Modeling of the adsorption kinetics of Basic Red 46 on single-walled carbon nanotube and carboxylate group functionalized single-walled carbon nanotube

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ABSTRACT

The present study was carried out to investigate the potential of single-walled carbon nanotube (SWCNTs) and carboxylate group functionalized single-walled carbon nanotube (SWCNT-COOH) as alternative adsorbents for the removal of Basic Red 46 (BR 46) from contaminated water by using batch adsorption studies. Effects of some key operating parameters such as pH, ionic strength and contact time on the dye removal were investigated and discussed. The experimental results show that SWCNTs and SWCNT-COOH are promising adsorbents for removing BR 46. Results showed that removal of BR 46 increased with increasing contact time, pH and ionic strength. Adsorption kinetics data were modeled using the first order, the pseudo-first and pseudo-second order, Elvoich equations and intra-particle diffusion models. Results show that the pseudo-first order kinetic model was found to correlate the experimental data well.

Keywords: Adsorption, Basic Red 46 removal, Single-walled carbon nanotube, Kinetic models

INTRODUCTION

Effluents from the textile industry contain various kinds of synthetic dyestuffs, and there has been increasing scientific interest in regard to decolorization of these effluents in the last few decades [1]. Removing color from wastes is often more important than other colorless organic substances, because the presence sence of small amounts of dyes (below 1 ppm) is clearly visible and influences the water environment considerably [2].

Physical, chemical and biological processes are the principles used in treating dyes in effluent wastewater [3]. Methods used to treat wastewater containing dye include coagulation-flocculation [4] and advanced oxidation process [5]. However, these methods are expensive and present operational problems such as development of toxic intermediates, lower removal efficiency, and higher specificity for a group of dyes, among others [6,7]. Adsorption is the most versatile and widely used method of water treatment because of its low cost, ease of operation, and efficiency in treatment [8].

Carbon nanotubes (CNTs) have attracted great attention in multidisciplinary areas due to their unique hollow tube structure and their many outstanding mechanical, electronic and optical properties [9]. CNTs have been proposed for various applications such as hydrogen storage devices, sensors and so on [10]. In comparison with classical adsorbents such as activated carbon and

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clay, CNTs is more attractive because of its favorable physicochemical stability, high selectivity, and structural diversity. Extensive experiments have been conducted on the adsorption of inorganic or organic contaminants on CNTs such as Zn^{2+} [11], Cd^{2+} [12], Pb^{2+} [13], Cu^{2+} [14], Cr^{6+} [15], fluoride [16] and dioxin [17]. Therefore, CNTs might be ideal sorbents for the removal of dyes from water. Earlier studies have obtained only equilibrium adsorption data and few works have measured the kinetics and thermodynamic parameters of adsorption on CNTs. Few investigations focused on the adsorption of organic pollutants on CNTs and simultaneously determined the kinetics equilibrium and thermodynamic parameters.

Therefore, the present objective of this study is to evaluate the Basic red 46 removal potential and adsorption ability of dye using single-walled carbon nanotube (SWCNTs) and carboxylate group functionalized single-walled carbon nanotube (SWCNT-COOH) was investigated. Finally, the rates and mechanism of the adsorption process were investigated. The objective of this study is to investigate the effect of Basic red 46 on contact time, initial concentration, pH and temperature on the adsorption process. Various kinetic evaluations have been used to describe the adsorption process. Here we attempted to apply a simple first order kinetic model for changing the bulk concentration, and pseudo first-order rate equation and pseudo second-order, Elovich model and intraparticle diffusion model for the adsorbent phase concentration.

EXPERIMENTAL METHODS
Chemicals and reagents
SWCNTs and SWCNT-COOH were purchased from NanoAmor Nanostructured & Amorphous Materials,
Inc, USA. SWCNTs (Armchair (6,6), Young's Modulus (0.94T TPa), Tensile strength (GPa 126.2T), purity, > 95; diameter 1-2 nm; length, 5-30 nm; surface area, ~ 400 m^2/g; and manufacturing method, catalytic chemical vapor deposition (CVD)) and SWCNT-COOH (content of COOH, 6 wt%; with purity > 95%; average diameter 1-2 nm; length 5-30 nm and SSA ~400 m^2/g). The BR 46 is from the commercial manufacturing company DyStar Co. (Germany).

Batch adsorption experiments
The adsorption experiments were conducted in 100 mL flasks containing 50 mL of BR46 solution of known concentration (50, 100,150 and 200 mg/L) prepared from the dilution of 250 ppm stock solutions. The initial pH of each flask solution was adjusted to optimum value (pH 9) with 0.1 M HCl or 0.1 M NaOH solution. Upon completion, the sample of the mixture was removed from the flask and separated by centrifuging at 4000 rpm for 5 min. The obtained solution was later analyzed for residual BR46. The adsorption capacities were calculated based on the differences of the concentrations of solutes before and after the experiment according to the following Eq. (1).

$$q_e = \frac{(C_i - C_f)V}{W} \tag{1}$$

where q_e is the concentration of the adsorbed solute, BR 46 (mg/g adsorbent); C_i and C_f are the initial and final (equilibrium) concentrations of the solute in solution (mg/ L); V (L) is the volume of the solution and W (g) is the mass of the adsorbent. To evaluate the fitness of kinetic and isotherm equations to the experimental data, the chi-square statistic (X^2) was used to measure the kinetic and isotherm constants. X^2 can be defined as

[18]:

$$X^2 = \sum_i^N \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \qquad (2)$$

If data from the model are similar to the experimental data, X^2 will be a small number; if they are different, X^2 will be a large number. The subscripts "exp" and 'calc" show the experimental and calculated values and N is the number of observations in the experimental data.

RESULTS AND DISCUSSION
Effect of contact time and temperature on adsorption

The contact time between BR 46 and each of adsorbents are the most important design parameter that effect the performance of adsorption processes. The effect of contact time on the performance of SWCNT-COOH and SWCNTs surfaces at various temperatures in adsorption of BR 46 was investigated individually. The solution pH and mass of adsorbents were fixed. The initial BR 46 concentration for all test solutions were 150 mg/L. Fig. 2 shows adsorption of BR 46 as a function of contact times ranging between 10 and 180 minute. These data indicate that adsorption started immediately upon adding SWCNT-COOH and SWCNTs surfaces as adsorbents to both solutions. The adsorption of BR 46 was rapidly increased from 22 and 39 mg/g in the 10 minute for SWCNTs and SWCNT-COOH surfaces as adsorbents, respectively. Thus, the contact time required achieving the equilibrium and complete adsorption for both adsorbents 80 and 100 minute for SWCNTs and SWCNT-COOH as adsorbents at 298 K, respectively. Therefore, the optimum contact time for SWCNTs and SWCNT-COOH surfaces in the tested dye was considered to be 100 minute. The shorter the contact time on the adsorption system, the lower would be the capital and operational costs for real-world applications.
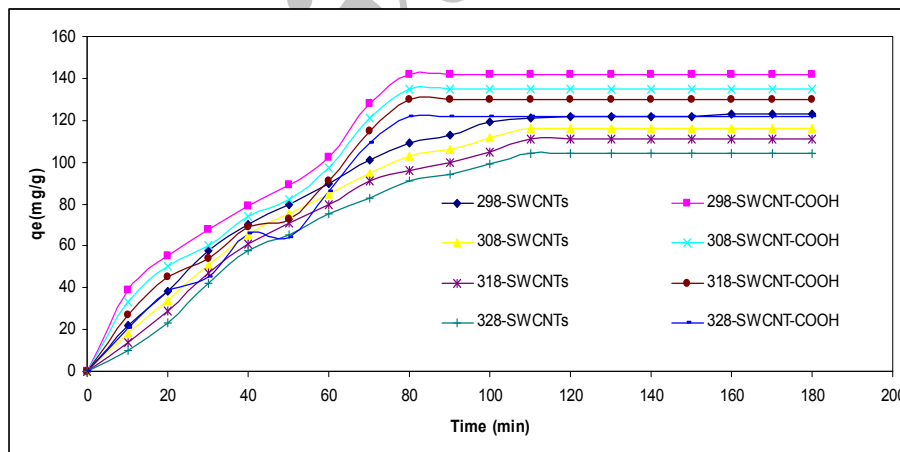

Fig. 1. Effect of contact time on the adsorption of BR 46 by SWCNT-COOH and SWCNTs surfaces at various temperatures, (Initial BR 46 concentration: 150mg/L, temperature: 298, 308, 318 and 328K, mass each of adsorbent: 0.05 g and pH 9).

Effect of pH

The pH is one of the most important factors controlling the adsorption of dyes onto suspended particles, because both adsorbed molecules and adsorbent particles may have functional groups which are affected by the concentration of hydrogen ions (H^+) in the solution and which are involved in the molecular adsorption process at the active sites of adsorbent. In order to investigate the effect of initial pH on the adsorption of BR46, equilibrium pH

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and effect of initial pH on amount adsorption in the presence of electrolyte, batch experiments were conducted at different initial pH values in the range 1– 11. Fig. 3 showed that equilibrium pH was not much affected in strongly acidic solution and the adsorption of BR46 was minimum but when initial pH was increased to 6 indicating that dye adsorbed

along with some H^+ ions. aqueous chemistry and surface binding-sites of the adsorbent. The equilibrium sorption capacity was minimum at pH 1 and increased up to pH 6, reached maximum over the initial pH 9. Further increase was noticed at pH 8–9.
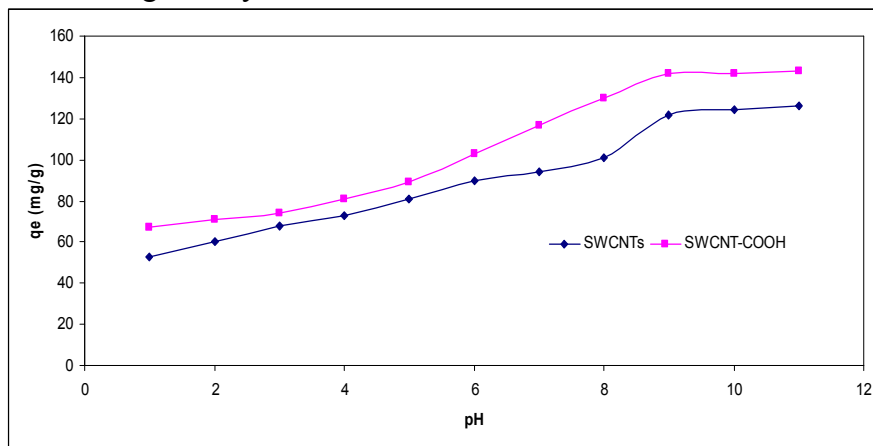

Fig. 2. Effect of initial pH of solution on adsorption of BR 46 by SWCNT-COOH and SWCNTs surfaces, mass each of adsorbents = 0.05 g, initial pH 9, contact time=100 minute, initial BR 46 concentration = 150 mg/L and Temperature 298 K.
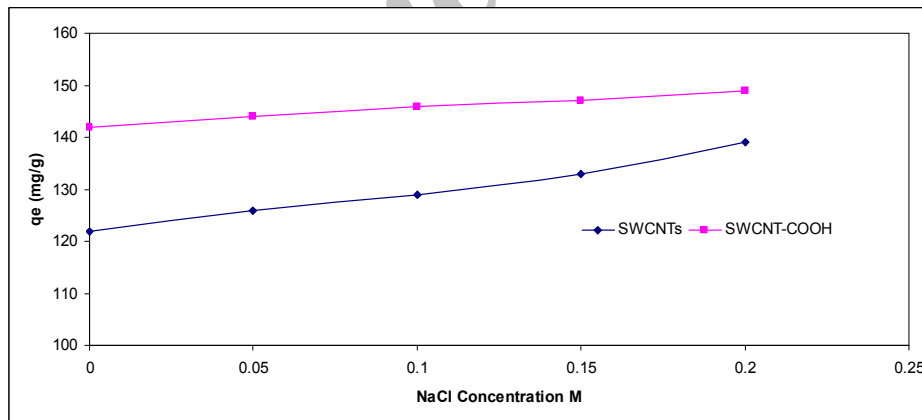

Fig. 3. Effect of NaCl concentration on BR 46 adsorption efficiency. Experimental conditions: BR 46 concentration 150 mg/L, mass each of adsorbent 0.05 g, initial solution pH 9, contact time 100 minute, and temperature 298 K.

Effect of ionic strength

The effects of NaCl with different concentrations ranging from 0.01M to 0.2 M on the BR 46 adsorption efficiencies of SWCNT-COOH and SWCNTs surfaces, shown in Fig. 4. It is observed that the variation of NaCl concentration exhibited a

significant effect on BR 46 adsorption and high salt concentration was contributive to BR 46 adsorbed. The presence of salt in wastewater lads to high ionic strength, which may significantly effect the performance of the adsorption process [19], and the facilitation for BR 46

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adsorption could be produced by two mechanisms [20]: one is the addition of salts resulting in the minimization of the repulsion among the negatively charged functional groups of BR 46.

Kinetics study

The adsorption process on a porous adsorbent in a stirring chamber generally involves several transport stages; external diffusion, internal diffusion, and actual adsorption. The model for the separation process should adequately account for the mass balance and the equilibrium isotherm if the system is isothermal. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (r^2, values close or equal to 1). A relatively high r^2 value indicates that the model successfully describes the kinetics of BR46 adsorption. Simple First Order Model

The sorption kinetics may be described by a simple first order equation [21]. The change in bulk concentration of the system using the following a linear form simple first order rate Eq. (2):

$$\log C_t = \frac{k_1}{2.303} t + \log C_0 \qquad (3)$$

Where C_t and C_o are the concentration of dye at time t and initially (mg/L), respectively, and k_1 is the first order rate constant, (1/min). The experimental results showed that the log C_t versus t (Fig. 4) for constant initial concentrations of dye was deviated considerably from the theoretical data. A comparison of the results with the correlation coefficient is shown in Table 1 and 2, which indicates the failure in expressing this adsorption process by the simple first order kinetics.
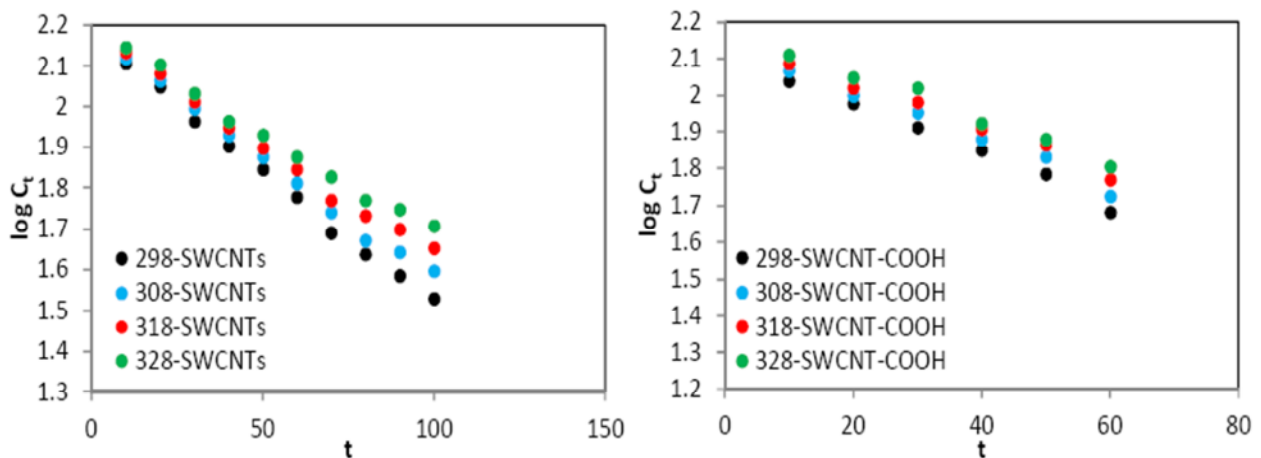

Fig. 4. Plot of the simple first order adsorption kinetics

Pseudo Firs-order Model

The sorption kinetics may be described by a pseudo first order equation [22]. The linear form equation is the following:

$$\log(q_e - q_t) = \log(q_e) - k_1 t \qquad (4)$$

where q_e and q_t are amounts of dye adsorbed at equilibrium and at time

(mg/g), respectively, and is the equilibrium rate constant of pseudo first-order adsorption, (1/min). Fig. 5 shows a plot of linearization form of pseudo first-order model. The slopes and intercepts of plots of versus were used to determine the pseudo first-order constant and equilibrium adsorption density. However, the experimental data deviated considerably

from the theoretical data. A comparison of the results with the correlation coefficients is shown in Table 1. The correlation coefficients for the pseudo first order kinetic model obtained at all the studies concentrations were low. This suggests that this adsorption system is not a pseudo first-order reaction.
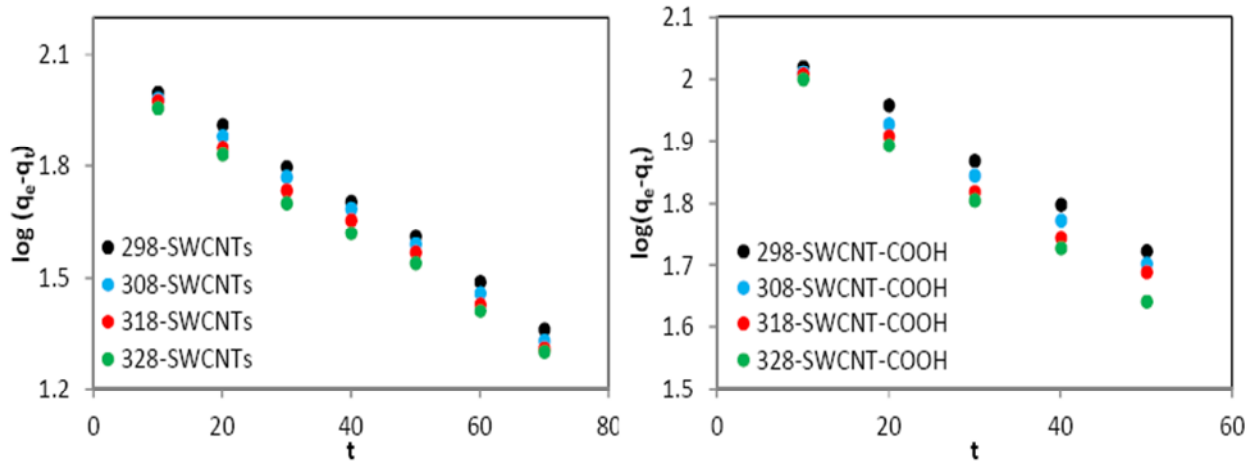

Fig. 5. Plot of the Pseudo Firs-order adsorption kinetics.

Pseudo Second-order Model

The adsorption kinetics may also be described by a pseudo second-order equation [23]. The linear form equation is the following:

$$t/q = 1/k_2 q_e^2 + t/q_e \qquad (5)$$

where k_2 is the equilibrium rate constant of pseudo second-order adsorption (g/mg.min). The slopes and intercepts of plots t / q versus t were used to calculate the pseudo second-order rate constants k_2 and q_e. The straight lines in plot of t / q versus t (Fig. 6) show good agreement of experimental data with the pseudo second-order kinetic model for different initial dye concentrations. Table 1 lists the computed results obtained from the pseudo second-order kinetic model. These indicate that the adsorption system studied belongs to the second order kinetic model.
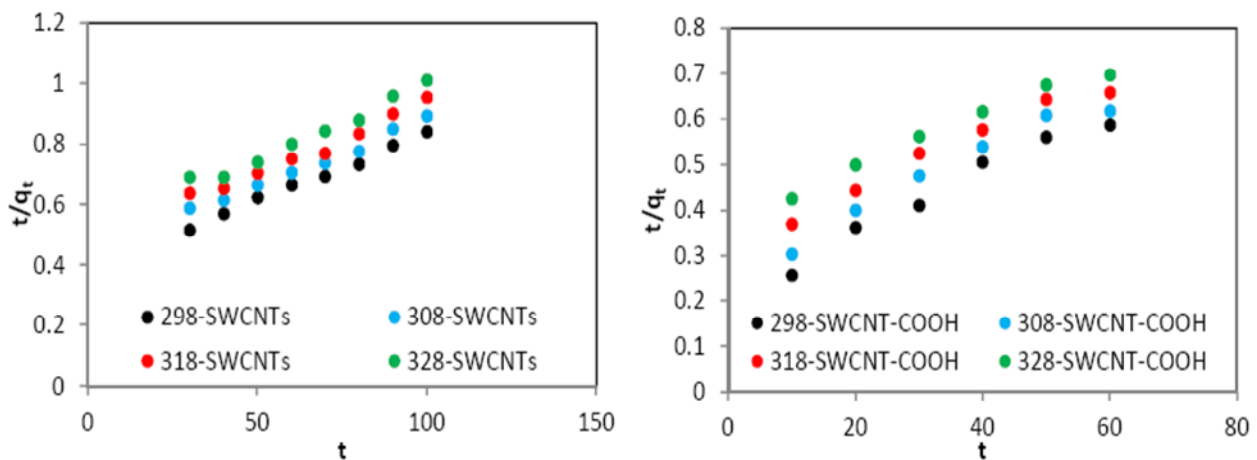

Fig. 6. Plot of the Pseudo Second-order adsorption kinetics.

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Elovich Model

The Elovich model equation is generally expressed as [24]:

$$\frac{dqt}{dt} = \alpha \exp(-\beta q^\mathsf{Y})$$ (6)

Where α is the initial adsorption rate (mg/g.min) and β is the adsorption constant (g/mg) during any experiment.
To simplify the Elovich equation, Chien and Clayton assumed $\alpha \beta \gg t$ and by applying the boundary conditions at and at equation (6) become $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ equation (7) become:

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t)$$ (7)

If metals ion adsorption fits the Elovih model, a plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $1/\beta$ and an intercept of $1/\beta \ln(\alpha \beta)$. Fig. 7 shows a plot of linearization form of Elovich model at constant concentrations studied. The correlation coefficients for the Elovich kinetic model obtained at all the studies concentrations were low. This suggests that this adsorption system is not an acceptable for this system.
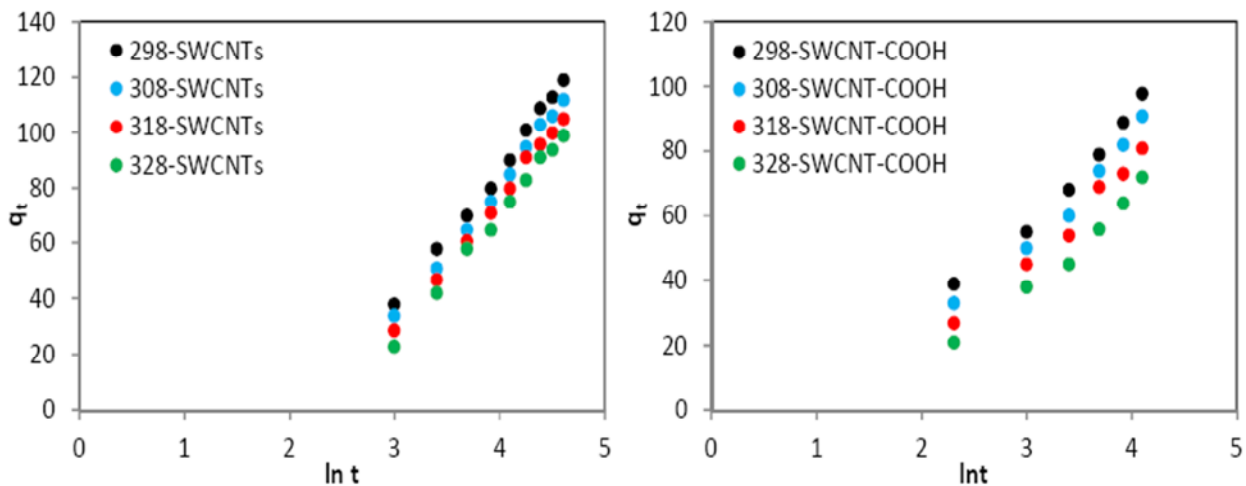

Fig. 7. Plot of the Elovich adsorption kinetics

The Intra-particle Diffusion Model

The intra-particle diffusion model is expressed as [25]:

$$q = k_i t^{1/2} + C$$ (8)

where C is the intercept and k_i is the intra-particle diffusion rate constant (mg/g h$^{0.5}$), which can be evaluated from the slope of the linear plot of q versus $t^{1/2}$. Fig. 10 shows a plot of the linearized form of the intra-particle diffusion model.

As can be seen from these figures, the pseudo first-order kinetic model provides the best correlation for all of the adsorption process, whereas the other models fits the experimental data well not for initial periods of the adsorption process only. Hence it was concluded that the pseudo second-first kinetic model was found to be rate limiting.
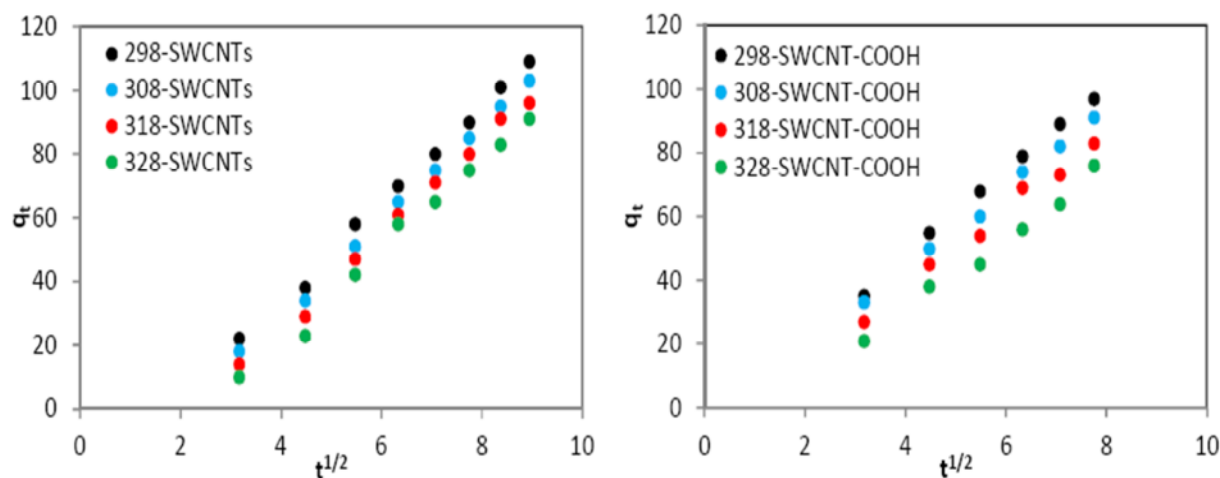
Fig. 8. Plot of the Intra-particle Diffusion adsorption kinetics.

CONCLUSIONS

single-walled carbon nanotube (SWCNTs) and carboxylate group functionalized single-walled carbon nanotube (SWCNT-COOH) can be used as effective adsorbenta for removing Basic red 46 from contaminated water sources. Increasing the temperature decreased the BR46 adsorption rate but the maximum adsorption capacity was similar. The pseudo first-order kinetic model accurately described the adsorption kinetics. The adsorption mechanism was found to be physic-sorption and the rate-limiting step was mainly surface adsorption.

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