



Equilibrium, kinetic and thermodynamic studies on the adsorption of 2-nitroaniline onto activated carbon prepared from cotton stalk fibre

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ABSTRACT

Activated carbon prepared from cotton stalk fibre has been utilized as an adsorbent for the removal of 2-nitroaniline from aqueous solutions. The influence of adsorbent mass, contact time and temperature on the adsorption was investigated by conducting a series of batch adsorption experiments. The equilibrium data at different temperatures were fitted with the Langmuir, Freundlich, Tempkin, Redlich–Peterson and Langmuir–Freundlich models. The Langmuir–Freundlich isotherm was found to best describe the experimental data. The adsorption amount increased with increasing temperature. The maximum adsorption capacity of 2-nitroaniline was found to be 383 mg/g for initial 2-nitroaniline concentration of 200 mg/L at 45 °C. The kinetic rates were modeled by using the Lagergren–first-order, pseudo-second-order and Elovich models. The pseudo-second-order model was found to explain the adsorption kinetics most effectively. It was also found that the pore diffusion played an important role in the adsorption, and intraparticle diffusion was the rate-limiting step at the first 30 min for the temperatures of 25, 35 and 45 °C. FTIR and ¹³C NMR study revealed that the amino and isocyanate groups present on the surface of the adsorbent were involved in chemical interaction with 2-nitroaniline. The negative change in free energy (ΔG°) and positive change in enthalpy (ΔH°) indicated that the adsorption was a spontaneous and endothermic process.

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1. Introduction

2-Nitroaniline is an important compound used as an intermediate or precursor in the manufacture of organic synthesis, such as azo dyes, latex, paint, pesticide and medicine. However, the presence of 2-nitroaniline in water even at a very low level would be harmful to aquatic life and human health in terms of its toxicity, potential carcinogenic and mutagenic effects [1]. Molecules derived from 2-nitroaniline are also very toxic and biorefractory [2]. So it has been identified as priority pollutants by US Environmental Protection Agency [3]. The widespread uses of 2-nitroaniline, which is little dissolvable and often at low concentrations in water, have resulted in environment contamination and public health problems. Therefore, the purification of wastewater polluted with 2-nitroaniline is a great challenge to environmental scientists and engineers, and the novel and cost-effective 2-nitroaniline removal technologies have to be developed.

Some methods such as advanced oxidation processes, biodegradation or adsorption have been employed to remove nitroanilines from water [2,4,5]. Among these methods, adsorption on activated

carbon has long been recognized to be one of the most effective methods for the removal of organic compounds from dilute aqueous solutions. However, commercially available activated carbon is still considered as expensive materials for many countries due to the use of non-renewable and relatively expensive starting material such as coal [6,7]. Therefore, in recent years, it has prompted a growing research interest in the production of activated carbon from renewable and cheaper precursors which are mainly agricultural by-products, such as corncob [8], rattan sawdust [9], rice straw [10], apricot shell [11], jute fibre [12], rubber wood sawdust [13,14], bamboo [15] and oil palm fibre [16].

Cotton is the main crop in China, and the planting area is more than 5.5 million hectare, and it is estimated that more than 20 million tonnes (dry weight) of cotton stalk are generated annually [17]. In order to make better use of the cheap and abundant agricultural by-products, it is proposed to make it into activated carbon. Production of activated carbon from agricultural by-products serves a double purpose. First, unwanted surplus agricultural waste is converted to useful value-added adsorbents, and second, the use of agricultural by-products provides a potential adsorbent for the removal of organic pollutants from wastewater.

In this study activated carbon was prepared from cotton stalk fibre and used as an adsorbent for the removal of 2-nitroaniline from dilute aqueous solutions. Effects of parameters such as adsor-

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bent mass, contact time and temperature of the solution on the adsorption process have been investigated. Equilibrium adsorption data have been fitted to five different isotherm equations to determine the best isotherm model to represent the experimental adsorption data. Three simplified kinetic models including Lagergren-first-order equation, pseudo-second-order equation and Elovich equation were used to determine the mechanism of adsorption. The thermodynamic parameters such as standard free energy, enthalpy, and entropy were also evaluated.

2. Experimental

2.1. Adsorbent

2.1.1. Preparation of adsorbent

The precursor used for the production of adsorbent was cotton stalk. A certain amount of raw cotton stalk fibre provided by Hubei Chemical Fiber Co., China was soaked with 4% potassium dihydrogen phosphate solution at impregnation ratio of 1:60 for 20 min. After drying in an oven at 105 °C, the dried cotton stalk fibre was stabilized in a stainless steel vertical tubular reactor placed in a tube furnace for 30 min at 250 °C. The carbonization of the cotton stalk fibre was carried out under a high purity nitrogen flow of 80 cm³/min by raising the temperature at a rate of 10 °C/min to 600 °C, and maintaining the temperature for 30 min. Thereafter, the gas flow was switched to water steam and activation was carried out at 800 °C for 20 min. At last, the activated product was cooled to room temperature under nitrogen flow.

2.1.2. Pretreatment of adsorbent

The cotton stalk activated carbon was boiled and washed three times in distilled water and dried at 105 °C for 24 h before being used as adsorbent. The pore structures of the activated carbon were investigated by using a computer controlled automated porosimeter (Micromeritics ASAP-2020, America). Nitrogen was used as the cold bath (77 K) and classical adsorption models BET theory was used. The porous structural parameters used in this paper were taken from BJH data. The pH at the point of zero charge (pH_{pzc}) of cotton stalk activated carbon was determined by batch equilibrium method described by Babic [18]. The elemental analysis of the activated carbon was obtained from a CHN-O-Rapid Elemental Analytical Instrument (Elementer, Germany).

2.2. Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR)

The surface functional groups of the activated carbon before and after adsorption were detected by FTIR (NEXUS870, America-Nicolet) and NMR (Avance 300, German-Bruker) spectra.

2.3. Scanning electron microscopy

A scanning electron microscope (Hitachi S4800, Japan) was used to visualize the surface morphology and structure of cotton stalk activated carbon before and after adsorption of 2-nitroaniline.

2.4. Chemicals

All the reagents used were of analytical grade and without further purification. The chemicals used in this study, i.e., phosphate, hydrochloric acid, sodium hydroxide, ammonium chloride and 2-nitroaniline, were purchased from Shanghai Chemical Reagent Co., China. 2-nitroaniline solution (200 mg/L) was prepared by dissolving required amount of 2-nitroaniline in distilled water in the adsorption test.

2.5. Adsorption studies

In batch adsorption experiments, certain amounts of the activated carbon was added into several 250 mL Erlenmeyer flasks, each containing 100 mL solution (200 mg/L 2-nitroaniline). And then the flasks were shaken at 150 rpm in a constant temperature shaker (Shanghai Scientific Instrument Co. Ltd., China) at a pre-settled temperature for 48 h. Samples were separated by a fast filtration, and then concentrations of 2-nitroaniline at equilibrium (C_e) were determined.

Different mass of adsorbent (0.02–0.13 g) was introduced to respective 100 mL 200 mg/L 2-nitroaniline solution at 15, 25, 35 and 45 °C, respectively, in order to determine adsorption isotherms and evaluate the effect of adsorbent mass. Batch experiments were conducted at different periods by adding 0.5000 g adsorbent into each 500 mL 2-nitroaniline solution, respectively, at 15, 25, 35 and 45 °C to evaluate adsorption kinetic and the effect of time on 2-nitroaniline adsorption.

The adsorbent phase concentrations of 2-nitroaniline (q_e) were calculated according to the following equation:

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

where C_0 and C_e are the initial and equilibrium concentrations of 2-nitroaniline (mg/L), respectively, V is the volume of the solution (L), and W is the mass of adsorbent (g).

2.6. Analysis

The concentrations of 2-nitroaniline were analyzed by using a Helios Beta UV-vis spectrometer (Unicam Co., UK) that gave good linearity for the absorbency versus 2-nitroaniline concentration at its maximum absorbency wavelength 223 nm.

3. Results and discussion

3.1. Characteristics of the adsorbent

The BET surface area (S_{BET}), t -Plot micropore area (S_{micro}), external surface area (including mesopores and macropores area S_{ext}), total pore volume (V_t), micropore volume (V_{micro}) and average pore width (D_w) are given in Table 1. It was found that the activated carbon had a remarkable BET surface area, which was primarily contributed by micropores. The average pore diameter was 2.073 nm, indicative of its micropores character defined by IUPAC (International Union of Pure & Applied Chemistry).

Fig. 1 shows the pore size distribution calculated in the standard manner by using BJH method. Percentage of micropores area and volume is 71.8% and 73.8% respectively, further showing that the activated carbon is dominantly micropores.

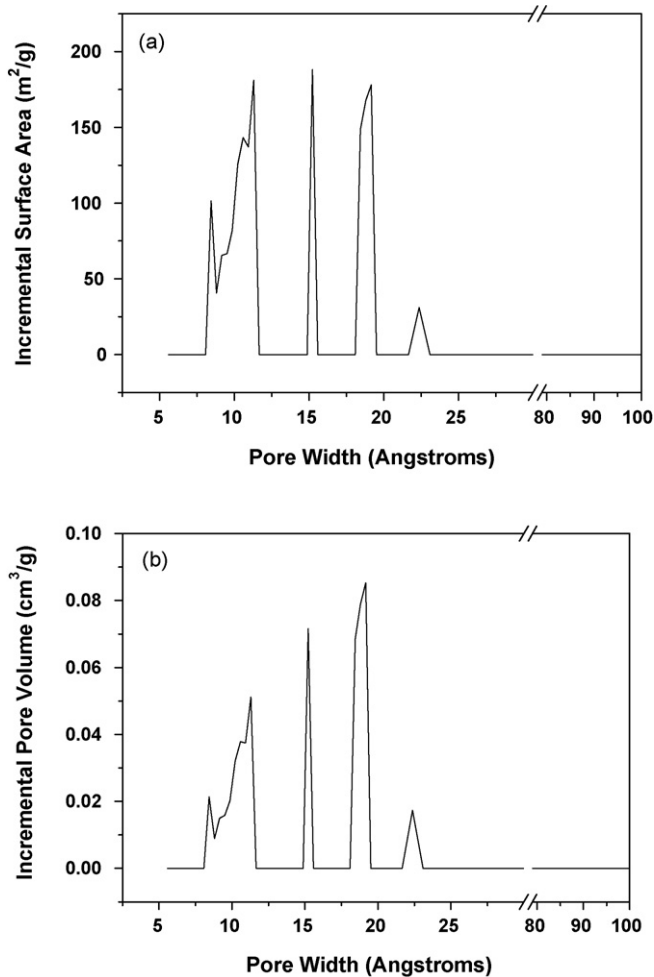
3.2. Fourier transform infrared spectroscopy (FTIR) before and after 2-nitroaniline adsorption

The FTIR spectra of carbon before and after 2-nitroaniline adsorption are shown in Fig. 2. The FTIR spectra of the adsorbent before adsorption indicated the presence of isocyanate (N=C=O) and amino groups (N-H). The peak at 2278 cm⁻¹ was assigned to the stretching bands of isocyanate groups (N=C=O), and the amino stretch (N-H) could be ascribed to the bend that appeared at 3430 cm⁻¹ [19–21]. On the other hand, the peak appeared at 1563 cm⁻¹ was the results of carbonyl groups (C=O), and the broad band at 1167 cm⁻¹ that represents haloalkyl groups (C-H) [19,22]. From Fig. 2, the peak intensity after adsorption at 3430 cm⁻¹ as well as 2278 cm⁻¹ was slightly lower than that before adsorption, suggesting that the isocyanate and amino groups played an important role in the adsorption [19–21].

Table 1

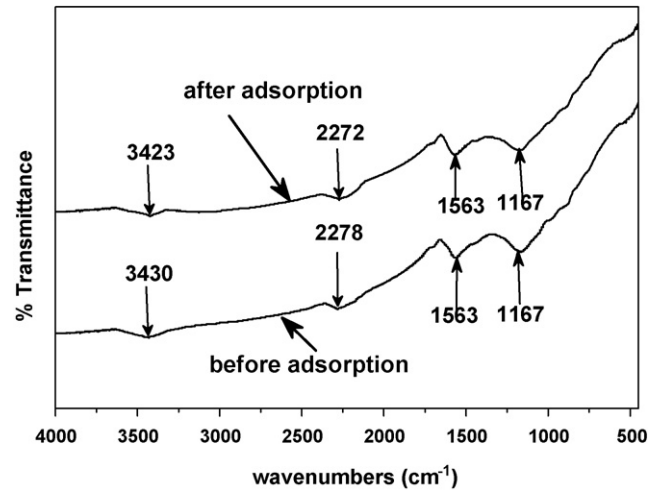
Main characteristics of cotton stalk activated carbon.

Parameters	S_{BET} (m ² /g)	S_{micro} (m ² /g)	S_{ext} (m ² /g)	V_t (cm ³ /g)	V_{micro} (cm ³ /g)	D_w (Å)	Bulk (g/cm ³)	pH _{pzc}	Elemental analysis (wt.%)			
									C	H	N	O
Values	1287	924	363	0.667	0.492	20.73	0.04	5.6	86.29	0.42	3.07	10.22

**Fig. 1.** Pore size distributions of cotton stalk activated carbon by DFT method.

3.3. Scanning electron microscopy (SEM) before and after 2-nitroaniline adsorption

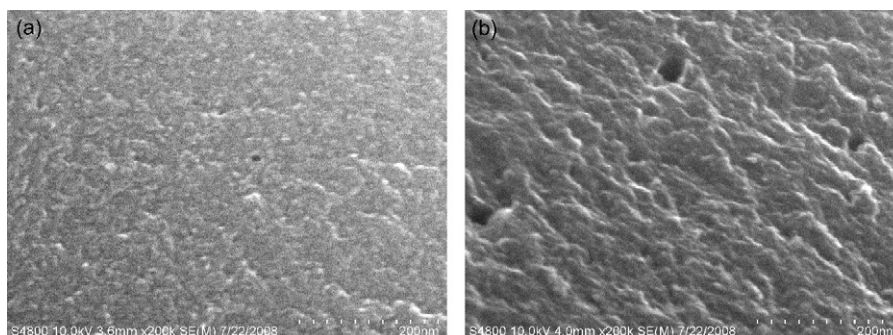
The SEM photographs of cotton stalk activated carbon before and after 2-nitroaniline adsorption are shown in Fig. 3. It was found

**Fig. 2.** FTIR spectra of cotton stalk activated carbon before and after 2-nitroaniline adsorption.

that the surface of cotton stalk activated carbon after 2-nitroaniline adsorption had many holes and looked rougher. Tansel and Nagaranjan [23] also found that the percentage of rough area on the external surface of granular activated carbon increased more than 70%. Tang et al. [24] explained this phenomenon as heterogeneous energy distribution of the activated adsorption sites on activated carbon surface.

3.4. Effects of temperatures and contact time

As we known, temperature has great effect on the adsorption process. Adsorption experiments were carried out for different contact time at different temperature by adding 0.5000 g adsorbent into each 500 mL 2-nitroaniline solution at natural pH. The results are shown in Fig. 4. It was found that equilibrium adsorption amount q_e increased from 188 mg/g to 233 mg/g with the increase of temperature from 15 to 45 °C, which indicated that the adsorption process was endothermic. This could result from two possible reasons. Firstly, intraparticle diffusion rate of adsorbate molecule into the pores increased with increasing temperature since diffusion was an endothermic process [25]. Secondly, it might be due to the increase in chemical interaction between adsorbate and surface

**Fig. 3.** The SEM photographs of cotton stalk activated carbon (a) before 2-nitroaniline adsorption (200 nm) and (b) after 2-nitroaniline adsorption (200 nm).

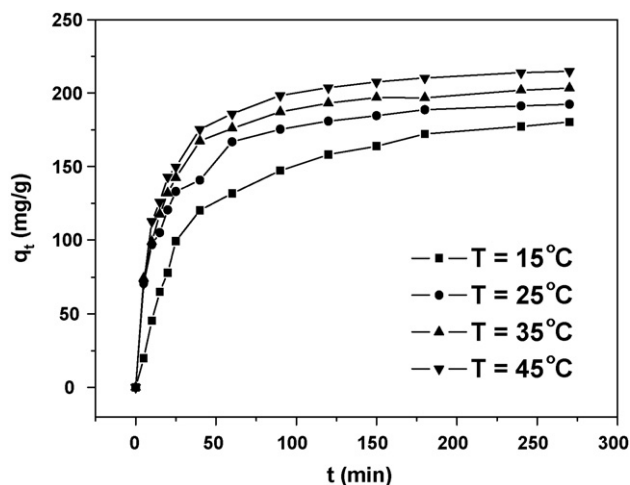


Fig. 4. Effect of temperature and time on 2-nitroaniline adsorption ($V_0 = 500$ mL; $C_0 = 200$ mg/L; $T = 15$ – 45 °C; adsorbent mass = 0.5000 g/500 mL; pH 7).

functionalities of adsorbent [26,27]. Marinovic et al. [27] found that physical adsorption predominated with temperature increasing up to 20 °C while the contribution of chemisorption became increasingly large with temperature increasing from 25 to 50 °C. On the other hand, shifts of the FTIR spectrum peaks for carbon surface after adsorption towards lower wavenumbers, suggested that chemisorption took place. Furthermore, the ^{13}C NMR spectra of the adsorbents before and after 2-nitroaniline adsorption were carried out. The major three peaks of the ^{13}C NMR spectra before adsorption were near 59 ppm (substituted saturated carbons), 123 ppm (olefinic and aromatic carbons), 189 ppm (carbonyls and allenes) [19]. Compared to the carbons before and after adsorption, the shift of peak intensity of the ^{13}C NMR spectra from 123 ppm to 120 ppm, and the appearance of new peak of the ^{13}C NMR spectra at 107 ppm further supported chemisorption mechanism.

From Fig. 4, it was also found that the adsorption curves of 2-nitroaniline varying with contact time at four different temperatures had similar trends. The curves could be divided into three parts. In the first 25 min, almost 70% of the adsorption occurred at temperatures of 25 , 35 and 45 °C, and 50% of the adsorption did at temperature of 15 °C. In the second part ($25 \text{ min} < t < 60 \text{ min}$), the slopes became gentle as 20% adsorption occurred. In the third part ($t > 60 \text{ min}$), the adsorption amount q_t was steady and the adsorption reached equilibrium. The initial faster increase of adsorption amount q_t may due to the large number of most active site available. The slower adsorption at the end is probably due to the saturation of active sites and decrease of 2-nitroaniline concentrations.

3.5. Effects of adsorbent mass

Fig. 5 shows the effect of adsorbent mass on the adsorption. The results showed that increasing the carbon mass increased the percent removal ($R\%$) but decreased the adsorption capacity. There are two factors, which can contribute to this adsorbent mass effect: (i) as the dosage of adsorbent is increased, the adsorption sites remain unsaturated during the adsorption reaction leading to drop in adsorption capacity [28]; (ii) the aggregation/agglomeration of adsorbent particles at higher mass, which would lead to a decrease in the surface area and an increase in the diffusional path length [29].

3.6. Equilibrium isotherms

Adsorption isotherms describe qualitative information on the nature of the solute–surface interaction as well as the specific

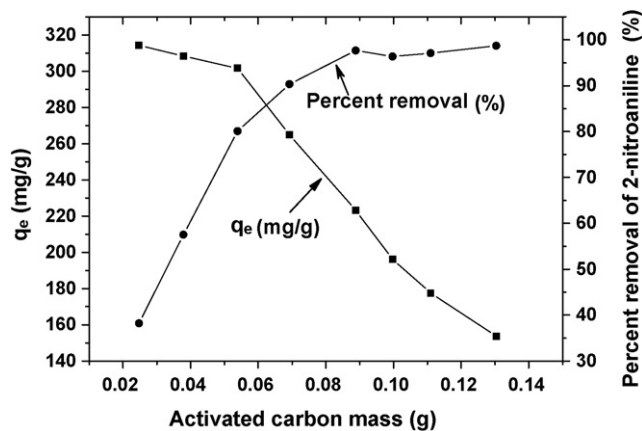


Fig. 5. Effect of adsorbent mass on adsorption ($V_0 = 100$ mL; $C_0 = 200$ mg/L; $T = 25$ °C; adsorbent mass = 0.0200 – 0.1300 g/100 mL; contact time = 24 h; pH 7).

relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. The equilibrium experiment was studied in the temperature range of 15 – 45 °C, adsorbent mass: 0.2 – 1.3 g/L, C_0 : 200 mg/L. The results are shown in Fig. 6.

In order to understand the adsorption mechanisms of 2-nitroaniline onto the activated carbon, five adsorption isotherm models, Langmuir, Freundlich, Tempkin, Redlich–Peterson and Langmuir–Freundlich, were used to fit the experimental data. These isotherm equations are given in Table 2. For determining the five isotherm parameters by using non-linear regression, Origin version 7.0, a window based statistical software, was used. Different adsorption isotherms obtained at various temperatures are illustrated in Fig. 7. The values of the parameters and the correlation coefficients obtained at various temperatures are listed in Table 3.

It is well known that the Langmuir model is usually used with an ideal assumption of an monolayer adsorption surface [30]; the Langmuir–Freundlich model is usually used with a heterogeneous adsorption surface [31]; the Redlich–Peterson model may be used to represent adsorption equilibrium over a wide concentration range, and can be applied either in homogeneous or heterogeneous systems due to its versatility [32]; the Freundlich model is appropriate for the description of multilayer adsorption with interaction between adsorbed molecules [33]; and the Tempkin model shows the effects of some indirect

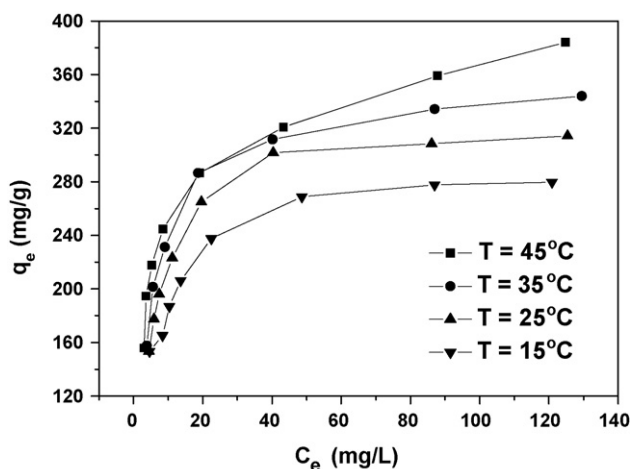
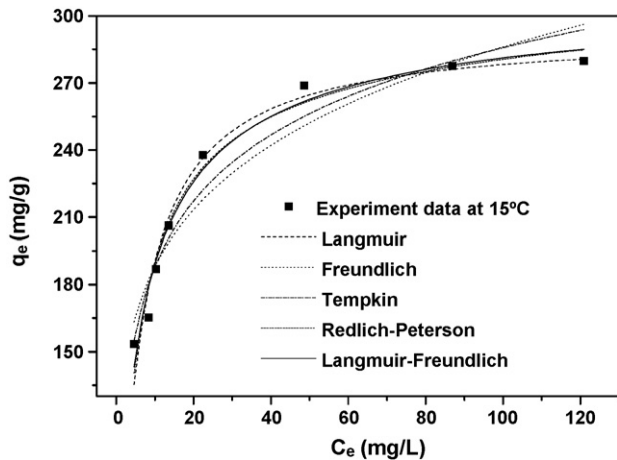


Fig. 6. Adsorption isotherm for 2-nitroaniline onto cotton stalk activated carbon at four different temperatures ($V_0 = 100$ mL; $C_0 = 200$ mg/L; contact time = 24 h; adsorbent mass = 0.0200 – 0.1300 g/100 mL; pH 7).

Table 2
Isotherm models adopted in this work and their parameters.

Isotherms	Equations	Parameters
Langmuir	$q_e = bq^0 C_e / (1 + bC_e)$	C_e : equilibrium liquid phase concentration (mg/L); q_e : equilibrium adsorption capacity (mg/g); b : constant of Langmuir (L/mg); q^0 : the maximum adsorption capacity (mg/g);
Freundlich	$q_e = K_F C_e^{1/n}$	K_F : the Freundlich constant for a heterogeneous adsorbent (L/mg); $1/n$: the heterogeneity factor;
Tempkin	$q_e = (RT/b_T) \ln(AC_e)$	A : the Tempkin constant (L/g); b_T : Tempkin constant;
Redlich–Peterson	$q_e = K_R C_e / (1 + aC_e^\beta)$	K_R : constant of Redlich–Peterson (L/g); a : constant of Redlich–Peterson (L/mg); β : constant of Redlich–Peterson;
Langmuir–Freundlich	$q_e = q^0 (K_{LF} C_e)^{\alpha_{LF}} / [1 + (K_{LF} C_e)^{\alpha_{LF}}]$	K_{LF} : constant of Langmuir–Freundlich (L/mg); α_{LF} : the heterogeneity parameter.

**Fig. 7.** Comparison of different isotherm models for 2-nitroaniline adsorption onto cotton stalk activated carbon at 15 °C.

adsorbate/adsorbate interactions on adsorption isotherms [34]. The value of correlation coefficients (R^2) for the five models at different temperatures shows that the goodness of fit of the models is temperature-dependant. For 15, 25 and 35 °C, the adsorption isotherm models fitted the data in the order of: Langmuir–Freundlich \geq Redlich–Peterson \geq Langmuir $>$ Tempkin $>$ Freundlich isotherm, but for 45 °C in the order of: Langmuir–Freundlich $>$ Redlich–Peterson $>$ Tempkin $>$ Freundlich $>$ Langmuir isotherm. The Langmuir–Freundlich model was found to best represent the equilibrium data, suggesting that the activated

Table 3
Isotherm parameters for 2-nitroaniline adsorption onto cotton stalk activated carbon at different temperatures.

Isotherms	Parameters	15 °C	25 °C	35 °C	45 °C
Langmuir	q^0 (mg/g)	293.22	330.38	352.48	370.71
	b (L/mg)	0.185	0.197	0.221	0.250
	R^2	0.968	0.996	0.996	0.960
Freundlich	K_F (L/mg)	123.49	136.99	150.62	151.45
	n	5.482	5.393	5.541	5.098
	R^2	0.922	0.891	0.905	0.964
Tempkin	A (L/g)	8.183	7.516	9.192	8.251
	b_T	56.2	50.81	50.39	47.79
	R^2	0.951	0.934	0.946	0.983
Redlich–Peterson	K_R (L/g)	66.96	59.18	80.79	167.83
	a (L/mg)	0.279	0.159	0.239	0.725
	β	0.957	1.026	0.991	0.895
Langmuir–Freundlich	R^2	0.972	0.997	0.996	0.988
	q^0 (mg/g)	312.60	325.90	353.44	451.38
	K_{LF} (L/mg)	0.174	0.198	0.220	0.144
Langmuir–Freundlich	a_{LF}	0.768	1.075	0.986	0.555
	R^2	0.977	0.997	0.996	0.991

carbon surface may be heterogeneous with a different energy distribution [31]. Furthermore, the Langmuir isotherm model fitted the experiment data better than Freundlich isotherm model at temperatures of 15, 25 and 35 °C, revealing that the adsorption of 2-nitroaniline onto the adsorbent was monolayer coverage more than multilayer adsorption [30]. The Tempkin and Freundlich isotherms were all better than the Langmuir isotherm for temperature of 45 °C, implying that the adsorption process involved multimolecular layers of coverage and the effects of some indirect adsorbate/adsorbate interactions might occur in high temperature [33,34].

3.7. Kinetic studies

In order to investigate the kinetics of adsorption of 2-nitroaniline, the Lagergren-first-order model [35], Ho's pseudo-second-order model [36], and Elovich model [37] were used. These kinetic models are given in Table 4.

The values of the parameters and the correlation coefficients obtained using non-linear regression by origin version 7.0 at four temperatures are listed in Table 5. Adsorption equation obtained at 15 °C and the fitting of the kinetic models are illustrated in Fig. 8. It was found that the fitting to Ho's pseudo-second-order model gave the highest values of correlation coefficients and predicted q_e more accurately than the other two models investigated. Therefore, Ho's pseudo-second-order model could be used for the prediction of the kinetics of adsorption of 2-nitroaniline on the activated carbon.

3.8. Adsorption mechanism

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber and Morris's intraparticle diffusion model [38], in which the rate of intraparticle diffusion is a function of $t^{0.5}$ and can be defined as follows:

$$q = f \left(\frac{D_t}{r_p^2} \right)^{0.5} = K_w t^{0.5} \quad (2)$$

Table 4
Kinetic models adopted in this work and their parameters.

Kinetic models	Equations	Parameters
Lagergren-first-order	$q_t = q_e - q_e e^{-k_1 t}$	t : time (min); q_e : equilibrium adsorption capacity (mg/g); q_t : adsorption capacity at time t (mg/g); k_1 : constant of pseudo-first-order (min^{-1}).
Pseudo-second-order	$q_t = t / [1 / (k_2 q_e^2) + t / q_e]$	q_t : adsorption capacity at time t (mg/g); k_2 : constant of pseudo-second-order (g/mg min).
Elovich	$q_t = (1/\beta_E) \ln(\alpha_E \beta_E) + (1/\beta_E) \ln(t)$	α_E : initial adsorption rate (mg/g min); β_E : desorption constant (g/mg).

Table 5
Kinetic parameters for 2-nitroaniline adsorption onto cotton stalk activated carbon at different temperatures.

Kinetic models	Parameters	15 °C	25 °C	35 °C	45 °C
Lagergren-first-order	q_e (mg/g)	170.00	181.46	193.03	204.01
	k_1 (min ⁻¹)	0.02979	0.05870	0.06224	0.06368
	R^2	0.988	0.955	0.974	0.975
	$q_{e,mea}$ (mg/g)	189.31	192.33	205.22	220.05
Pseudo-second-order	q_e (mg/g)	199.22	198.34	210.35	222.43
	k_2 (g/mg min)	0.00017	0.00042	0.00043	0.00041
	R^2	0.995	0.981	0.997	0.998
	$q_{e,mea}$ (mg/g)	189.31	192.33	205.22	220.05
Elovich	α_E (mg/g min)	14.62	70.69	84.71	89.12
	β_E (g/mg)	0.02416	0.03167	0.03041	0.02864
	R^2	0.991	0.988	0.981	0.980

$q_{e,mea}$, the equilibrium adsorption amount by experiment.

where r_p is particle radius, D_t is the effective diffusivity of solutes within the particle, and K_w intraparticle diffusion rate. K_w values can be obtained by linearizing the curve $q = f(t^{0.5})$. Such types of plots may present a multi-linearity, implying that the overall adsorption process may be controlled by one or more steps, such as film or external diffusion, intraparticle diffusion and a chemical reaction on the pore surface, or a combination of more than one step. Weber and Morris [38] reported that if intraparticle diffusion was involved in the adsorption process, then a plot of the square root of time versus the adsorption amount would result in a linear relationship, and that the intraparticle diffusion would be the controlling step if this line passes through the origin.

Fig. 9 shows the intraparticle diffusion plot of the adsorption of 2-nitroaniline on the activated carbon at four different temperatures. As can be seen from Fig. 9, the plots of 25, 35 and 45 °C show similar features that have two linear segments followed by a plateau. In the first 25 min, the first linear portion passed through the origin, implying that the intraparticle diffusion played an important role and controlled the rate of the adsorption. In the followed 60 min, the regression was nearly linear but did not pass through the origin, suggesting that the intraparticle diffusion was not the sole rate-controlling step in this stage. The K_w value evaluated from the first linear parts of these curves at 25, 35 and 45 °C was 27.681, 29.814 and 32.84 respectively. The K_w value increased with the increasing temperature, which showed that the adsorption rate increased with the increasing temperature in the first stage at 25, 35 and 45 °C. Comparing to the plots of 25, 35 and 45 °C, the plot of 15 °C had an added curved portion in the first 5 min, showing that film diffusion played an important pole in this stage [38].

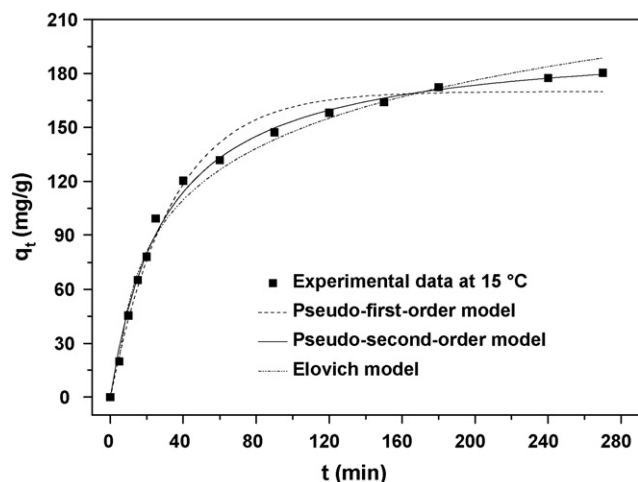


Fig. 8. Comparison of different kinetic models for 2-nitroaniline adsorption onto cotton stalk activated carbon at 15 °C.

3.9. Adsorption thermodynamics

Thermodynamic parameters can be evaluated from the variation of the thermodynamic equilibrium constant K_D at different temperature. It is defined as Eq. (3) for adsorptive reactions [39].

$$K_D = \frac{\alpha_s}{\alpha_e} = \frac{v_s q_e}{(v_e C_e)} \quad (3)$$

where α_s and α_e refer to the activity of adsorbed 2-nitroaniline and the activity of 2-nitroaniline in solution at equilibrium, v_s and v_e denote the activity coefficient of the adsorbed 2-nitroaniline and the 2-nitroaniline in solution, respectively. As the 2-nitroaniline concentration in the solution decreases and approaches to zero, K_D can be obtained by plotting q_e/C_e versus q_e and extrapolating q_e to zero [40].

The adsorption standard free energy changes (ΔG°), can be calculated according to Eq. (4). The average standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) be calculated plotting of $\ln K_D$ versus $1/T$ according to Eq. (5).

$$\Delta G^\circ = -RT \ln K_D \quad (4)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{(\Delta H^\circ/R)}{T} \quad (5)$$

where R refers to the universal gas constant, T denotes the different adsorptive Kelvin temperatures.

Thermodynamic parameters of different samples are listed in Table 6. It is well known that these parameters can evaluate the orientation and feasibility of the physicochemical adsorptive reaction [39]. The negative adsorption standard free energy changes (ΔG°)

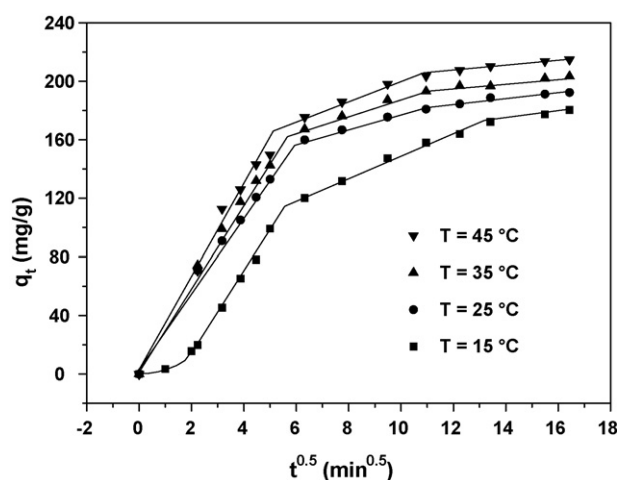


Fig. 9. Weber–Morris plots for 2-nitroaniline adsorption onto cotton stalk activated carbon at different solution temperatures.

Table 6

Thermodynamic data for 2-nitroaniline adsorption onto cotton stalk activated carbon evaluated at different temperatures.

T (°C)	K_D	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/kmol)
15	56.22	−9.65	12.94	78.06
25	64.36	−10.32	12.94	78.06
35	77.18	−11.13	12.94	78.06
45	93.42	−12.00	12.94	78.06

and positive standard entropy changes (ΔS°) at all temperatures indicated that the adsorption reactions were general spontaneous process. The positive value of entropy showed the increased randomness at the solid liquid interface during the adsorption process, and also suggested the process was entropy driven and not enthalpy driven. The decrease of Gibbs free energy (ΔG°) with increasing temperature indicated a higher adsorption impetus in higher temperature. The positive value of enthalpy indicated that the adsorption was endothermic. As we know, the physical adsorption is generally exothermic reaction. Hence, logical cause of the observation is that the adsorption should include some endothermic chemical reactions, which are supported by increasing adsorptive capacity with rising temperature. Xie et al. [41] reported a similar result that the adsorption capacity for aniline on carbon nanotube increased with increasing temperature.

4. Conclusions

The present investigation showed that the cotton stalk activated carbon was an effective and low-cost adsorbent for the removal of 2-nitroaniline from dilute aqueous solution. The surface area of the prepared activated carbon was relatively high with large pore volume and was found to be microporous. The adsorption amount increased with increasing temperature. The maximum adsorption for initial 2-nitroaniline concentration 200 mg/L was found to be 383 mg/L at temperature of 45 °C. The Langmuir, Freundlich, Tempkin, Redlich–Peterson and Langmuir–Freundlich isotherm equations were used to interpret the adsorption phenomenon of the adsorbate, and the Langmuir–Freundlich isotherm was found to best describe the experimental data. The kinetic rates were modeled using the Lagergren-first-order, pseudo-second-order and Elovich equations, and the pseudo-second-order equation was found to explain the adsorption kinetics most effectively. Amino and isocyanate groups present on the surface of the adsorbent were involved in chemical interaction with 2-nitroaniline as revealed from FTIR and ^{13}C NMR study. It was also found that the pore diffusion played an important role in the adsorption. Thermodynamic study showed the adsorption was a spontaneous and endothermic process.

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