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Removal of chlorophenol from aqueous solutions by multi-walled carbon nanotubes: Kinetic and thermodynamic studies

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ABSTRACT

Kinetics and thermodynamic studies were conducted for the adsorption of 2,3-dichlorophenol, as an example of persistence organic pollutants, on pristine multi-walled carbon nanotubes (MWCNTs) in aqueous solution. The adsorption of 2,3-dichlorophenol was found to be dependent on mass of MWCNTs, concentration, solution pH, and adsorption temperature. MWCNTs were found to be an excellent adsorbent for the removal of 2,3-dichlorophenol from aqueous solutions in a very short period of time. A comparison of the kinetic models and the overall adsorption capacity was best described by the pseudo second-order kinetic model. The kinetics of the adsorption showed that the adsorption is mainly due to the diffusion of 2,3-dichlorophenol from the aqueous phase to the solid phase. The adsorption of 2,3-dichlorophenol on pristine MWCNTs at different temperatures was studied. The thermodynamic parameters showed that the adsorption process is product favored, and becomes more so at lower temperature, since the adsorption is exothermic. The magnitude of the enthalpy suggests a weak type of bonding between the 2,3-dichlorophenol and the MWCNTs. The entropy values were negative, indicating that 2,3-dichlorophenol is more ordered on the aqueous phase than at the MWCNTs surface.

1. Introduction

There has been increasing concern and more stringent regulation standards pertaining to the discharge of persistence organic pollutants to the aquatic environment, due to their toxicity and detriment to living species including humans. Persistence organic pollutants are non-degradable and can accumulate in living tissues, so they must be removed from polluted water. Chlorophenols are one of these harmful and toxic persistence organic pollutants, which are commonly used in a number of industrial applications such as biocides and wood preservation, in addition produced as bi-products of many other processes. Chlorophenols are sparingly soluble in water (less than 1 g/l at 25 °C) but the removal of these toxic compounds from aqueous systems represents a problem, especially when it is present at very low concentrations. Current methods for removing chlorophenols from polluted water include microbial degradation, adsorption on activated carbon, biosorption, chemical oxidation, deep-well injection, incineration, solvent extraction and irradiation [1–6]. Among these methods, adsorption is a promising and widely applied method due to its cost-effectiveness and the ability to recycle both of the pollutants (adsorbate) and the adsorbents. A number of materials, including activated carbon [1], fungus [3], hollow fiber [4], red mud [7], fly ash [8], and many other adsorbents, have been reported to be capable of adsorbing chlorophenols from aqueous solutions. But efforts dedicated to exploring new effective adsorbents continue to grow. Carbon nanotubes (CNTs), a new member in the carbon family, were first reported following arc-discharge synthesis of C_{60} by Iijima in 1991 [9]. Carbon nanotube is one of the most suitable candidates because it has a wide range of length scale and it is capable of forming a carboxylic group on the surface [10]. Different diameter and chirality of nanotubes give rise to diverse chemical, physical and mechanical properties [11–13]. Many research studies have showed the ability of carbon nanotubes to adsorb different pollutants from various aqueous samples [14–20]. This ability of CNTs; compared with other adsorbents, is due to strong interaction between the CNTs surface and the pollutants due to the unique structure of CNTs as a result of the delocalized π-electrons on the hexagonal arrays of carbon atoms in grapheme sheets of CNTs surface. Despite of the fact that the cost of carbon nanotubes is quite expensive compared with other conventional treatment methods, but there production cost is getting lower and the unique properties of these tubes made them a promising material for environmental remediation. In spite of this very strong adsorption capability of carbon nanotubes towards different pollutants, the studies on the adsorption of organic pollutants such as chlorophenols by MWCNTs are still scarce in literature. Kinetic studies are very important factors for understanding the mass transfer of different analytes for

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the bulk phase to an adsorbent such as MWCNTs and to determine the different conditions affecting this transfer. Thermodynamics calculation of the adsorption process is required to understand the mechanism of adsorption and spontaneity, as well, the heat of adsorption by calculating different thermodynamic parameters of the adsorption. In this research work, kinetic and thermodynamic studies were performed for the adsorption of 2,3-dichlorophenol (DCP), as an example of persistence organic pollutants, on pristine multi-walled carbon nanotubes (MWCNTs) in aqueous solution in order to achieve a better understanding of the adsorption process and enhance the efficiency of chlorophenols removal from polluted water.

2. Experimental details

2.1. Materials

Multi-carbon nanotubes (>80% purity) produced using chemical vapour deposition and iron as catalysts were purchased from Sun Nanotech (China) and they were used as received without any pretreatment. A scanning electron microscope (SEM); JEOL JSM-5600 Digital Scanning Electron Microscope, was used to characterize the MWCNTs for its morphological information. Texture properties of the prepared samples were determined from nitrogen adsorption/desorption isotherms measurements at 77 K using a model NOVA 3200e automated gas sorption system (Quantachrome, USA). Prior to measurement, each sample was degassed for 3 h at 200 °C. The specific surface area, S_{BET}, was calculated by applying the Brunauer–Emmett–Teller (BET) equation [21]. Pore size distribution was generated by the Barrett–Joyner–Halenda (BJH) [22] analysis of the desorption branches, and values of the average pore size were calculated. Microporosity was assessed from the *t*-plot method, using Harkins–Jura correlation [23] for a *t*-plot as a function of the normalized pressure, p/p^o. Surface areas obtained by the *t*-plot method, S_t were calculated from slope analysis of the *t*-plots. 2,3-dichlorophenol was obtained from Merck (>98%) was chosen as the target compound to represents chlorophenols and persistent organic pollutants.

2.2. Kinetic adsorption experiments

The determination of 2,3-dichlorophenol concentration was performed using Lambda EZ150 UV/Vis Spectrophotometer at a wavelength of 276 nm. The blank used in the experiment was distilled water without any 2,3-dichlorophenol. Kinetic adsorption experiments were carried out to establish the effect of time on the adsorption process and to identify the adsorption rate. The experimental procedures are described as follows. (1) Prepare a series of 1-L solutions containing different DCP concentrations. (2) Measure initial pH and then add a given amount of the MWCNTs (0.5 g/l) into the solution. (3) Agitate these solutions on a magnetic stirrer at 400 rpm for 2 h at room temperature (298 ± 2 K). (4) At the completion of preset time intervals, a 5 mL of solution was taken and immediately filtered through a 0.45 µm membrane filter (supor-450, 25 mm, Gelman Sciences Ann Arbor, MI, USA) to collect the supernatant. (5) Determine the residual DCP concentration in the supernatant. The residual DCP concentration in the supernatant was analyzed using a Lambda EZ150 UV/Vis Spectrophotometer. The amount of DCP adsorbed was determined as the difference in concentration between samples withdrawn at two consecutive time intervals during the course of the adsorption experiments. The adsorption capacity of the MWCNTs, q_t (mol g^{-1}), which represents the amount of DCP adsorbed per amount of MWCNTs, was then calculated by a mass–balance relationship using Eq. (1):

$$q = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 and C_t are the concentrations of DCP in solution (mol l^{-1}) at time $t = 0$ and t, respectively, V is the volume of the solution (l), and m is the mass of the dry adsorbent used (g).

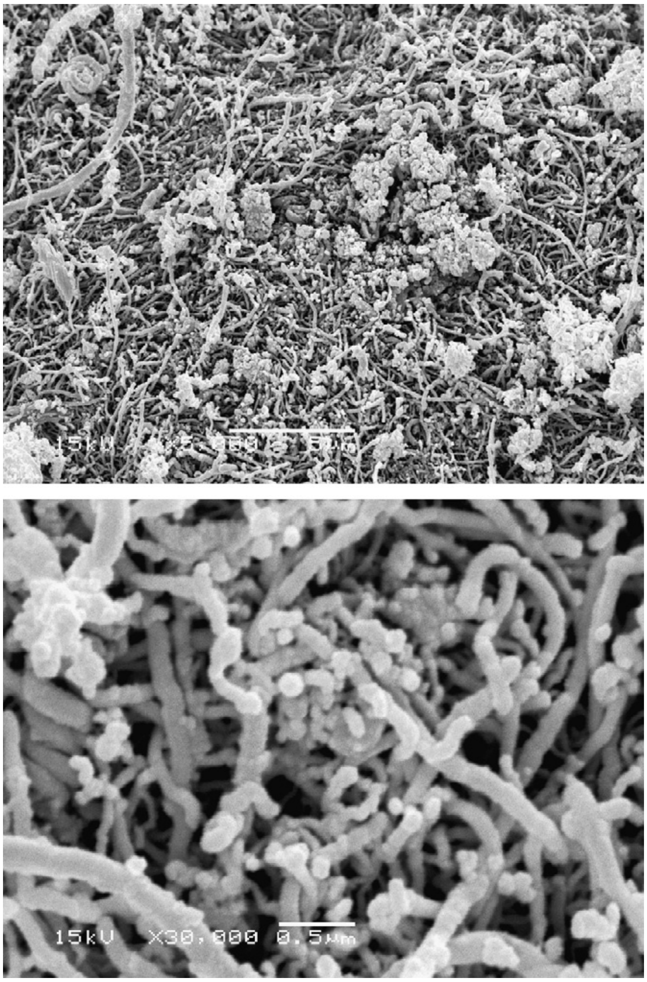

Fig. 1. SEM images of pristine MWCNTs.

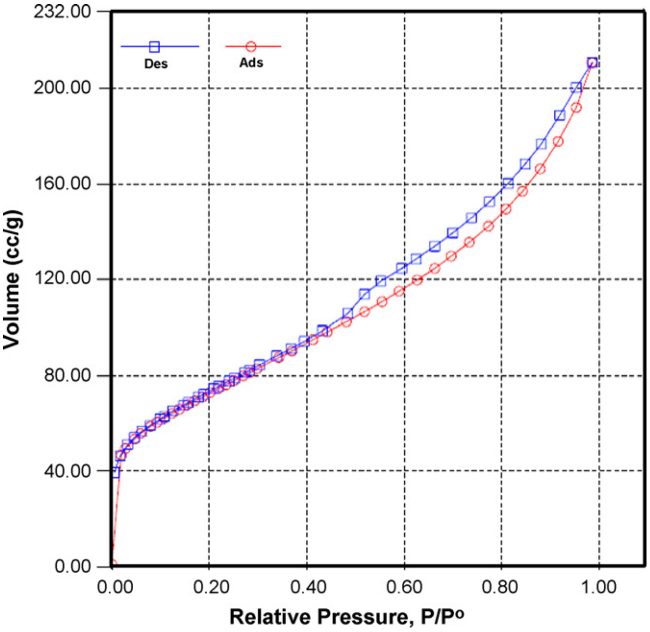

Fig. 2. N_2 adsorption/desorption isotherm of MWCNTs.

3. Results and discussion

3.1. Characterization of multi-walled carbon nanotubes

Scanning electron microscope imaging was used to study the morphological surface of the pristine MWCNTs and a representative image is presented in Fig. 1. It is clear from the figure that the pristine MWCNTs are highly tangled tubes with average diameter between 80 and 150 nm. Nitrogen adsorption/desorption isotherm for pristine MWCNTs were determined from N_2 adsorption isotherm measured at 77 K and the results are presented in Fig. 2. The isotherm obtained is classified as type IV isotherm with

Table 1
Figures of merit for the determination of the 2,3-dichlorophenol using UV–vis spectrophotometer from aqueous solution.

Figure of merit	Value
Linear dynamic range (LDR) (M)	1×10^{-5} M to 1×10^{-3} M
Sensitivity (Slope of the calibration curve)	1581
Correlation coefficient (R^2)	0.999
Limit of detection LOD (ng/ml)	1×10^{-6} M
LOQ: limit of quantification (ng/ml)	3.3×10^{-6} M

H3 type hysteresis loops according to the original IUPAC classification [24]. However, according to the extended classification of adsorption isotherms [25] the isotherm is classified as type IIb isotherms. The specific surface area for the pristine MWCNTs was calculated from the BET-equation and was found to be 258 $m^2\,g^{-1}$. The total pore volume V_p, and pore size W_p were obtained for the pristine MWCNTs and were found to be 0.32 cc g^{-1} and 25–27 Å, respectively.

3.2. Method development for the determination of 2,3-dichlorophenol

The analytical figures of merit for the determination of the 2,3-dichlorophenol using UV–vis spectrophotometer were calculated from its calibration curve and the results are presented in Table 1. The calibration curves were linear for 2,3-dichlorophenol within the experimental concentration range from 1×10^{-5} M till 1×10^{-3} M with a correlation coefficient (R^2) greater than 0.995 and the sensitivity of the spectrophotometer for the target analyte in aqueous solution was 1581; slope of the calibration curve. The limit of detection (LOD), defined as the concentration giving a signal three times the standard deviation of blanks (signal/noise ratio of 3), was measured by integrating blank peak areas for each analyte in ten (10) independent performances in distilled water as the blank was found to be 1×10^{-6} M. The limit of quantification (LOQ) was the lowest analyte concentration that could be quantified in a sample with acceptable relative standard deviation (RSD) under the stated operational conditions of the method. LOQ was determined as the analyte concentration corresponding to a signal/noise ratio of 10 and it was found to be 3.3×10^{-6} M. The average relative standard deviation was 9.0%, showing the good reproducibility of the UV–vis spectrophotometer for the determination of the 2,3-dichlorophenol.

3.3. Adsorption study

The adsorption of any analyte into a solid adsorbent is mainly affected by different factors such as the adsorbent mass, the analyte concentration, as well as the pH of the solution, especially when the target analyte contains acidic hydrogen ion such as chlorophenols.

3.3.1. Effect of mass

The effect of MWCNTs mass on the % DCP adsorbed from aqueous solution was studied at a DCP concentration of 1×10^{-4} M solution and the results are shown in Fig. 3. Three different masses of MWCNTs were used: 50 mg, 100 mg, and 200 mg. It is clear from the figure that increasing the amount of adsorbent leads to increasing the % of the analyte adsorbed. The % DCP adsorbed from aqueous solution increased from 50% to 71% and to 94% when 50 mg, 100 mg, and 200 mg of MWCNTs were used, respectively. This may be due to the fact that increasing the adsorbent mass may affect the adsorption as it increases the exposed surface area and the number of binding sites which are available for adsorption and hence increased the % DCP adsorbed from aqueous solution.

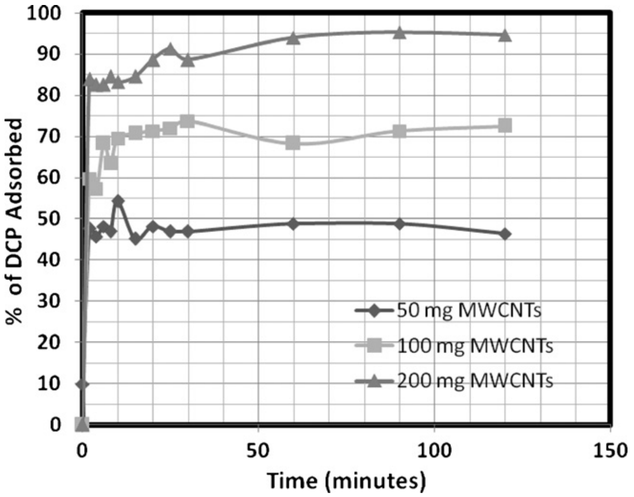

Fig. 3. Effect of MWCNTs mass on the adsorption of DCP from aqueous solution.

3.3.2. Effect of 2,3-dichlorophenol concentration

The effect of DCP concentration on the adsorption behavior of MWCNTs was studied at a mass of 100 mg and the results are shown in Fig. 4. Generally, it is clear from the figure that increasing the concentration of 2,3-dichlorophenol while keeping the amount of the adsorbent constant leads to the reduction in the % adsorbed. The % of 2,3-dichlorophenol adsorbed from aqueous solution decreased from 72% to 42% and to 35%, when 1.0×10^{-4} M, 4.0×10^{-4} M, and 8.0×10^{-4} M solution were used, respectively. In other words, increasing the concentration of the DCP eight folds (×8), from 1.0×10^{-4} M to 8.0×10^{-4} M, resulted in 50% reduction in the adsorbability of the pristine MWCNTs; from 72% to 35%. This may be due to the saturation of the active sites of the MWCNTs with the 2,3-dichlorophenol molecules at higher concentrations.

3.3.3. Effect of pH

One of the most important factors which affect the adsorption of analytes from aqueous solution is the pH. This is because it plays an important role in the adsorption process as the OH^- and H^+ ions might compete with the other analyte for the adsorption on the active site and/or a strong water hydration sphere around the analyte molecule. In general, it is well known that chlorophenols are characterized by the presence of acidic H^+ which might be ionized when the pH of the solution is equal or more than its pK_a. For our target analye, 2,3-dichlorophenol, had pK_a value equal to 7.8 [26]. The effect of the pH on the adsorption 2,3-dichlorophenol from aqueous solution was studied at different pHs and the results are

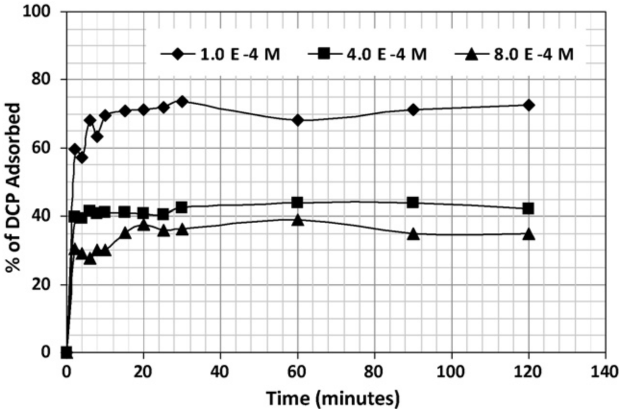

Fig. 4. Effect of DCP concentration on the adsorption from aqueous solution.

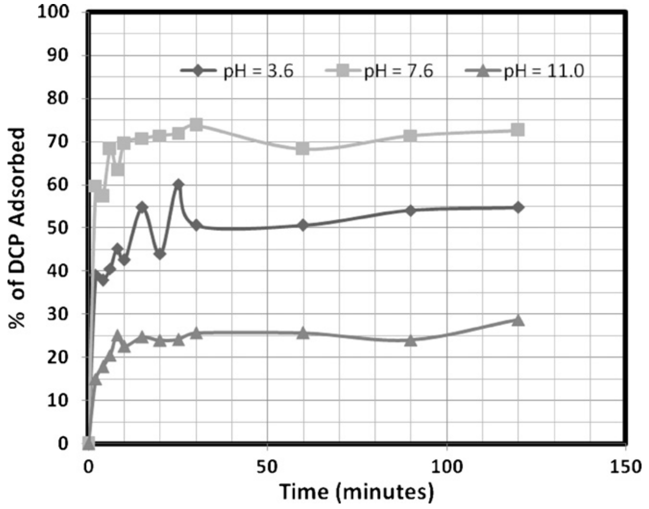

Fig. 5. Effect of the solution pH on the adsorption of DCP by MWCNTs.

presented in Fig. 5. Three different pHs were used: a 3.6 which is very acidic and much lower than the pK_a value, a 7.6 which is almost the same like the pK_a value and similar to the pH of the natural waters, and finally at pH 11.0 which is basic and much more than the pK_a value. At pH 3.6, the adsorption of the 2,3-dichlorophenol was considerably low and this may be due to the fact that H$^+$, which have almost the same concentration (1×10^{-4} M) out-compete with the chlorophenol for the same active sites [27,28]. When the pH of the solution increased from 3.6 to 7.6 the adsorption was greatly enhanced, increased from 54% to 72%. At this pH, which is slightly lower than the pK_a value, most of the chlorophenol molecules were not ionized and there were not any competitions with any other species which existed in the solution for the active sites available on the MWCNTs surface. Meanwhile, when the pH of the solution was increased from 7.6 to 11.0; higher than the pK_a value, most of the chlorophenol molecules were present in their ionized; negative ions. This leads to the drastic decrease in the adsorption from 72% to 26%. This decrease was mostly due to the repulsion between the MWCNTs surface and the anionic chlorophenolide ions as well as the competition between the analytes and the hydroxyl ions present (higher in concentration than the chlorphenol), on the solution at such high pH, for the adsorption on the MWCNTs active sites [29,30].

3.3.4. *Effect of the solution temperature*

The temperature of the solution is considered as another critical factor which may affect the adsorption process greatly. Also, if the removal efficiency of a certain pollutant from aqueous solution is temperature dependent, which is the case most of the time, it might affect the suitability of the adsorbent as increasing the temperature mostly consumes fuel and time. Generally, the adsorption depends on the temperature in two different ways. High temperature, generally increases the rate of diffusion of the adsorbate molecules through the solution to the external and internal surface of the adsorbent, and may change the equilibrium adsorption capacity of the adsorbent for a particular adsorbate. The effect of the solution temperature on the adsorption and removal of chlorophenol was studied at three different temperatures: 278 K, 298 K, and 313 K. The results are presented in Fig. 6. It is obvious from the figure that showed increasing in temperature had a great effect on the % of chlorophenol removed from the solution. Increasing the temperature from 278 K to 298 K, and to 313 K accompanied with a sharp and significant decrease in the % of 2,3-dichlorophenol adsorbed and removed from the solution, as it decreased from 87% to 72% and to 48%, respectively. This suggested that the adsorption and removal of DCP from aqueous solution is an exothermic process, which will be discussed in detail at the thermodynamic section.

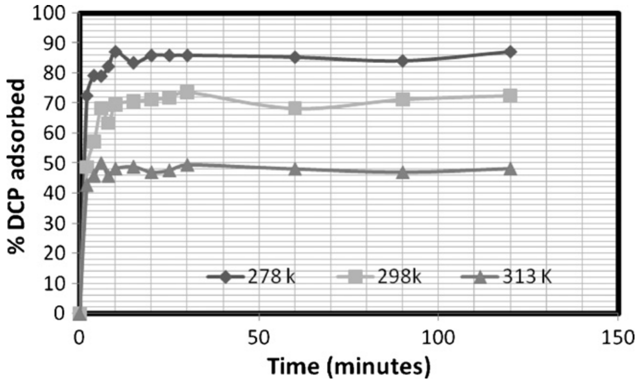

Fig. 6. Effect of the solution temperature on the adsorption of DCP by MWCNTs.

3.4. *Kinetics study and evaluation of the thermodynamic parameters*

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. Successful application of the adsorption demands innovation of cheap, easily available and abundant adsorbents of known kinetic parameters, and sorption characteristics. Adsorption kinetics can be modeled by several models – the pseudo first-order Lagergren equation and pseudo second-order rate equation given below as Eqs. (2) and (3), respectively.

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1}{2.303}t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e}t \qquad (3)$$

where k_1 is the rate constant of pseudo first-order adsorption (min^{-1}), k_2 (g mol^{-1} min) the rate constant of pseudo second-order adsorption, q_e and q_t are amount of analyte adsorbed on adsorbent (mol g^{-1}) at equilibrium and at time t, respectively.

For the pseudo first-order kinetic model, plotting $\log(q_e - q_t)$ vs. time (t), did not give straight lines for all the studied temperatures. Whereas, when the pseudo second-order adsorption equation was used, it converged with clear straight line and high correlation coefficient (R^2). From the results, it is clearly seen that the equilibrium adsorption from the pseudo second-order model are much close to the experimental data, suggesting better application of the second-

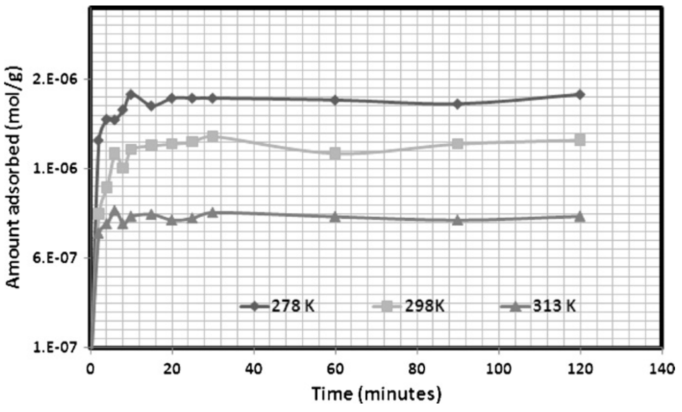

Fig. 7. Adsorption of DCP on pristine MWCNTs as amount adsorbed (mole of 2,3-dichlorophenol/g of MWCNTs) vs. time (minutes).

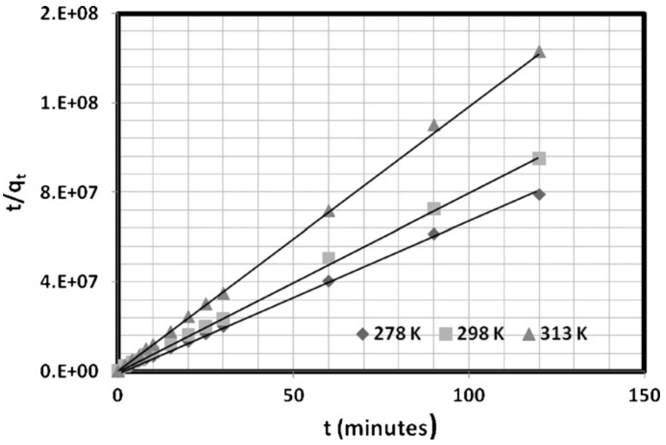

Fig. 8. Plots of pseudo second-order kinetics of 2,3-dichlorophenol on pristine MWCNTs (linear form).

order kinetics as shown in Figs. 7 and 8. The rate constant of pseudo second-order adsorption; k_2 (g mol^{-1} min), were calculated from the plots and their values are presented in Table 2. It is obvious from the table that increasing the temperature from 278 K to 298 K and then to 313 K, associated with decreasing the amount of chlorophenols adsorbed at equilibrium (q_e) and increase the rate constant of pseudo second-order adsorption (k_2). The pseudo second-order rate constant of chlorophenols adsorption is expressed as a function of temperature by the Arrhenius type relationship as it is expressed in Eq. (4).

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{4}$$

where E_a is the Arrhenius activation energy of sorption, representing the minimum energy that reactants must have for the reaction to proceed, A the Arrhenius factor, R the gas constant and is equal to 8.314 J mol^{-1} K^{-1}, and T is the solution temperature. When $\ln k_2$ is plotted vs. $1/T$ (K^{-1}), a straight line with slope $-E_a/R$ is obtained and shown in Fig. 9. The activation energy is obtained as 27.1 kJ mol^{-1}. This suggests that the adsorption is not a chemically activated process but a physical diffusion process.

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were determined by using the following equations [31–33]:

$$K_C = \frac{C_A}{C_s} \tag{5}$$

$$\Delta G^\circ = -RT \ln K_C \tag{6}$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

where K_C is the distribution coefficient for the adsorption, C_A the amount of chlorophenol (mol) adsorbed on the adsorbent per liter of the solution at equilibrium, and C_S is the equilibrium concentration (mol l^{-1}) of the chlorophenol in the solution. T is the solution temperature (K) and R is the gas constant. ΔH° and ΔS° were calculated from the slope and intercept of van't Hoff plots of $\ln K_C$ vs. $(1/T)$ as it shown in Fig. 10 and the calculated values of ΔG°, ΔH°, and ΔS° are presented in Table 3. It is seen that the adsorption process is spontaneous with the negative values of ΔG° within the experimental temperature and it became less spontaneous as the temperature increased from 278 K to 298 K, and to 313 K, as the ΔG° values were −4.43 kJ mol^{-1}, −2.19 kJ mol^{-1}, and −1.02 kJ mol^{-1}, respectively. The standard enthalpy change (ΔH°) for the adsorption on the pristine MWCNTs were negative and indicate that the process is exothermic in nature and the same effect was reported for p-chlorophenol and phenol on activated charcoal [34] and chitosan [35]. The magnitude of ΔH° (−38.3 kJ mol^{-1}) suggests a weak type of bonding between the DCP and the MWCNTs such as physical adsorption. The values obtained in this study agreed with the other values found in the literature for adsorption of chlorophenols, in general, on different adsorbents [34–36]. Also, the small value of ΔH° suggested that the process is not a surface chemical reaction but a diffusion process. The negative value of ΔS° shows decreased disorder at the solid–solution interface during the adsorption of chlorophenol. The adsorption decreases randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent, and an affinity of the MWCNTs toward chlorophenols. The values of the thermodynamic parameters estimated in this study agreed well with a previous published study [37], which focus on the adsorption of pentachlorophenol (PCP) by pristine MWCNTs. The ΔG° for the DCP was less negative (−2.19 kJ mol^{-1} at 298 K) compared with PCP in the previous study [37] (−33.7 kJ mol^{-1} at 298 K), while the ΔH° for the DCP was more negative (−38.3 kJ mol^{-1}) compared with

Table 2
Parameters of the pseudo second-order kinetic model for the adsorption of 2,3-dichlorophenol on pristine MWCNTs.

Temperature (K)	k_2	q_e	R^2
278	2.1×10^7	1.52×10^{-6}	0.999
298	3.1×10^7	1.26×10^{-6}	0.999
313	6.9×10^7	8.35×10^{-7}	0.999

k_2 (g mol^{-1} min) the rate constant of pseudo second-order adsorption, q_e is amount of analyte adsorbed on adsorbent (mol g^{-1}) at equilibrium.

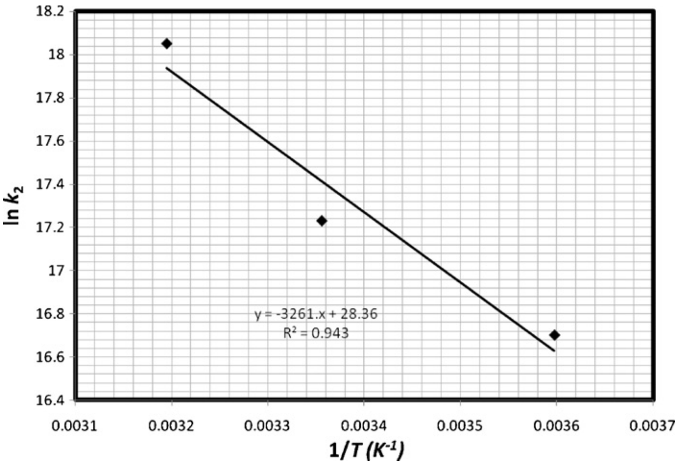

Fig. 9. Arrhenius plot of the pseudo second-order kinetics.

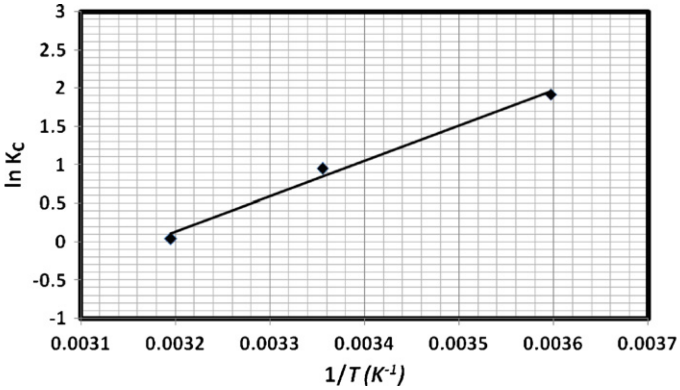

Fig. 10. Plot of $\ln K_C$ vs. $1/T$ for estimation of thermodynamic parameters.

Table 3
Values of the thermodynamic parameters for the adsorption of 2,3-dichlorophenol on pristine MWCNTs.

Temperature (K)	K_c	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})
278	0.082	−4.43	−38.3	−121.8	27.1
298	0.067	−2.19	−38.3	−121.1	27.1
313	0.044	−1.02	−38.3	−119.1	27.1

PCP in (−23.7 kJ mol^{-1}), whereas, the ΔS° for the DCP was negative (−121.1 J mol^{-1} K at 298 K) compared with PCP which was found to be positive (33.5 J mol^{-1} K at 298 K). This indicates that the DCP adsorption was entropy driven whereas it was enthalpy driven for the PCP.

4. Conclusion

Multi-walled carbon nanotubes as adsorbent was used for the removal of 2,3-dichlorophenol from aqueous solution. SEM images showed the well defined and entangled MWCNTs which varies in diameter and length. The BET surface area measurement indicated that the specific surface area of the MWCNTs was 258 m^2 g^{-1} and the total pore volume and average pore size were found to be 0.32 cc g^{-1} and 25–27 Å, respectively. Many of the factors that greatly affect the adsorption process was studied and optimized such as the mass of adsorbent, analyte concentration, pH and temperature of the solution. The % DCP adsorbed from aqueous solution was 94% for 200 mg of MWCNTs were used. At a pH lower or higher than the natural pH (7.0), the % removed was decreased. The kinetics studied was performed and the results suggested that the adsorption process was found to be a pseudo second-order process. Different thermodynamic parameters were calculated for the adsorption process and the results revealed that the adsorption process was spontaneous within the experimental temperature used as was indicated from the negative ΔG° (−2.19 kJ mol^{-1} at 298 K) and it became less spontaneous as the temperature increased. The adsorption process was found to be exothermic and the negative value of ΔH° (−38.3 kJ mol^{-1}) suggests that the adsorption is physical in nature. Also, the change in entropy was negative in value (−121.1 J mol^{-1} K at 298 K) which suggests that the adsorption of the chloropheol on carbon nanotubes decreased the randomness at the solid/solution interface.

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