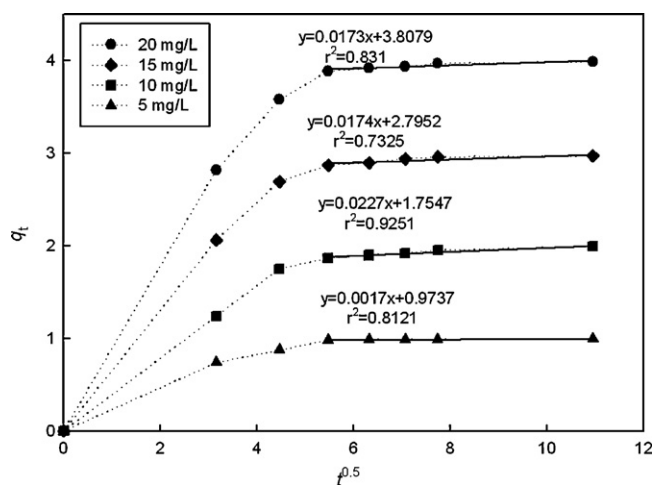


Fig. 5. Plot of intraparticle diffusion model for adsorption of PFOA onto PAC (T , 298 K; V , 100 mL; PAC, 0.5 g; agitation rate, 120 rpm).

The two regions in the q_t versus $t^{0.5}$ plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion. The initial curved portion is due to the PFOA diffused through the solution to the external surface of PAC or the boundary layer diffusion. And followed linear portion represents the gradual adsorption stage, in which intraparticle diffusion of PFOA on PAC takes place. k_i values were determined by the slope of the straight-line portion of plots. On the other hand, the intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate-controlling step. And it can be seen that the linear portions did not pass through the origin, which indicates the intraparticle diffusion was not the only rate-controlling step.

And the slow step in this system can be examined by Bahangam's equation which is used to describe particle diffusion during adsorption process [42]:

$$\log \log \left(\frac{c_0}{c_0 - q_t M} \right) = \log \left(\frac{k_0 M}{2.303 V} \right) + \alpha \log t \quad (15)$$

where c_0 is the initial concentration of the adsorbate in solution (mg/L), V is the volume of the solution (mL), M is the weight of adsorbent used per liter of solution (g/L), q_t is the amount of adsorbate retained at time t (mg/g), α (<1) and k_0 which are constants of the system were examined. The plot $\log \log(c_0/(c_0 - q_t M))$ ver-

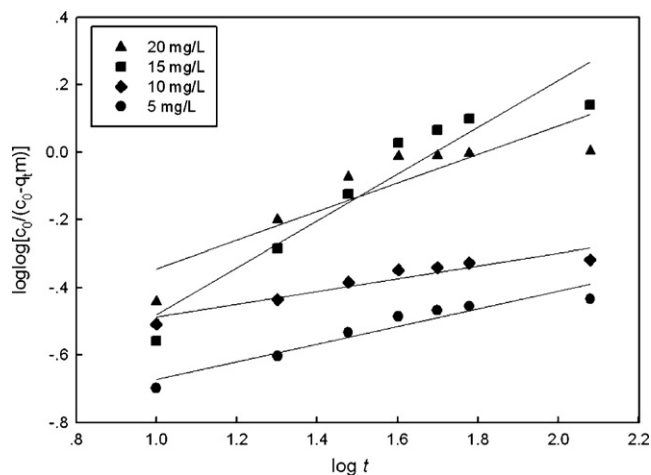


Fig. 6. Plot of Bahangam's equation for adsorption of PFOA onto PAC (T , 298 K; V , 100 mL; agitation rate, 120 rpm).

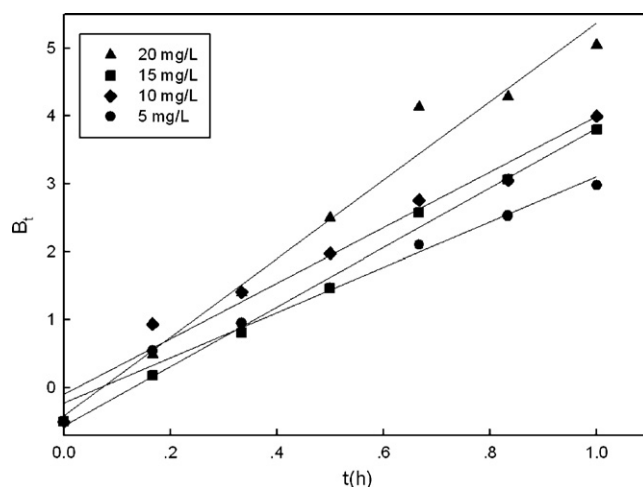


Fig. 7. Boyd plot for the adsorption of PFOA onto PAC (T , 298 K; V , 100 mL; agitation rate, 120 rpm).

sus $\log t$ is shown in Fig. 6. The plot gives a straight line showing that kinetics confirmed to Bahangam's equation and therefore the adsorption of PFOA on PAC was particle diffusion controlled.

In order to further identify the controlling step in the sorption process, adsorption kinetic data were also analyzed by the procedure given in the Boyd model. Boyd equation contains one single constant, B_t , the value of which was determined by the ratio of the internal diffusion constant, for the particle to the square of the particle radius. Boyd equation described the diffusion in and through the adsorbent particle, which is particle diffusion. The description of equation is as below [43]:

$$F = 1 - \left(\frac{6}{\pi^2} \right) \exp(-B_t) \quad (16)$$

and

$$F = \frac{q_t}{q_e} \quad (17)$$

where q_e (mg/g) is the amount of PFOA adsorbed at equilibrium time and q_t (mg/g) is the amount of PFOA 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 .

From above two equations, Boyd model can be expressed as below:

$$B_t = -0.4977 - \ln(1 - F) \quad (18)$$

The calculated B_t values were plotted versus time t (h), as shown in Fig. 7. The linear lines for all PFOA concentrations move towards the origin which indicates the particle diffusion to be the rate-controlling parameter [36]. This conclusion was in accordance with the result tested by Bahangam's equation.

4. Conclusions

The present research strongly indicates that the PAC can be used as an effective, economic and favorable adsorbent for the removal of PFOA from aqueous solution.

1. At the experimental condition the adsorption reaction reaches equilibrium within 60 min in all cases. Under the prevailing conditions, the maximum PFOA removal tended to be 99%.
2. The equilibrium data are best fitted to Langmuir isotherm model.
3. Thermodynamic parameters (ΔH° , ΔS° and ΔG°) are determined and their values indicate that the adsorption process is spontaneous and endothermic in nature. As the temperature increases from 293 K to 323 K, the ΔG° values decrease,

indicating less driving force and hence resulting in lesser adsorption capacity at higher temperatures. The positive value of the entropy change suggests the increased randomness at the solid–solution interface during the fixation of the PFOA on the active sites of PAC.

4. The pseudo-first-order model, pseudo-second-order model and Elovich equations are applied to identify the kinetics of PFOA adsorption onto PAC. The result proves that the adsorption of PFOA on PAC follows pseudo-second-order kinetics.
5. The adsorption of PFOA on the PAC is mainly governed by particle diffusion.
6. Above results indicate that PAC sorption is a promising treatment for the removal of PFOA from dilute aqueous streams.

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