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Adsorption potential of 2,4-dichlorophenol onto cationic surfactant-modified phoenix tree leaf in batch mode

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ABSTRACT

It is essential and important to remove chlorophenols from solution. The natural phoenix tree leaf (NTL) was modified by a cationic surfactant, hexadecylpyridinium chloride monohydrate (CPC), and applied as an adsorbent (modified phoenix trees' leaf (MTL)) to enhance the capability to remove 2,4-dichlorophenol in aqueous solutions. Analysis of elemental composition, SEM and FTIR indicated that CPC was adsorbed on the surface of NTL. 2,4-dichlorophenol (2,4-DCP) was selected as adsorbate and the adsorption experiments were carried out in batch mode. Effects of physical–chemical parameters such as solution pH, coexisted salt, and contact temperature were investigated. The optimum pH was 6.3 and the effect of salt concentration is not significant. The adsorption quantity was up to 188.8 mg g^{-1} at experimental condition. The equilibrium adsorption data were fitted adequately to Freundlich and Henry isotherms, and the corresponding constants were calculated for these models. In addition, the adsorption kinetic data were analyzed using the pseudo-first-order and pseudo-second-order kinetic equations. The results showed that the pseudo-second-order model was better to fit the experimental data, which indicated that the adsorption of 2,4-DCP was controlled predominantly by a chemical adsorption process. Thermodynamic study suggested that the adsorption of 2,4-DCP on CPC–MTL was an endothermic process. Furthermore, the adsorbed 2,4-DCP was desorbed effectively up to 83% and the exhausted adsorbent could be regenerated and reused, making the adsorption process more feasible and economical. The results indicated that MTL can be used as an efficient adsorbent for the removal of 2,4-DCP from aqueous solutions.

Keywords: Modified phoenix tree leaf; 2,4-dichlorophenol; Adsorption; Regeneration

1. Introduction

Among various organic pollutants, phenols and its derivatives are extremely harmful environmental contaminants owing to their bioaccumulation, recalcitrance, high toxicity, and persistence in environment. Chlorophenols have been extensively used in the manufacture of pharmaceuticals, paint, insecticides, leather, fungicides, plastic, and cosmetics [1] as well as the pesticides and paper industries are dominating sources containing phenolic derivatives [2].

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As common environmental pollutants, phenol and phenolic derivatives can disturb the use of water, producing obnoxious odor and taste to drinking water. Moreover, substituted phenols bring lethal effect on human beings even at low concentrations. The structure of cellular bilayer phospholipids can be disturbed by highly toxic 2,4-dichlorophenol (2,4-DCP), which acted as a common and typical phenolic derivatives, and this proper structure of cellular bilayer phospholipids plays a significant role in the normal function of cell membrane [3], leading to mutagenic and carcinogenic effects. Generally, 2,4-DCP is more troublesome to dechlorinate than other polychlorinated phenols from wastewater.

Phenol and phenolic derivatives have been designated as priority pollutants due to ubiquitous features in environment and high toxicity even in trace amount. Various purification technologies have been reported to keep waters free from phenol and substituted phenols, such as photocatalytic degradation, membrane filtration [4], electrochemical degradation, biological degradation [5], incineration, extraction, and adsorption on activated carbons [6].

Because of economic feasibility and simple implementation, adsorption has been employed as an effective method for the removal of phenolic compounds. In addition, most contaminants-laden adsorbents produced from the adsorption process do not sustain safe disposal environmentally [7]. Currently, activated carbon has been widely used in adsorption process because of its vast surface area and great affinity for organic compounds. However, tedious procedures of preparation, high cost, and inevitable regeneration may restrict widespread applications of activated carbon in wastewater treatment.

From the point of pollution control, efforts have been exerted to develop economic and environment-friendly adsorbent for the removal of chlorophenols. These alternative materials include *Punica granatum* peel [7], bentonite [8], rice husk [9], cyclodextrin polymers [10], palm piths [11], red mud [12], maize cobs [13], coal fly ash [14] and so on. Among these substitutes, various agricultural byproducts have drawn particular attention in the adsorption system due to its relative cheapness, abundance in nature, and by avoiding complex pretreatment steps before applications. Hence, the interest of researchers has been provoked by one type of plant waste.

The phoenix trees' are widely cultivated in China. Traditionally, fallen leaves have been incinerated, landfilled, or used as natural compost. However, owing to huge production, restricted ability of landfills and air pollution created by burning, it was urgent to explore feasible treatment technology. The natural phoenix trees' leaf (NTL) demonstrated potential advantage when used as adsorbent material because of its large content of lignin, cellulose, pectin, hemicellulose, and low cost. In previous studies, it was noted that plant leaves smoothly got rid of dyes and heavy metals from contaminated water [15,16].

Nevertheless, the direct utilization of raw agricultural byproducts will release much soluble organic compounds like cellulose, pectin, and lignin, which contribute to the increase of biological chemical demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC). As a result, higher BOD, COD, and TOC can aggravate the consumption of oxygen content in solution and the aquatic life would be threatened to a certain extent. Consequently, surface modification is necessary to overcome these problems and enhance the adsorption capacity of plant wasters.

Surfactants are amphipathic agents along with a hydrophilic head group and a hydrophobic tail chain. They can change the surface properties of solid adsorbents, particularly at the interface. In this paper, hexadecylpyridinium chloride monohydrate (CPC), a kind of cationic surfactant, was applied to modify phoenix trees' leaf for adsorption of 2,4-DCP.

The chemical structure of CPC is shown in Fig. 1 and critical micelle concentration (CMC) of this surfactant is about 0.9 mol L^{-1} [17]. At concentrations above CMC, bilayer or admicelle can be formed on the surface of solid. The hydrophilic pyridine head group tends toward the aqueous environment and hydrophobic tail is inside the admicelle or bilayer. This 16-carbon alkyl chain provides hydrophobic environment for the retention of low-polarity contaminations. The surfactant-modified sawdust and barley straw were reported for removal of dyes [18,19]. The hydrophobic interaction is conducive for adsorption of phenolic compounds. In fact, it has been noted that the surfactant-treated adsorbents were selected to remove chlorophenols, such as montmorillonite [20] and bentonite [21].

The aim of this study is to evaluate the potential of CPC-modified phoenix trees' leaf (MTL) as adsorbent to enhance the ability of removal of 2,4-DCP from aqueous solution. The system variables including initial pH and salt concentration were investigated.

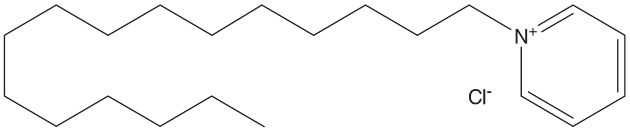


Fig. 1. Chemical structure of CPC.

Adsorption equilibrium and kinetic process were carried out in batch mode and thermodynamic was calculated according to isotherm data.

2. Materials and methods

2.1. Preparation of adsorbent

Fresh biomass of phoenix trees' leaf used was obtained from campus of Zhengzhou University. The collected leaf was washed extensively with tap water, and then dried in an oven for 4 h at 343 K. Dried phoenix trees' leaf was crushed and sieved through 20–40 mesh size. The sample NTL was preserved in glass bottle for use.

The surfactant MTL was prepared as following steps: Five gram of MTL and 0.5% CPC solution (200 mL) were shaken in 250 mL conical flask for 24 h at 303 K. The supernatant was filtered and modified leaf was washed by deionized water for removal of retained CPC superficially. Finally, the treated leaf was dried at 343 K in an oven overnight and stored in glass container.

2.2. Characterization of adsorbent

The elemental contents of nitrogen, carbon, and hydrogen were determined using an element analyzer (Thermo Electron Corporation Flash EA1112, USA). The specific surface areas of samples were measured by the N_2-BET method using a Quanta-chrome NOVA 1000e instrument. All samples were degassed at room temperature for 1.5 h, prior to N_2 adsorption analysis. The surface morphology of NTL and MTL was observed using a SEM instrument (JSM-6700F, Japan). IR spectra of samples were determined between 4,000 and 400 cm^{-1} using a FTIR instrument (PE-1710 FTIR, USA) in KBr pellets.

2.3. Preparation of 2,4-DCP solution

2,4-DCP ($C_6H_4Cl_2O$, FW = 163.00) used in this study was purchased from Shanghai Aladdin Industrial Corporation (China). Stock solution (1,000 $mg\,L^{-1}$) was prepared by dissolving 2,4-DCP in distilled water. Working solutions of different concentrations could be obtained by diluting stock solution with double-distilled water to required concentrations.

2.4. Adsorption experiments

Adsorption experiments were conducted in an orbital shaker at 150 rpm. Ten milliliters of 2,4-DCP solution (100 $mg\,L^{-1}$) was agitated with 8 mg of MTL in 50 mL conical flasks for 255 min until adsorption equilibrium was reached. Effect of solution pH was carried out in the range of 2–12. The initial pH was adjusted with HCl and NaOH solutions. Influence of salt concentration (0–0.1 $mol\,L^{-1}$) was also investigated.

Kinetic experiments were proceeded in 10 mL 2,4-DCP solutions (100, 200, and 300 $mg\,L^{-1}$) by introducing 8 mg of adsorbent for predetermined intervals of time. In adsorption isotherm experiments, 8 mg of MTL was added to 10 mL of 2,4-DCP solutions at different concentrations (20–350 $mg\,L^{-1}$) and agitated time was 400 min in order to reach equilibrium. A series of conical flasks were shaken at 308, 318, and 328 K, respectively.

After equilibrium, the samples were filtered and the concentration of 2,4-DCP in supernatant solution was analyzed spectrophotometrically at a wavelength of maximum absorbance (285 nm). The measurement was done in duplicates and the average values were shown. Adsorptive quantity of 2,4-DCP was calculated as the following expression:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e is the amount of 2,4-DCP adsorbed onto unit weight of MTL ($mg\,g^{-1}$); C_0 is the initial 2,4-DCP concentration ($mg\,L^{-1}$); C_e is 2,4-DCP concentration at equilibrium ($mg\,L^{-1}$); and m is the dry weight of MTL (g).

2.5. Regeneration studies

In order to assess the reusability of exhausted MTL, desorption and regeneration tests were carried out. The spent adsorbent MTL saturated with 2,4-DCP was filtered after adsorption equilibrium and separated with the solution, and 2,4-DCP attached to the leaf surface was washed with distilled water. The loaded MTL was then dried in oven at about 333 K for 5 h. Then, 20 mg of the resulting adsorbent was agitated with 20 mL of desorption solutions in three flasks, respectively. The three desorption solutions were deionized water, 0.1 $mol\,L^{-1}$ sodium hydroxide, and 75% ethanol. Next, these flasks were shaken at 308 K for about 4 h. After desorption, MTL was filtered again and desorbed 2,4-DCP was measured in the filtrate. Three successive adsorption–desorption cycles were conducted using the same procedure. The desorption rate and regeneration rate were calculated in the following equations:

$$\rho = \frac{C_e \times V}{q_e \times m} \times 100\% \tag{2}$$

$$\eta = \frac{q_i}{q_b} \times 100\% \tag{3}$$

where ρ is desorption rate of the adsorbent (%); C_e is the concentration of desorbed 2,4-DCP in solution (mg L^{-1}); V is the volume of desorption solution (L); m is the dry weight of loaded adsorbent (g); η is the regeneration efficiency of the adsorbent (%); q_i and q_b are the adsorption capability of regenerative MTL and MTL in the same experimental conditions, respectively.

For the kinetics of desorption test, the 20 mg of MTL saturated with 2,4-DCP was agitated with 75% ethanol (20 mL) in a series of flasks at 308 K. Then, each sample in the flasks was withdrawn at predetermined time. The adsorbed 2,4-DCP in filtrate was measured using a UV spectrophotometer.

2.6. Error analysis

In this paper, the nonlinear regressive method was applied. In order to estimate the feasibilities of adsorption models, experimental data were analyzed by the average relative error (ARE), along with the values of the determined coefficient (R^2). The calculated expression of ARE was given as following:

$$\text{ARE} = \frac{\left(\sum |(q_c - q_e)/q_e|\right)}{n} \tag{4}$$

where q_c was the calculated amount of 2,4-DCP adsorbed onto MTL according to kinetic and isotherm models; q_e was the experimental value; and n was the number of experimental points.

3. Results and discussions

3.1. Characterization of adsorbent

3.1.1. Elemental composition

The percentages of nitrogen, carbon, and hydrogen for NTL and MTL were presented in Table 1.

From Table 1, phoenix tree leaf was rich in carbon. As expected, the content of nitrogen significantly increased after modification, which indicated that cationic surfactant, CPC, was coated on the surface of NTL successfully.

Table 1
Chemical composition of NTL and MTL

	Elemental compositions (%)		
Sample	Nitrogen	Carbon	Hydrogen
NTL	0.367	46.1	5.94
MTL	1.12	55.1	7.14

In order to obtain an accurate loading of surfactant onto the leaf surface, the concentration of CPC solution was determined by monitoring the absorbance at λmax of 259 nm using ultraviolet–visible spectrophotometer. The CPC impregnated onto NTL was calculated as 241.2 mg g^{-1}. Besides, it was found that 251.2 mg g^{-1} of CPC was adsorbed on the leaf based on the nitrogen content before and after modification. Similar results from these two methods demonstrated that the difference in nitrogen content was almost entirely owing to the loading of surfactant.

3.1.2. BET analysis

The BET surface areas of samples can be obtained from nitrogen adsorption isotherms at 77 K by applying BET equation. The surface areas for NTL and MTL were found to be 2.08 and 1.32 m^2 g^{-1}, respectively.

Apparently, the loading of CPC on phoenix tree leaf caused the decrease in surface area compared to NTL. This result was mainly because of the constriction of pore channels, as a result of the attachment of surfactant to internal structure of NTL. Subsequently, the diffusion of N_2 was hindered throughout these channels.

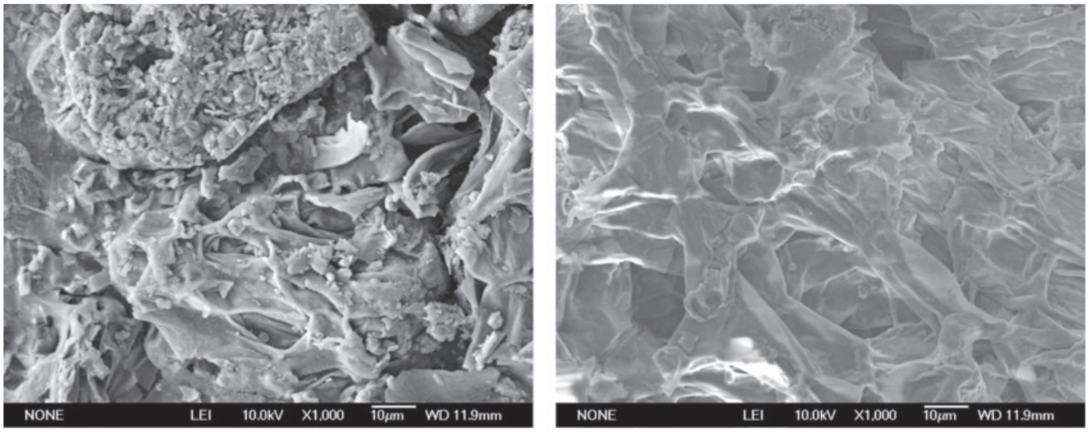
3.1.3. SEM analysis

SEM reveals significant information on surface characteristics and morphological features of adsorbent materials. Typical SEM photographs of NTL and MTL were taken at 1,000× magnification (Fig. 2(a) and (b)).

From Fig. 2(a), NTL had porous and irregular external surface with a lot of heterogeneous cavities, holes, and protrusions. After the introduction of CPC, the surface of NTL was apparently occupied by cationic surfactant and the main channels of NTL were obstructed by CPC. Hence, this was sufficiency indicatives of expected loading of CPC on the surface of phoenix tree leaf.

3.1.4. FTIR analysis

The FTIR was significant to identify the major functional groups which were involved in the adsorption of 2,4-DCP. The FTIR spectrum of NTL and CPC–MTL were illustrated in Fig. 3. Various peaks relative



(a) **(b)**

Fig. 2. SEM images of NTL (a) and MTL (b).

to functional groups existed in Fig. 3 showed the complex nature of phoenix tree leaves.

A strong and broad band at 3,426 cm^{-1} was attributed to free or hydrogen-bonded O–H stretching vibrations in cellulose, lignin, and pectin on the surface of adsorbent [22]. But after modification, this absorption peak weakened and shifted to lower wave number 3,419 cm^{-1}. The intensity of the peaks at 2,923 and 2,852 cm^{-1} enhanced sharply after the modifying process. This was owing to the increase in the content of aliphatic carbon for MTL, which in turn indicted that surfactant molecules CPC were combined with NTL. The peak observed at 1,732 cm^{-1} was indicative of the stretching vibration of unionized C=O, and may be attributed to carboxyl groups in carboxylic acids or corresponding esters [23]. While, the stretching of C=O from carboxylic group contained intermolecular hydrogen bond was associated with the absorption bands close to 1,615 cm^{-1}.

The region below 1,550 cm^{-1} was the fingerprint region, representing complex interacting vibration systems [24]. The bands at 1,516 and 1,447 cm^{-1} were assigned the stretching of aromatic skeletal vibrations (from lignin). The peak located at 1,377 cm^{-1} may be assigned to asymmetric bending vibration of $–CH_3$ groups. The absorption peak at 1,063 cm^{-1} was due to the asymmetric stretching vibrations of Si–O−Si. The peak associated with the stretching of C–O was verified at 1,316 cm^{-1}. Moreover, the wave number observed at 1,240 cm^{-1} was due to the stretching vibrations of −OH from phenols. In addition, the band at 780 cm^{-1} was one of the characteristics of aromatic skeletal groups. The absorption band ranged from 600−700 cm^{-1} was attributed to bending vibration of Si–O−Si bonds.

Abundant hydroxyl and carboxyl groups were presented on the surface of phoenix tree leaves from FTIR analysis. It was also found from Fig. 3 that the positions of absorption peaks of MTL were substantially similar to those of NTL's, and small differences were observed for the relative width and intensity of absorption bands.

3.2. Batch adsorption performance

3.2.1. Effect of solution pH on adsorption

The pH of the adsorption medium fundamentally affected the surface charge of adsorbent as well as the extent of ionization of the phenolic adsorbate. The optimal experiments were performed in the pH ranges of 2–12. And the plot of adsorption capacity vs. pH was represented graphically in Fig. 4.

As revealed in Fig. 4, the greatest uptake was obtained at pH 2.41. When pH increased from 2.40 to 11.6, the amount of 2,4-DCP adsorbed dropped distinctly from 62.6 to 18.6 mg g^{-1}.

The surface charge of leaf was dependent on its pH_{PZC} and the solution pH. And the adsorbent surface was negatively charged at $pH > pH_{PZC}$ and positively charged at $pH < pH_{PZC}$. Moreover, the existence of molecular and ionic forms of phenolic in aqueous solution compounds should also be considered to explain this phenomenon. The percentages of these two forms relied heavily on the solution pH. According to the following reaction and the equilibrium constant, the value of pKa was calculated and the speciation diagram of 2,4-DCP was represented in Fig. 5.

$$2,4\text{-DCP} \leftrightarrow 2,4\text{-DCP}^- + \text{H}^+ \quad \text{p}K\text{a} = 7.85$$

where 2,4-DCP$^-$ indicated phenolate anions.

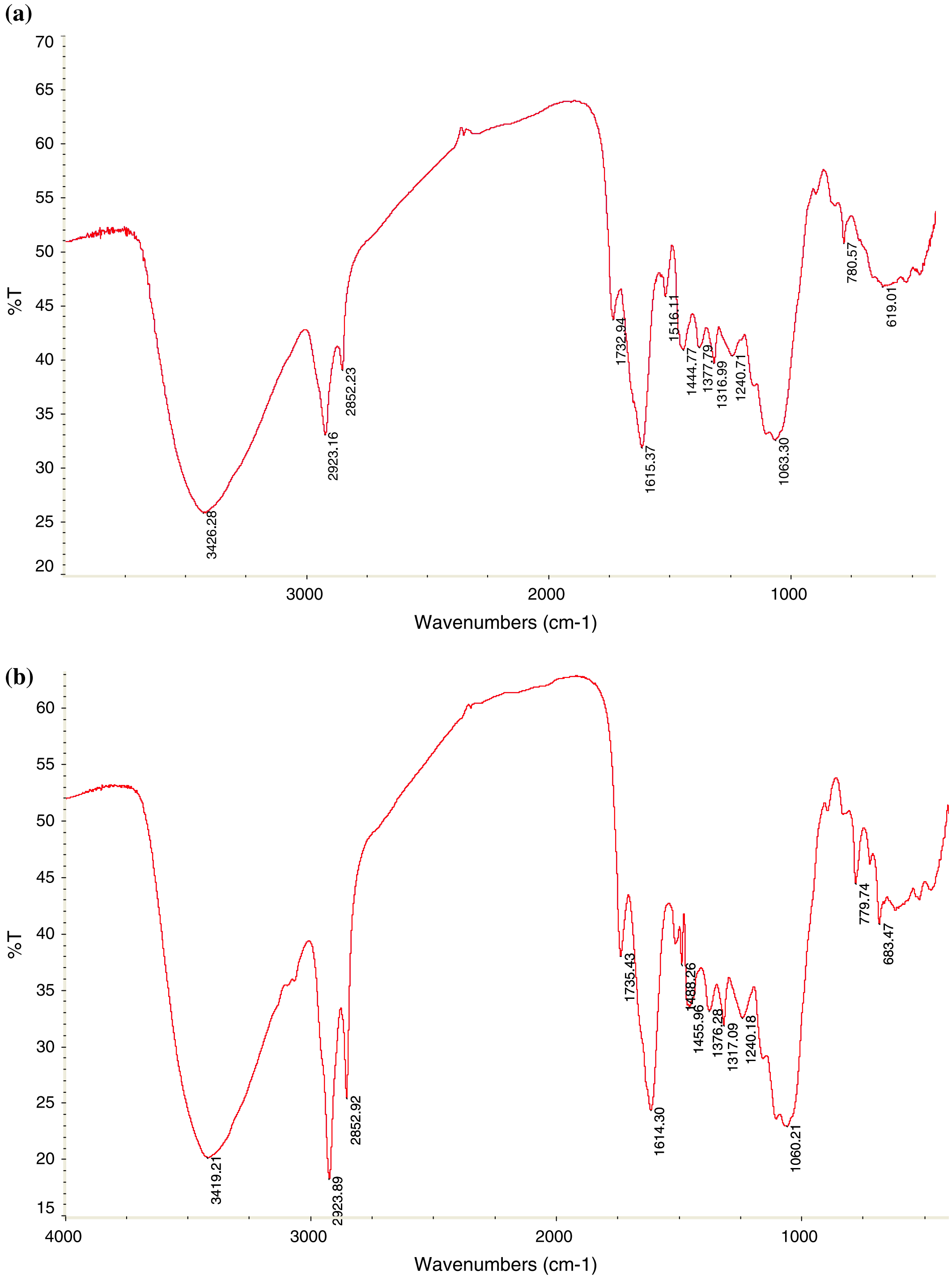


Fig. 3. FTIR spectrum of NTL (a) and MTL (b).

Correspondingly, approximate 99% of all 2,4-DCP was existed as neutral molecules at pH < 6.0. Nevertheless, at pH > 9.0, almost 95% of all 2,4-DCP was existed as phenolate anions. When the pH value was below pH_{pzc} (5.1), the surface of MTL was positively charged. In this case, 2,4-DCP exists prevailingly as the neutral species. Consequently, there was nearly no electrostatic repulsion between the adsorbent and the adsorbate. And 2,4-DCP molecules were adsorbed to alkyl chains of MTL mainly via van der Waals forces.

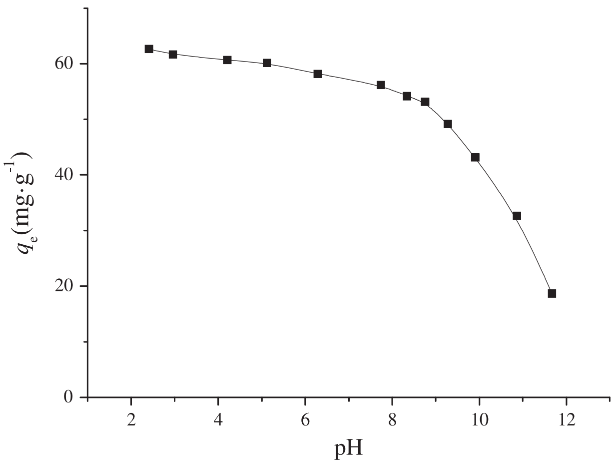


Fig. 4. Effect of solution pH on the adsorption of 2,4-DCP by MTL.

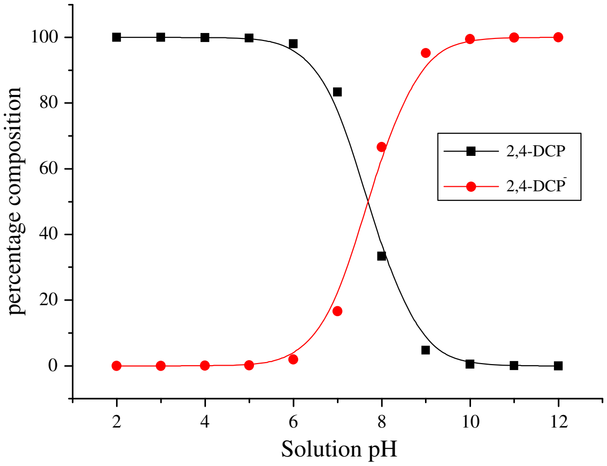


Fig. 5. Speciation diagram of 2,4-DCP at 25℃.

As a result, the uptakes of chlorophenol did not significantly altered in the acidic solution.

At pH > p*K*a (7.85), 2,4-DCP dissociated and gradually formed phenolate anions, while the surface functional groups on MTL were negative. As a result, the electrostatic repulsion caused by the identical charges of active sites and target molecules impeded the adsorption of 2,4-DCP on MTL. With the increase of pH, more phenolate anions were dissociated and the MTL surface was charged more negatively, resulting in greater electrostatic repulsion. Besides, the decrease in hydrophobicity assigned to dissociation of 2,4-DCP would interfere with affinity of the adsorbate and active sites. And stronger water–adsorbate bonds were formed in aqueous solution associated with higher solubilities of the phenolate anions. Thus, adsorption efficiency radically lowered at basic pH. Similar observations were reported in the adsorption of 2,4-DCP onto rice husk [25], *Posidonia oceanica* (L.) seagrass [26] and maize cob carbon [13] as well as adsorption of 2,4,6-trichlorophenol with cattail fiber-based activated carbon [27] and 2,4-DCP by anaerobic granular sludge [28].

Initial pH of 2,4-DCP solution was about 6.3 without adjustment using acids and bases, when a considerable removal (58.2 mg g^{-1}) was observed. Hence, the optimum pH of 6.3 was used in further experiments.

3.2.2. *Effect of salt concentration*

The influence of salt concentration on the adsorption of 2,4-DCP was carried out by adding different doses of sodium chloride and calcium chloride to initial solutions. As shown in Fig. 6, there was mild undulating on the adsorption capacity with increase in concentration of electrolyte. When ionic strength changed from 0 to 0.1 mol L^{-1}, the uptakes of the phenols varied from 53.1 to 45.6 mg g^{-1} and 48.6 mg g^{-1} for sodium chloride and calcium chloride, respectively.

With the existence of salt, this slight decrease of 2,4-DCP adsorption verified that electrostatic interaction was not dominating during the adsorption process. Otherwise, prominent negative impact would be manifested if the primary mechanism be electrostatic attraction. The minor reduction in adsorption uptakes could be comprehended as follows: ionic strength had a significant influence of the thickness of electrical double layer (EDL) formed on the particle surface. EDL thickness became thinner at higher concentration of electrolyte and led to increasing amount of 2,4-DCP

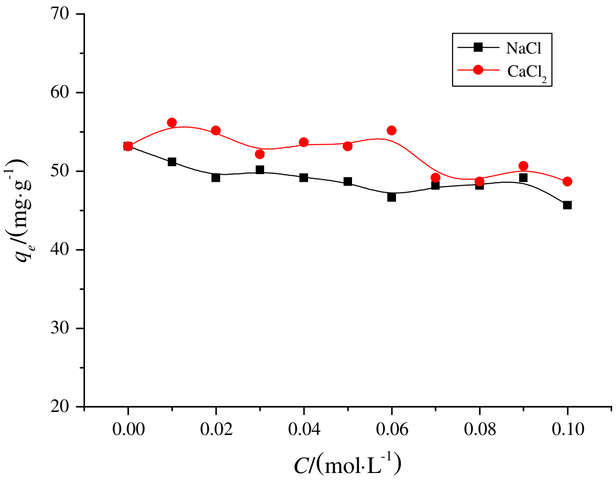


Fig. 6. Effect of salt concentration on the adsorption of 2,4-DCP by MTL.

molecules approaching MTL surface. Furthermore, the presence of salt in solution may reduce the number of water molecules in free form then the solubility of organic adsorbate (2,4-DCP) was lower, which was the phenomenon of salting-out effect. Hence, the diffusion process for phenolic compounds to hydrophobic leaf surface was greatly facilitated. On the other hand, the activity of 2,4-DCP molecules and the active sorption sites decreased with the increase in salt concentration , and then the nearness of adsorbate and active sites may be restrained, making adverse contributions to the adsorption process. Taking all these factors into consideration, the reducing uptakes owing to lower activity may be only partially compensated by the enhanced adsorption associated with EDL thickness and salting-out effect. Similar trend were reported by Wang et al. [29] in their study of adsorption of 2,4-DCP onto Mn-modified activated carbon.

Consequently, it was concluded that MTL was suitable to remove 2,4-DCP from wastewater-containing salt.

3.2.3. Adsorption kinetics

Kinetic study, acted as a crucial approach for assessing adsorption efficiency, can accurately estimate equilibrium time for the maximum absorption capacity. The influence of contact time on adsorptive uptake of 2,4-DCP at various initial concentrations (100, 200, and 300 mg L^{-1}) was demonstrated in Fig. 7.

As seen from Fig. 7, the same curve character was found for all different concentrations. The amount of adsorption increased fast at the initial stage (0–30 min), and then gradually increased to reach a plateau till dynamic equilibrium, then negligible increment in removal was obtained, although the contact time was extended further. To be specific, approximately 79.7, 74.9, and 81.1% of equilibrium capacity for 2,4-DCP was acquired within 30 min at 308 K for 100, 200, and 300 mg L^{-1}, respectively. The adsorption quantity increased at higher initial concentration.

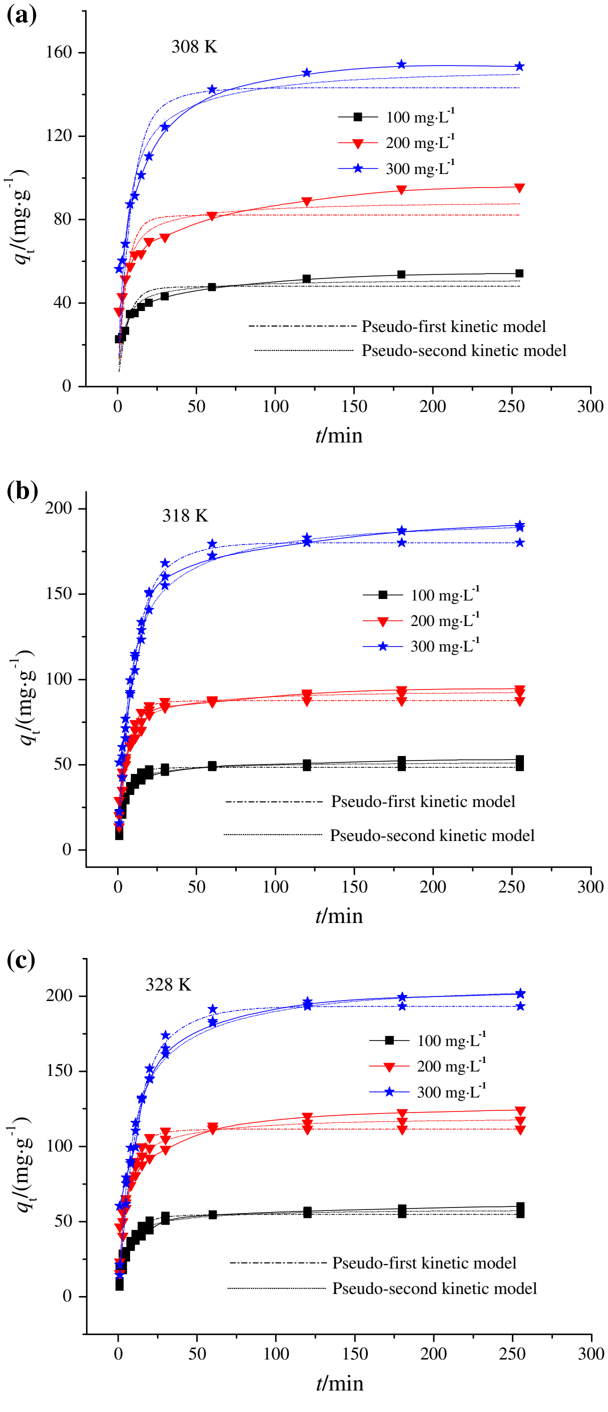


Fig. 7. Adsorption kinetics of 2,4-DCP onto MTL and fitted curves at 308 K (a), 318 K (b), and 328 K (c).

This phenomenon may be explained that abundant vacant active sites were available for adsorption at the initial stage, and there was great concentration gradient between the adsorbate on the surface of leaf and the adsorbate in bulk solution. As a result, 2,4-DCP was rapidly attached to the surface of MTL by surface mass transfer, which was called external surface adsorption or instantaneous adsorption stage. But after a lapse of time, a number of available external sites was already filled and repulsive forces between the adsorbate molecules on the solid phase was greater. Consequently, the remaining vacant active sites were hard to be occupied and the adsorption process became slower and more stable [30]. Based on this, all samples were agitated for 255 min to ensure that the equilibrium was reached. Thus, a fast adsorption process was confirmed from the rapid kinetics study due to about 80% of 2,4-DCP adsorbed within 30 min, revealing the benefit of this low-cost adsorbent. This observation was in agreement with Shaarani et al. who reported the adsorption of 2,4-DCP onto activated carbon derived from agricultural waste [31].

As an orbital shaker was at 150 rpm, the diffusional resistance is not an important factor and diffusional resistance is assumed to be absent.

Compared to Fig. 7(a)–(c), the adsorption quantity became larger with the increase of temperature at same initial 2,4-DCP concentration. This showed that the process was endothermic.

From Fig. 7(a), the adsorption quantity for MTL was 53.2 mg g^{-1} at 308 K with initial concentration 100 mg L^{-1}. But for NTL, it was only 1.88 mg g^{-1} at same condition (the kinetic curve was not shown). This showed that the adsorption quantity of NTL was significantly enhanced through CPC modification.

Cationic surfactants-modified adsorbents are extensively studied and used to remove pollutants from solution [21,24]. The mechanism was due to adsorption of cationic surfactants onto adsorbent surface. The nonpolar portion of CPC may interact with the solid surface through hydrophobic bonding and the polar head group directed toward the bulk of the solution, so the surface is potential positive. In solution, some groups in leaf, such as lignin and cellulose, lose hydrogen ions and form a potential negative surface. So another possible mechanism is the electrostatic attraction of surfactant cations on the leaf surface. The property of leaf surface change and the chemisorption and hydrophobic interactions were involved between CPC molecules impregnated on the leaf surface and 2,4-DCP.

In order to estimate the controlling mechanism of the adsorption process, the pseudo-first-order and the pseudo-second-order kinetics models were used to analyze the experimental data of 2,4-DCP adsorption by MTL.

The pseudo-first-order equation of Lagergren was generally given as [32]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{5}$$

The pseudo-second-order equation was represented as the following [33]:

$$q_\mathrm{t} = \frac{k_2 q_\mathrm{e}^2 t}{1 + k_2 q_\mathrm{e} t} \tag{6}$$

where q_e and q_t (mg g^{-1}) were the amounts of 2,4-DCP adsorbed on adsorbent at equilibrium and at any time t, respectively; k_1 was the rate constant of pseudo-first-order reaction (min^{-1}); k_2 was the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}).

The kinetics parameters could be calculated from nonlinear regressive analysis using Origin 7.5 software. The experimental and calculated parameters of the pseudo-first-order equation and pseudo-second-order equation together with determined coefficient (R^2) and ARE were all listed in Table 2. Furthermore, the comparison between experimental data and fitted curves at 308, 318, and 328 K were also illustrated in Fig. 7.

As shown in Table 2, higher correlation coefficients, lower ARE and a good agreement between the experimental and theoretical uptakes indicated the applicability of the pseudo-second-order model to describe the adsorption kinetics. In literature, some researchers revealed that the adsorption of 2,4-DCP

Table 2
Kinetic parameters for adsorption of 2,4-DCP on MTL from nonlinear method

	T (K)								
	308 K			318 K			328 K		
$C_0/(\mathrm{mg\,L^{-1}})$	100	200	300	100	200	300	100	200	300
Pseudo-first-order model									
$k_1(\mathrm{min}^{-1})$	0.163	0.179	0.108	0.185	0.171	0.0901	0.129	0.150	0.0769
$q_{\mathrm{e(cal)}}/(\mathrm{mg\,g^{-1}})$	47.9	82.2	143.1	48.4	87.6	180.1	54.8	111.6	193.2
$q_{\mathrm{e(exp)}}/(\mathrm{mg\,g^{-1}})$	54.2	95.7	153.3	55.2	94.7	190.3	60.2	124.2	201.3
R^2	0.668	0.654	0.780	0.768	0.861	0.929	0.760	0.723	0.895
ARE	0.145	0.162	0.160	0.120	0.118	0.119	0.159	0.160	0.112
Pseudo-second-order model									
$k_2 \times 10^{-3}$ ($\mathrm{g\,mg^{-1}\,min^{-1}}$)	5.12	3.09	1.13	5.95	2.95	6.7	3.72	2.01	0.54
$q_\mathrm{e}/(\mathrm{mg\,g^{-1}})$	51.4	88.7	153.0	51.6	93.6	194.7	58.3	119.6	208.9
R^2	0.848	0.855	0.895	0.912	0.964	0.958	0.898	0.888	0.929
ARE	0.0950	0.0987	0.0997	0.0684	0.0613	0.0903	0.104	0.0963	0.0847

R^2: determined coefficient; ARE: average relative error.

onto CTAB/bentonite [21] and palm pith carbon [11] as well as adsorption TCP on activated clay [34] followed well the pseudo-second-order kinetic model. Previously, Wu et al. [35] reported that the pseudo-second-order model was adequate for general adsorption systems, because in most cases the adsorbents were small particles and molecular weights of adsorbates were lower (such as heavy metal ions, phenols and its derivatives), which account for its feasibility in present study.

On the contrary, the first-order model was not applicable to the data, which could be concluded from lower R^2, higher ARE and notable variances between the calculated and experimental q_e. The inadequacy of pseudo-first-order equation for this kinetic was possibly owing to the limitations of the boundary layer which controlled the adsorption process. However, the study carried out by Bhatnagar and Minocha found that the first-order model gave a better fit than the second-order model on the adsorption of 2,4-DCP using *punica granatum* peel waste [7].

From Fig. 7, a good fitting was achieved for the pseudo-first-order model within the first stage, but this model gradually deviated from the experimental data after the initial phase, suggesting that the pseudo-first-order model was generally applicable to the initial rapid stage, but not the whole adsorption process. In the whole range, this system followed the pseudo-second-order model predominantly, indicating that the rate determining step could be chemical adsorption in the adsorption process for 2,4-DCP [33]. This implied that valency forces may be involved during this process by exchange or sharing electrons between the adsorbent and adsorbate.

3.2.4. Equilibrium study

The equilibrium adsorption studies were conducted by varying initial concentrations of 2,4-DCP solution and adsorption isotherms were presented in Fig. 8. As depicted in Fig. 8, the amount of 2,4-DCP adsorbed increased markedly from 6.33 to 188.8 mg g^{-1} with increasing initial 2,4-DCP concentration from 20 to 350 mg L^{-1} and corresponding equilibrium concentration changed from 14.9 to 198.9 mg L^{-1} at 308 K.

This behavior may be attributed to higher driving force from the concentration gradient with increase in initial concentration, which was for overcoming the resistances to mass transfer of 2,4-DCP molecules between the solid and aqueous phases. Moreover, the active sites of leaf would be surrounded by much more 2,4-DCP molecules with higher concentration of 2,4-DCP in solution. As a result, the adsorption phenomenon was proceeded more smoothly. Besides, the probability of collisions between the adsorbent and adsorbate was vastly elevated with increasing initial 2,4-DCP, which caused enhancive adsorptive ability in some degree. Wang et al. reported similar result for the adsorption of 2,4-DCP by Mn-modified activated carbon [29].

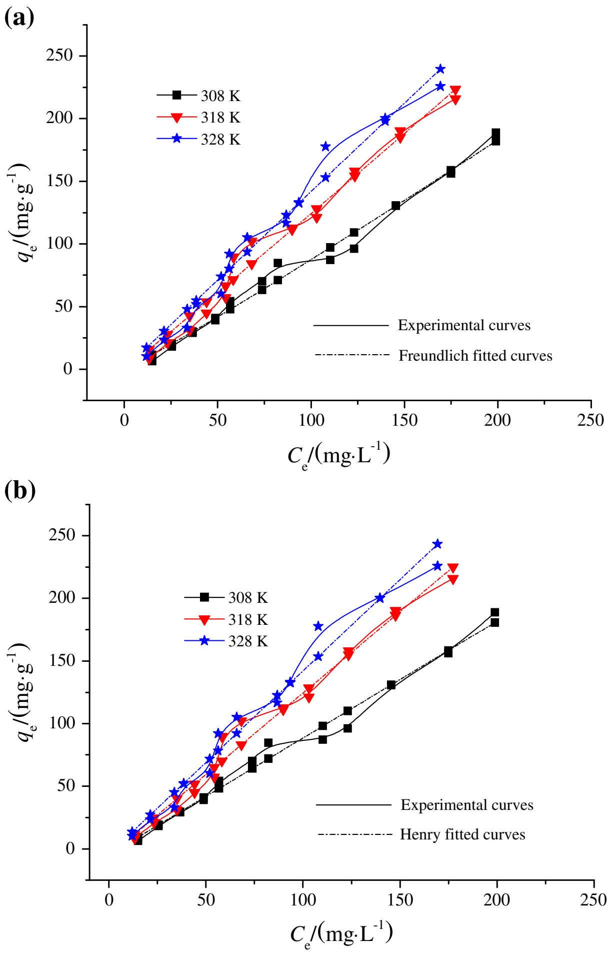


Fig. 8. The isotherm of 2,4-DCP adsorption onto MTL and nonlinear fitted curves of Freundlich model (a) and Henry equation (b).

A comparison of adsorption isotherms in Fig. 8 manifested that the adsorption quantity of 2,4-DCP slightly elevated with increase in temperature. The amount of 2,4-DCP adsorbed changed from 188.8 to 225.8 mg g^{-1} when temperature increased from 308 to 328 K, implying the endothermic nature of the adsorption process. The enhancement in adsorption capacity at higher temperature was owing to the following factors. The rate of 2,4-DCP molecules to pass the external boundary layer and diffuse in the internal pores of MTL was increased, caused by lower viscosity of the solution as increasing the temperature. Furthermore, temperature had positive effect on the porosity and the total pore volume of the adsorbent. Hence, a mass of new available active sites were created due to the opening of the cellulose fiber network at higher temperatures. Similar trend was observed by Bhatnagar and Minocha for the adsorption of 2,4-DCP onto *punica granatum* peel waste [7].

The adsorption isotherms express specific relationship between the amount of adsorbate which was dissolved in solution and adsorbed on the surface of adsorbent under equilibrium conditions. The equilibrium isotherm is significant to design and optimize the adsorption system for the removal of phenolic derivatives from wastewater. In the present study, adsorption equilibrium data at various temperatures (308, 318, and 328 K) were analyzed with Freundlich and Henry isotherms, two of the most commonly used models.

The Freundlich model was empirical equation based on the assumption of adsorption on highly heterogeneous surface. The nonlinear form of Freundlich isotherm was given by the following equation [36]:

$$q_e = K_F C_e^{1/n} \tag{7}$$

where C_e was the equilibrium concentration of 2,4-DCP in solution (mg L^{-1}); q_e was the amount of 2,4-DCP adsorbed on MTL (mg g^{-1}); K_F was empirical constant, related to the adsorption capacity[mg g^{-1} (L mg^{-1})^n]; the other empirical parameter $1/n$ (dimensionless) represented the adsorption intensity, varying with the degree of heterogeneity.

According to the Henry model, the amount of 2,4-DCP adsorbed onto unit weight of MTL (q_e) was related to the equilibrium concentration (C_e) by the following equation:

$$q_e = A + KC_e \tag{8}$$

where A and K represented isotherm constants, respectively.

The Freundlich fitting parameters K_F and $1/n$ together with correlation coefficients (R^2) and ARE were presented in Table 3. The corresponding Henry parameters of A and K at various temperatures were also shown in Table 3. Besides, the simulated curves according to Freundlich and Henry models were illustrated in Fig. 8.

As seen in Table 3, the values of R^2 were larger than 0.970 at different temperatures, and the corresponding values of ARE were negligible (<0.205). Then the adaptabilities of Freundlich and Henry models were confirmed according to the calculated values of R^2 and ARE. This conclusion was highly consistent with the model fitting curves (Fig. 8). From Table 3, the values of K_F indicated high adsorption capacity of 2,4-DCP by MTL and obvious difference in adsorptive uptakes owing to temperatures, and this suggested that increasing temperature was advantageous for this adsorption process. In addition, the values of exponent $1/n$ calculated from Freundlich equation were equal to unity, implying a favorable chemisorption. The behavior was in agreement with previous studies for adsorption of chlorophenols on various adsorbents, such as fungal mycelia [37] and surfactant-modified natural zeolite [38], which were adequately described by Freundlich isotherm. Furthermore, the constant K of Henry equation increased with the temperature increasing.

Table 3
Parameters of adsorption isotherm model for 2,4-DCP adsorption onto MTL

T/K	308	318	328
Freundlich			
K_F	0.644	1.11	1.45
$1/n$	1.07	1.02	0.99
ARE	0.141	0.205	0.187
R^2	0.982	0.975	0.970
Henry			
A	−4.68	−5.55	−3.99
K	0.932	1.30	1.46
ARE	0.104	0.142	0.134
R^2	0.982	0.977	0.971

R^2: determined coefficient; ARE: average relative error.

The feasibility of Freundlich model was possibly due to its assumption of the multilayer adsorption on heterogeneous adsorbent surfaces. Therefore, a multimolecular layer adsorption may be involved in the sorption of 2,4-DCP and the surface of MTL was a bit heterogeneous. The heterogeneity could be caused by variety of functional groups on the leaf surface along with interactions between adsorbate molecules and active sites of adsorbent. Additionally, the Henry equation was adequate to model the adsorption isotherm, suggesting this heterogeneous adsorption was processed in dilute solution. According to adsorption isotherm curves, there may be partition effect about 2,4-DCP between the solid phase and liquid phase.

3.2.5. Adsorption thermodynamics

The thermodynamic parameters such as change in enthalpy (ΔH°), entropy (ΔS°), and free energy (ΔG°) were determined to estimate the impact of temperature on the adsorption of 2,4-DCP by MTL.

The apparent equilibrium constant (K_c) was calculated adopting the following equation [39–41]:

$$K_c = \frac{C_{ad,e}}{C_e} \tag{9}$$

where $C_{ad,e}$ was the amount of 2,4-DCP adsorbed on the adsorbent at equilibrium (mg L^{-1}); C_e was the equilibrium concentration of 2,4-DCP in solution (mg L^{-1}).

The value of Kc was used to compute free energy change (ΔG°) in the following relational expression:

$$\Delta G^\circ = -RT \ln K_c \tag{10}$$

The enthalpy change (ΔH°) and entropy change (ΔS°) were determined from the intercept and slope of plot between ΔG° and T.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{11}$$

where T was the absolute temperature, K; R was universal gas constant, 8.314 J mol^{-1} K^{-1}.

The magnitudes of ΔH°, ΔS°, and ΔG° at different temperatures for adsorption of 2,4-DCP on MTL were listed in Table 4.

The values of ΔH° and ΔS° were found to be 19.8 kJ mol^{-1} and 0.0595 kJ mol^{-1} K^{-1}, respectively. The positive ΔH° further confirmed endothermic nature of adsorption on 2,4-DCP–MTL system. The obtained ΔS° (0.0595 kJ mol g^{-1} K^{-1}) suggested the increasing randomness at the solid/solution interface and structural changes of adsorbate and adsorbent during the adsorption process. In other words, these adsorbed 2,4-DCP molecules on the surface of MTL were organized more randomly than those in solution. Similar phenomenon of positive ΔH° and ΔS° for 2,4-DCP adsorption onto *punica granatum* peel waste was reported by Bhatnagar [7].

Values of the Gibbs free energy change (ΔG°) were 1.50, 0.774, and 0.313 kJ mol^{-1} at 308, 318, and 328 K, respectively. And, positive ΔG° revealed this adsorption process was nonspontaneous in the range of studied temperatures. Similar results were observed in the adsorption of 2,4-DCP on palm pith carbon [11] and maize cob carbon [13]. In addition, the values of ΔG° decreased with temperature increasing.

Table 4
Thermodynamic parameters of 2,4-DCP adsorption on MTL

ΔH°/(kJ mol^{-1})	ΔS°/(kJ mol^{-1} K^{-1})	ΔG°/(kJ mol^{-1})		
		308 K	318 K	328 K
19.8	0.0595	1.50	0.774	0.313

3.2.6. Desorption studies

Degradation of pollutants and regeneration of saturated adsorbent was crucial to evaluate the reusability of the adsorbents and to elucidate the mechanism of adsorption [42–44].

If 2,4-DCP adsorbed on the adsorbent surface was desorbed easily by deionized water, the attachment of phenolic derivatives and leaf surface was by means of feeble binding force. The mechanism of adsorption may be ion exchange if alkali liquor was effective during desorption process. The chemisorption would be verified if high desorption rate was obtained using organic solution, such as ethanol. In this paper, three different desorption solutions were tested in batch system to find optimal reagent. The desorption percentages were found to be 23.1, 31.8, and 83.3% for deionized water, 0.1 mol L^{-1} sodium hydroxide, and 75% ethanol, respectively. Thus, it was rational to refer that the reaction between 2,4-DCP and MTL was controlled predominantly by chemisorption, and hydrophobic interactions were involved between surfactants molecules impregnated on the leaf surface and 2,4-DCP.

The regenerated MTL was repeatedly used to remove 2,4-DCP when 75% ethanol served as elution solution. The results in Table 5 definitely displayed that the adsorption capacity of spent MTL did not decline noticeably after three adsorption–desorption cycles.

The kinetics of desorption of 2,4-DCP from saturated MTL using 75% alcohol as desorption solution was shown in Fig. 9. Approximate 80.8% of 2,4-DCP was desorbed rapidly within the first 60 min. Thereafter, the rate of desorption slowed down until equilibrium was reached after 120 min. And desorption efficiency was obtained above 83% eventually. This phenomenon was explained by the following facts. At the beginning of desorption, all 2,4-DCP was loaded on MTL, and no adsorbate was present in alcohol solution. Rate of desorption was proportional to the

Table 5
The adsorptive capacity of regenerated MTL

Cycle	q_e (mg g^{-1})	Regeneration efficiency (η, %)
1	31.6	62.8
2	22.9	45.3
3	20.1	39.5

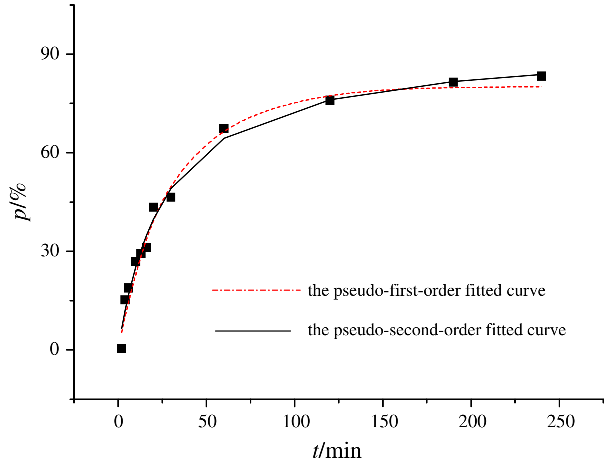


Fig. 9. Desorption kinetics of 2,4-DCP from spent MTL and fitted curves.

driving force [45]. As a result, great concentration gradient at initial stage facilitated the diffusion of 2,4-DCP from the leaf surface to the desorbing solution. But after a lapse of time, the adsorbate in solution and remained adsorbed would acquire equilibrium.

Fig. 9 also gave the nonlinear fitted kinetic curves of the pseudo-first-order model and pseudo-second-order model for desorption of 2,4-DCP by 75% alcohol. It showed a good agreement between the fitted curves and experimental data, indicating both the pseudo-first-order and pseudo-second-order models were suitable for this desorption system. Thus, the desorption of 2,4-DCP by 75% alcohol was a complicated reaction and both chemisorption and physisorption may be involved during the process.

Consequently, the excellent performance conducted using 75% ethanol demonstrated that phoenix tree leaf modified by surfactant CPC acted as low-cost adsorbent was feasible and economical to remove 2,4-DCP from wastewater.

4. Conclusion

The main purpose of this study was to assess the performance of the surfactant-modified phoenix tree leaf to adsorb 2,4-DCP from wastewater. FTIR and elemental analysis showed that CPC was successfully modified onto surface of NTL. The adsorption quantity was up to 188.8 $\mathrm{mg\,g^{-1}}$ at experimental condition. Adsorption kinetics, isotherms, and thermodynamics of this adsorption process were investigated. The Freundlich and Henry models provided good correlation of the equilibrium adsorption data, while the kinetic process was fitted better by the pseudo-second-order equation. The thermodynamic parameters showed that 2,4-DCP adsorption process was endothermic in nature. Desorption studies indicated that chemisorption was main mechanism during this adsorption process. Due to high adsorption capacity, low cost, abundant availability and easy modification, it could be concluded that MTL was a promising alternative biomass to remove 2,4-DCP from aqueous solution.

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