Adsorption Thermodynamics, Kinetics and Mechanism for the Adsorptionof Erythromycin OntoMulti-Walled Carbon Nanotubes

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ABSTRACT

The ability of multi-walled carbon nanotubes (MWCNT) to adsorb the Erythromycin antibiotic from aqueous solution was studied through the batch experiments. The adsorption of Erythromycin onto MWCNT was found to be dependent on adsorbent dose, initial concentration and contact time. The experiments were carried out at natural solution pH. Based on the observed results, the highest removal efficiency was achieved to be 99.4% under optimum conditions. The adsorption kinetic results showed that the pseudo-second order model was more suitable to explain the adsorption of Erythromycin onto MWCNT. The adsorption mechanism results showed that the adsorption process was controlled by both the internal and external diffusion of Erythromycin molecules. The values of free energy change (ΔG^0) and enthalpy change (ΔH^0) revealed that the adsorption process has the spontaneous, feasible, and endothermic nature.

Keywords: Batch adsorption; MWCNT; Erythromycin; Kinetic; Thermodynamics.

1. INTRODUCTION

In recent years, antibiotics have been recognized as one of the most important water contaminants [1, 2]. Antibiotics are designed specifically as a drug to treat or to prevent the infectious diseases in human or animal body [3, 4]. The use of antibiotics has become an indispensable in human life and the global market consumption of these drugs increase steadily every year [5, 6]. For preventing or treating infections in humans or animals, only some parts of the antibiotics given dose are metabolized and the rest is excreted as the active compound [7, 8]. The emergence of resistant bacterial strains is considered as an issue associated with the abuse of antibiotics, which it can lead to serious public health crisis in the future [9, 10]. Antibiotics have been found in the water environment, including in wastewater, seawater treatment plants, surface water, groundwater, and even in drinking water [11].

Erythromycin, a 14-carbon macrolide, is generated by fermentation of Streptomyces erythreus and is used for treatment of various infections, especially the respiratory and skin diseases [12]. The similarity in its activity to penicillin is led to be considered as a substitute for penicillin against the Gram-positive bacteria in the people who are sensitive to penicillin. . Furthermore, it is also consumes against Mycoplasma, Campylobacter and Legionella [13].

Although the elimination of the antibiotics from the wastewaters has been reported to be expensive; however this wastewater must be satisfactorily treated prior to the release into the environment [14]. , The adsorption process, among the various process applied for treatment of wastewater containing antibiotics, is found as the most effective and efficient method [15, 16].

Compared to other process, e.g., the distillation or solvent extraction from diluted aqueous solutions, this process has achieved a great endorsement for large-scale separation from

liquid, since it is a process that need to low energy for adsorptive separation [17, 18]. Adsorption is a physical–chemical process that involves the mass transfer of a solute (adsorbate) from the fluid phase to the sorbent surface till the thermodynamic equilibrium of the adsorbate concentration is attained, with no further net adsorption [19].
Carbon Nanotubes (CNTs) have been studied extensively in last decade for different applications including water purification due to their extraordinary physiochemical properties associated with their small size, tubular morphology and ease of functionalization [20]. CNTs have been used for removal of antibiotics, dyes and heavy metals from its aqueous solution [21-23].
The major goal of this study is the evaluation of the MWCNTs ability for removal of Erythromycin from aqueous solution. The effects of several operating parameters such as adsorbent dose, initial Erythromycin concentration, mixing rate,contact time, and temperature on the Erythromycin adsorption at fixed pH=7 were investigated. The adsorption behavior of MWCNT towards Erythromycin removal was studied using kinetics and thermodynamic viewpoints.

2. MATERIALS AND METHODS

The multi-wall carbon nanotubes (MWCNT) used in this study had the purity more than 98% and provided from Research Institute of Petroleum Industry (RIPI), Tehran, Iran). The size and morphology of MWCNT were examined by scanning electron microscope (JEOL JSM 6500F) and transmission electron microscopy (TEM) (using a Philips XL30).The specific surface area of the adsorbent was determined by the BET method using a Gemini 2357 surface area analyzer (Micromeritics Instrument Corporation, USA).
Erythromycin (Fig. 1), an antibiotic, with a molecular formula of $C_{37}H_{67}NO_{13}$, molecular weight 733.93, λ_{max} of 280 nm, and C.I. number of 114-07-8, was chosen as a model antibiotic for the present experimental studies. The stock solution of Erythromycin (500 mg/L) was prepared by dissolving 500 mg of Erythromycin powder in 1000 mL of distilled water. The stock solution was diluted with distilled water to obtain the solutions with desired concentrations (10–100 mg/L).

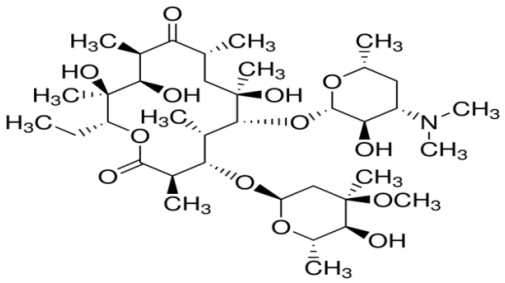


Fig 1. Chemical structure of Erythromycin

Batch Adsorption Test and Optimization of Conditions

The adsorption experiment was carried out in batch system inside 250 mL Erlenmeyer flasks containing 100 mL of synthetic Erythromycin solution. Initial pH of the samples was set by 0.1 molar NaOH and HCl. Afterwards, 0.4 g/L of adsorbent were added to the solutions with Erythromycin initial concentration of 25 ppm. The final solution was stirred at 30 °C and 120 rpm for 75 min. The solutes were filtered through the filter paper and 5 mL of the solution was analyzed to measure the adsorbed Erythromycin concentration. The optimization process

was also repeated for other parameters. These parameters were adsorbent dosage (0.1–1 g/L), mixing rate (0–200 rpm), and initial concentration of Erythromycin ion in the solution (10–100 ppm). To obtain the optimum condition, after adjusting the contact time to equilibrium condition, the desired parameter was varied at the determined range while other parameters were kept constant. The optimum condition of each parameter was selected and the investigation continued to define the optimum condition of other parameters. The Erythromycin concentration was identified by spectrophotometer at 280 nm (model DR-5000). In this research, all of the tests performed twice and the best results were reported.
The amount of adsorbed ions by adsorbent for each gram of adsorbent is identified by following Eq[23, 24]:

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

Where q_e is the amount of adsorbed Erythromycin per gram of MWCNT (mg/g) in the equilibrium state, C_0 and C_e are initial and equilibrium concentrations of Erythromycin (mg/L), V is the solution volume and W is the weight of the MWCNT.

3. RESULTS AND DISCUSSION

Fig. 2 displays the surface morphology of MWCNTs. The SEM and TEM figures show that the MWCNTs were cylindrical and the range of main external and internal diameters was 2-3.5 and 1.2-1.7 nm, respectively. The specific surface area of the adsorbent used in this study was 782.8 m^2/g.

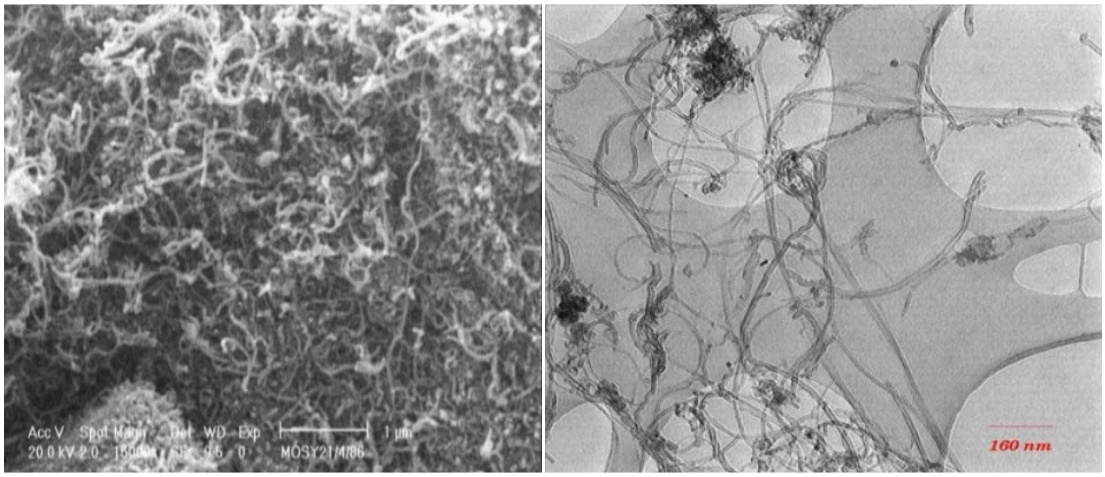


Fig. 2. Micrographs of MWCNTs (a) SEM and (b) TEM.

Effect of contact time and temperature: In order to establish the equilibrium time for Erythromycin adsorption onto MWCNT, the effect of contact time during the process was investigated until equilibrium reached. As shown in Fig. 3 the removal efficiency increases rapidly (in the first 75 min) due to the abundant availability of active binding site of the adsorbent and then remained almost constant with the occupancy of these sites [25-27]. Since the removal efficiency did not increase by increasing the time after 75 min, this time was applied as the equilibrium time for further experiments.

The effect of temperature on adsorption of Erythromycin onto MWCNT was conducted at 15, 25, 35 and 45 ℃ (288-318 K). Results presented in Fig. 3 and showed that the adsorption increases significantly with an increase in temperature from 288 K (adsorption capacity= 104.8 and removal efficiency= 83.71%) to 318 K (adsorption capacity= 124.6 and removal efficiency= 99.68%), which it illustrates that the adsorption process is endothermic. The increase in the adsorption capacity with temperature may be attributed to either change in pore size of the adsorbent improving intra-particle diffusion within the pores or enhancement in the chemical affinity of Erythromycin to the surface of the adsorbent [28]. This leads to increasing the disorder at the MWCNT surface and intensification of chemical interactions that take place during the adsorption process and as a result, increasing the adsorption capacity [29, 30].

Effect of Mixing Rate: The mixing rate and turbulence inside the aqueous solution is an important parameter in adsorption process because an increase in mixing rate increases the possibility of contact between the adsorbent and Erythromycin molecules which it results in higher efficiency. In order to examine the mixing rate on adsorption process, the parameters were determined in laboratory conditions as mixing rate of 0–200 rpm, initial Erythromycin concentration of 100 ppm, time of 75 min, temperature of 30 °C, adsorbent dosage of 0.8 g/L and pH = 7. The magnetic mixer was used for mixing process and the effect of this parameter is shown in Fig. 4. According to the Fig. 4, increasing the mixing rate in the range of 0–200 rpm increases the Erythromycin adsorption efficiency by the adsorbent. Higher mixing rate means the possibility of higher contact between the active sites and Erythromycin [30, 31]. The optimum removal was observed to be 98.9% at mixing rate of 200 rpm.

Effect of Adsorbent Dose: The adsorbent dosage is a considerable parameter in the adsorption process, as it determines the adsorption capacity in a certain concentration of adsorbed material. The experimental parameters for evaluation of the effect of MWCNT dosage (0.2–2 g/L) to remove the Erythromycin were the initial concentration of 100 ppm, temperature of 30 °C, contact time of 75 min, mixing rate of 200 rpm, pH of 7. Fig 5 shows the effect of MWCNT dose on adsorption of Erythromycin. The findings revealed that increasing the amount of used adsorbent leads to increase the Erythromycin adsorption, as the higher dosage increases the number of active sites for adsorption of Erythromycin ion [32, 33]. Increase in the amount of adsorbent up to 1 g/L results in the higher Erythromycin adsorption efficiency that is 92.7% . Higher dosages of adsorbent in aqueous solution, more than 1 g/L, show a negligible increase in adsorption because of saturation inactive sites [34].Even, in some cases, the final adsorption is reduced because there was the higher possibility of contact between adsorbent particles and active sites and this factor makes flocculation on the sites and, ultimately, it decreases the number of active sites and adsorbent surfaces and, consequently, the final efficiency.

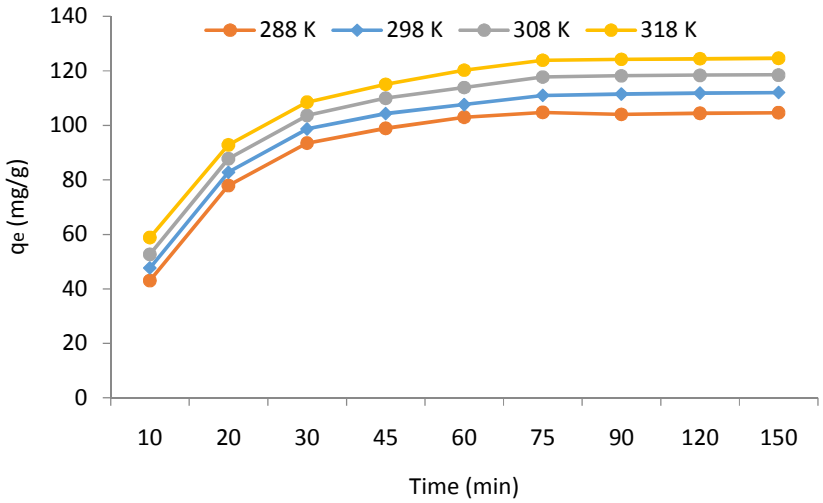


Fig 3. Effect of contact time and temperature on Erythromycin removal (pH =7, Adsorbent dosage 0.8 g/L, mixing rate 200 rpm, C_0 = 100 mg/L)

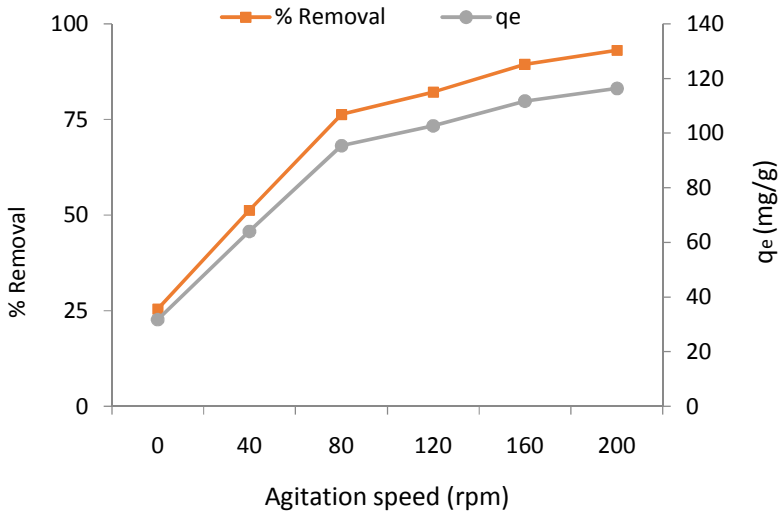


Fig. 4. Effect of mixing rate on Erythromycin adsorption (C_0 = 100 mg/L, temp= 25± 2◦C, time 75 min, adsorbentdosage 0.8 g/L, pH = 7)

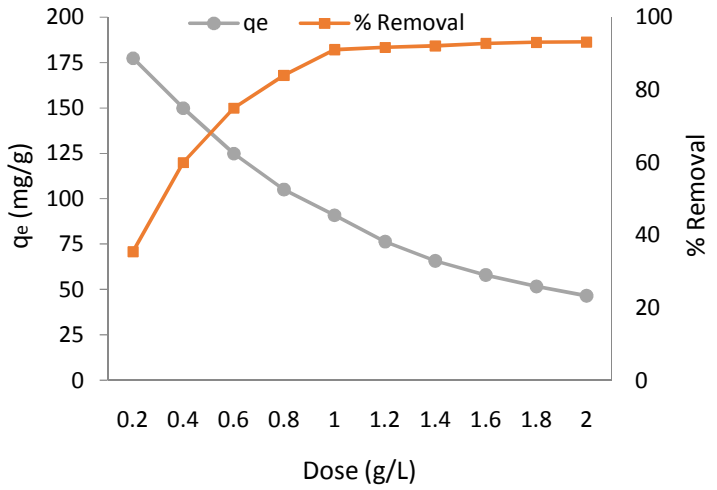


Fig 5: Effect of adsorbent dosage on Erythromycin adsorption (C_0 = 100 mg/L, time = 75 min, pH = 7, temp= 25± 2◦C and mixing rate 200 rpm)

Adsorption thermodynamics

The thermodynamics for Erythromycin removal by MWCNTs was investigated in the temperature range of 288-318 K, and the influence of temperature on the adsorption capacity is shown in Fig. 3. It can be found that there is an increase in the adsorption capacity of MWCNTs with increasing the temperature. Thermodynamic parameters such as the change in Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined using the following equation [34, 35]:

$K = q_e / C_e$

$\Delta G = - RT \ln K$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

Table 1 summarizes the thermodynamic parameters associated with the adsorption process. Values of ΔG^0 were calculated from the values of adsorption equilibrium constant (K) using above equations. The negative values of ΔG^0 at the three temperatures show that the adsorption process is spontaneous and the degree of spontaneity increases with increasing the temperature [36, 37]. The values of ΔH^0 and ΔS^0 are calculated from the slope and the intercept of the linear plot of Ln K vs. 1/T. The overall adsorption process seems to be endothermic (ΔH^0= 76.25 KJ/mol). This result also supports the suggestion that the adsorption capacity of MWCNTs increases with increasing temperature. Table 1 also reveals that the ΔS^0 value is positive (entropy increases as a result of adsorption). A positive value of ΔS^0 reflects the affinity of the adsorbent to the Erythromycin, which it is due to redistribution of energy between the adsorbate and adsorbent [38].

Table 1: Thermodynamic parameters of the Erythromycin adsorption onto MWCNT

T (K)	ΔG◦ (kJ mol^{-1})	ΔS◦ (J mol^{-1} K^{-1})	ΔH◦ (kJ mol^{-1})
288	-4.54	0.277	76.25
298	-5.71		
308	-8.24		
318	-13.11		

Adsorption kinetics

Fig. 3 demonstrate the effect of contact time on Erythromycin adsorption onto MWCNTs It is found that the adsorption kinetics of Erythromycin onto MWCNT included two steps: a fast initial adsorption followed by a slow gradual adsorption. The initial rapid phase (first 30 min) accounted for a considerable portion of the adsorption. During this stage, about 80% of Erythromycin was adsorbed, which can be attributed to the rapid diffusion of Erythromycin molecules from the solution to the external surface of MWCNT. Adsorption in the subsequent time was slower and was probably due to the diffusion of Erythromycin molecules into the porous structures of the adsorbent.
To evaluate the differences in the adsorption kinetic rates, the pseudo-first-order, pseudo-second-order, intraparticle diffusion and Boydmodels were used to fit the results.

The pseudo-first-order kinetic model is generally expressed as follows [39, 40]:

$$\log (q_e - q_t) = \log q_e - \frac{K}{2.303} t$$

Where q_e is the amount of Erythromycin adsorbed per unit mass of MWCNT at equilibrium (mg/g), q_t is the amount of Erythromycin adsorbed per unit mass of MWCNT at any time t (mg/g), t is the time (min), and K is the pseudo-first-order rate constant (1/min). The values of K and q_e were estimated from the slope and intercept of the linear plot of log (q_e-q_t) versus t (Fig 6a), and these values are listed in Table 2.

The pseudo-second-order kinetic model is given as follows [41, 42]:

$$\frac{t}{q_t} = \frac{1}{K_2}\frac{1}{q_e^2} + \frac{1}{q_e} t$$

Where K_2 is the pseudo-second-order rate constant (g/mg.min) and $K_2.q^2_e$=h is the initial adsorption rate (mg/g.min). The values of K_2 and q_e were estimated from the slope and intercept of the linear plots of t/q_t versus t (Fig 6b), and the values are listed in Table 2.

The calculated q_e values for all the studied initial Erythromycin concentrations from the pseudo-first-order kinetic model differed appreciably from the experimental q_e values. However, in the pseudo-second-order kinetic model, the calculated q_e values were very close to the experimental qe values for all the studied initial Erythromycin concentrations. Furthermore, the obtained coefficient of determination (R^2) values of the pseudo-second-order kinetic model are higher than the obtained R^2 values of the pseudo-first-order kinetic model, indicating that the pseudo-second-order kinetic model better obeys the adsorption kinetic data than the pseudo-first-order kinetic model.

Intraparticle diffusion model

The intraparticle diffusion equation is given as [43, 44]:

$q_t = K\, t^{0.5} + C$

Where $q_t$is the amount of solute on the surface of thesorbent at time t (mg/g) and Kis the intraparticle diffusion rate constant (mg/g.min$^{1/2}$). If intraparticle diffusion is the rate-limiting step in the adsorption of Erythromycin onto MWCNT, then the plot of qt versus $t^{1/2}$ should be a straight line and pass through the origin. The deviation of the plot of q_t versus $t^{1/2}$ from linearity indicates that the rate-limiting step should be film diffusion controlled [45, 46]. It was observed from Figure 6 C that the plots consist of two linear portions: the first linear portion is due to film diffusion and the second is due to intraparticle diffusion. The straight line does not pass through the origin, therefore, intraparticle diffusion is not only the rate-limiting step, and film diffusion control may be involved in the adsorption process. The values of K and C were estimated from the slope and intercept of the plot of q_t versus $t^{1/2}$, and the constants of the intraparticle diffusion model are presented in Table 2 with R^2 values.

The dual nature of the intraparticle diffusion plot (Fig 6 C) confirms the presence of both film and intraparticle diffusion. To anticipate the actual slowest step in the Erythromycin adsorption process, the obtained adsorption kinetic data were further analyzed using the Boyd kinetic model. The Boyd kinetic expression is given as [47, 48]:

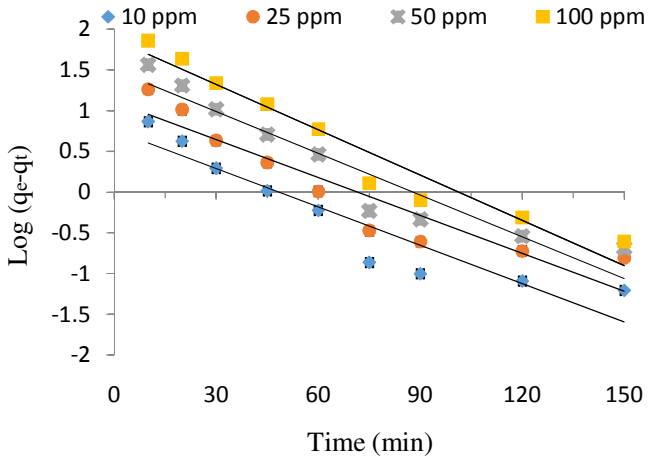
$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \exp(-Bt)$$

Equation can be modified and rearranged into the following form of theexpression [49-51]:

$$B = -0.4977 - \mathrm{Ln}(1-F) \qquad F = \frac{q_t}{q_e}$$

Where $q_e$is the amount of adsorbate adsorbed at finitetime (mg/g) and $q_t$represents the amount of Erythromycin adsorbedat any time t (min), F represents the fraction of soluteadsorbed at any time t, and Bis a mathematical functionof F. The Bvalues at different contact times can becalculated using equation above for various time intervals. The calculated B values were plotted against time t.

Figure 6d is used to identify whether the film diffusion or intraparticle diffusion controls the overall rate of the adsorption process. If the plots of [(0.4977 – Ln (1-F) or B versus time t] are linear and pass through the origin, then the actual slowest step in the process of the adsorption of Erythromycin onto MWCNT is intraparticle diffusion. From Figures 6d, it was observed that the plots are linear but do not pass through the origin, which confirms that film diffusion mainly control the adsorption process.


10 ppm
25 ppm
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100 ppm
Log (qe-qt)
2
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30
60
90
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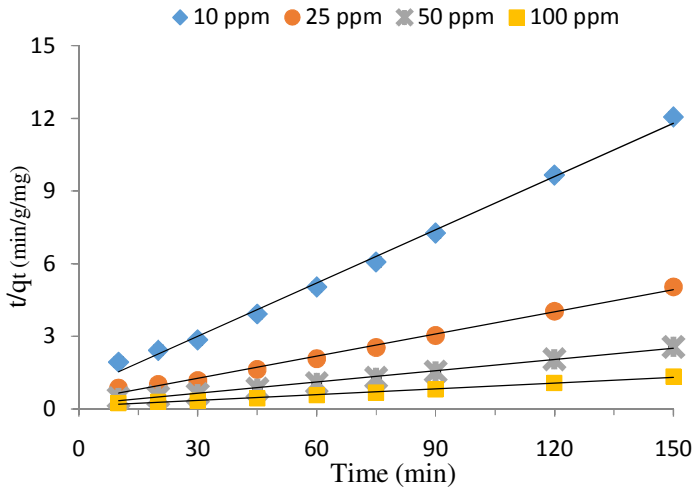
Time (min)


10 ppm
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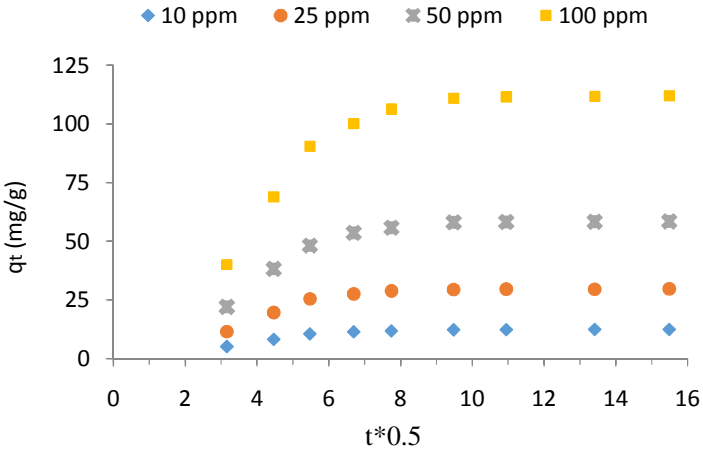
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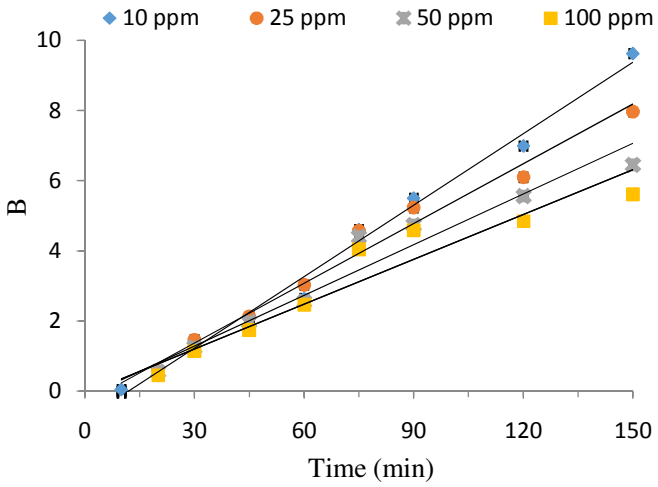

Fig. 6.Kinetic plots for the adsorption of Erythromycin onto MWCNT a: Pseudo-first order b: Pseudo-second order C:Intraparticle diffusion d: Boyd model

Table 2: Kinetic parameters for the adsorption of Erythromycin onto MWCNT at various concentration

C_o (mg/L)	q_e (exp) mg/g	Pseudo-first order			Pseudo-second order			Intraparticle diffusion			Boyd
		K_1	q_e	R^2	K_2	q_e	R^2	K	C	R^2	R^2
10	12.43	0.024	4.91	0.892	0.0066	13.69	0.995	0.464	6.80	0.741	0.972
25	29.75	0.031	9.17	0.874	0.0026	33.33	0.993	1.13	16.11	0.756	0.956
25	58.44	0.034	25.16	0.909	0.0011	66.65	0.994	2.32	30.27	0.723	0.949
100	125.5	0.036	52.71	0.942	0.0004	142.8	0.993	4.73	54.33	0.784	0.962

4. CONCLUSION

The kinetics and thermodynamics of Erythromycin adsorption onto the MWCNT were studied. The Erythromycin adsorption of onto the MWCNT was rapid during the first 30 min and the equilibrium attained at 75 min. The kinetic of Erythromycin adsorption was described by applying the pseudo-first-order, pseudo-second-order, Intraparticle diffusion and Boyd models. The kinetic data for the adsorption process obeyed the pseudo-second-order kinetic model which it suggests that the adsorption process is chemisorption. The MWCNT studied showed the superb potential for the removal of Erythromycin from aqueous solution

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