



Kinetics Study of Removal Doxycycline Drug from Aqueous Solution Using Aluminum Oxide Surface



Hawraa Kassem Hami, Ruba Fahmi Abbas*, Ala'a Abdullwahid Jasim, Dhifaf A. Abdul Abass, Marwa A. Abed, Asma A. Maryoosh

Department of Chemistry, College of Science-University of AL-Mustansiriyah-Baghdad-Iraq.

THE batch adsorption of doxycycline from aqueous solution using aluminum oxide under different experimental conditions was investigated in this study. The effect of initial concentration, sample volume, contact time and pH have been reported. A comparison of kinetic models applied to the adsorption of doxycycline on the adsorbents was evaluated for the pseudo first-order, the pseudo-second-order, Elovich, Fractional power and intra particle diffusion kinetic models were utilized to the adsorption data in respect of investigating the kinetic process; kinetic data were best fitted to the pseudo-second-order model validated by normalized standard deviation (NSD), average relative error (ARE) and chi-square test (Chi-X2). The result suggested that the intra particle diffusion was one of the rate-limiting steps.

Keywords: Kinetics, Doxycycline, Adsorption, Aluminum Oxide.

Introduction

Antibiotics are among the most important pharmaceutical compounds found in the aquatic environment. They have been discovered in different aquatic environments such as groundwater, agricultural drainage water and drinking water [1-3]. Animal waste used as fertilizer is a major source of water pollution. Antibiotics are usually poorly absorbed by the human body and thus come out either unchanged or altered, by urine and stool [4]. In recent years, attention has grown to know the fate of the environment because low levels of antibiotics can help spread antibiotic-resistant bacteria. Doxycycline belongs to a group of medicines called tetracycline antibiotics, DOH drugs have the same extensive spectrum antibiotics for activity against nearly all gram-positive and gram-negative bacteria but it is preferably on other tetracycline's in the remediation of certain infections because of its trustworthy absorption and the lengths of the half-time, it is used to treat chronic prostatic, syphilis and pelvic inflammatory malady, It also adversely affects the environment when it is present in industrial wastewater [5].

Doxycycline appears in three forms hyclate, monohydrate and hydrochloride, a hyclate group is solved in water and neutralized with sodium hydroxide becomes doxycycline monohydrate. These sub-edits with hydrochloric acid become doxycycline hydrochloride. Doxycycline hyclate ($C_{22}H_{24}N_2O_8HCl \cdot \frac{1}{2} C_2H_5OH \cdot \frac{1}{2} H_2O$) more dissolvable than doxycycline monohydrate, this is one of the main reasons for its frequent usage in pharmaceutical samples [6, 7]. This study shows the ability and behaviour of adsorption of DOH on Al_2O_3 surface. The adsorption information is examined for three kinetic equations. The impact of experimental qualifications, contact time, pH solution and initial DOX concentration on the adsorption process.

Materials and Methods

Equipment

The spectrophotometric analysis was carried out using Shimadzu (Model: CARY 100, VARIAN Co.) at the region (200-800 nm), pH Meter (Model: Hana) and shaking water path

*Corresponding author e-mail: rubaf1983@uomustansiriyah.edu.iq

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(Model: BS-11degetal, JEIO Korea, TECH) were also used in this study.

Materials

Preparation of solutions

Doxycycline Hyclate (DOH) stock standard solution (1000 mg. L⁻¹) was prepared by dissolving 0.25 gm of DOH in 250 ml distilled water, and then a series of DOH concentrations in the range of (50-125 mg. L⁻¹) was made. HCl (0.1 M) solution was prepared by diluting (1.54 ml) of concentrated hydrochloric acid (37%) and diluted to (250 ml) in a volumetric flask by distilled water. NaOH (0.1M) was prepared by dissolving (1 gm) of NaOH in (250 ml) volumetric flask with distilled water as solvent. The pH of each of the solution was adjusted by the dropwise addition of (0.1 M) HCl or (0.1 M) M NaOH when required [8].

Adsorption Experiments

Batch experiments were implemented in (100 ml) a volumetric flask comprise (10 ml) of DOH solution with variant concentration (50-125 mg. L⁻¹) and (0.1 gm) of the Al₂O₃ (Sigma-Aldrich) adsorbent surface. All experiments were performed in a constant temperature of 37.5°C to determine the equilibrium concentrations and the contact time of DOH adsorption on Al₂O₃ powder, pH values of DOH solutions were adjusted by 0.1 M HCl and NaOH in the range between (1.2 to 10) [9].

Analytical Methods

The amount of DOH solution adsorbed (mg. g⁻¹) according to the equation [10]

$$qt = \frac{(C_0 - C_t)v}{m} \dots \dots (1)$$

C₀ (mg. L⁻¹) is the initial concentration of drug (mg. L⁻¹), C_t (mg. L⁻¹) is the concentration at any time and q_t (mg. g⁻¹) is the adsorption capacity of DOH adsorbed onto Al₂O₃ powder at any time. At equilibrium, q_e = q_t and C_e = C_t; therefore the amount of adsorbed q_e (mg. g⁻¹), calculated from

$$qe = \frac{(C_0 - C_e)v}{m} \dots \dots (2)$$

V (L) is the solution volume and m is the weight of Al₂O₃ powder [11, 12].

Removal percentage (g) for DOH can be calculated as follows:

$$\text{Removal\%} = \frac{(C_0 - C_t)}{C_0} \times 100 \dots \dots (3)$$

Validity of kinetic model

Four different error functions namely coefficient of determination (R²), Chi-square test (X²), normalized standard deviation (NSD) and average relative error (ARE) were used to analyze the impact of various error functions of the kinetic model. The coefficient of determination R² is calculated by using the Microsoft Excel Software program while the other error function is defined as:

$$\text{Chi } X^2 = \sum_{i=1}^n \frac{(q_{cal} - q_{exp})}{q_{exp}} \dots \dots (4)$$

$$\text{NSD} = 100 \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left[\frac{q_{exp} - q_{cal}}{q_{exp}} \right]^2} \dots \dots (5)$$

$$\text{ARE} = \frac{100}{N} \sum_{i=1}^N \left| \frac{q_{exp} - q_{cal}}{q_{exp}} \right| \dots \dots (6)$$

Where q_{calc} is the theoretical concentration of doxycycline drug on the aluminum oxide surface, q_{exp} is the experimentally measured doxycycline drug concentration adsorbed on the aluminum oxide surface, p is the number of parameters, and N is the number of experimental measurements. The smaller values of (Chi X², NSD and ARE) and the high value of the coefficient of determination R² indicate that there is more a good accuracy for the method.

Result and Discussion

Calibration curve

DOH stock stander solution (1000 mg. L⁻¹) was prepared by dissolving of a certain weight of the DOH in water. Several solutions in the range (25 to 200 mg. L⁻¹) was made and their absorbance measured at λ_{max} = 345 nm, the value of molar absorptivity was found to be (0.0087 gm⁻¹. L. cm⁻¹) (Fig. 1).

Adsorption Studies

1-Effect of initial concentration and contact time of DOH drug

Variation of percentage removal of DOH with contact time at a different initial concentration range from (50-125 mg. L⁻¹), times in the range of (15 to 120) minutes, 0.1gm Al₂O₃ and temperature 37.5°C [2]. From Table 2, it was observed that with a rise in the initial DOH concentration from 50 to 125 mg. L⁻¹, the capacity of DOH adsorption increases, while the removal percentage was larger for low initial DOH concentration, this can be explained by the accessibility of vacant binding sites on the adsorbent. Since the binding sites were almost fully covered at high DOH concentrations, removal efficiency decreased with increasing

Nomenclature

k	fractional power kinetic model constant($\text{mg. g}^{-1}.\text{min}^{-1}$)
k_1	pseudo-first order kinetic model constant (l. min^{-1})
k_2	pseudo-second order kinetic model constant($\text{gm.g}^{-1}.\text{min}^{-1}$)
k_{id}	intraparticle diffusion kinetic model constant($\text{gm.g}^{-1}.\text{min}^{-0.5}$)
R^2	coefficient of determination
ARE	average relative error
NSD	normalized standard deviation
X^2	chi-square test
p	number of parameters
N	number of experimental measurements
C_e	equilibrium concentration (mg. L^{-1})
C_0	initial concentration (mg. L^{-1})
C_t	concentration at time t (mg. L^{-1})
q_e	amount of cyanide adsorbed at equilibrium (mg. g^{-1})
q_m	monolayer sorption capacity (mg. g^{-1})
m	mass of Al_2O_3 (g)
t	time (min.)
V	volume of the solution (L)
h	the initial adsorption rate ($\text{mg. g}^{-1}.\text{min}^{-1}$)
$t^{1/2}$	half-equilibrium time

Greek letters

A	Elovich kinetic model constant ($\text{mg. g}^{-1}.\text{min}^{-1}$)
B	Elovich kinetic model constant (g. mg^{-1})
v	Fractional power kinetic model constant

TABLE 1. Properties of DOH drug

Properties	Structure
Formula	$C_{22}H_{24}N_2O_8.HCl. \frac{1}{2} C_2H_5OH.$ $\frac{1}{2}H_2O$
Molar mass	512.94 g mol ⁻¹
Melting point	201 °C
Source	Iraq (S . D . I)
Solubility	Very soluble in water
Appearance	Yellow crystalline

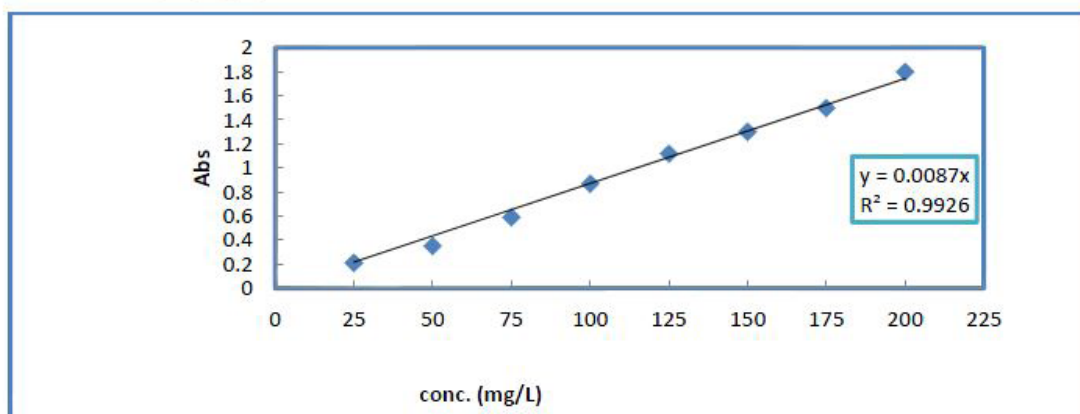
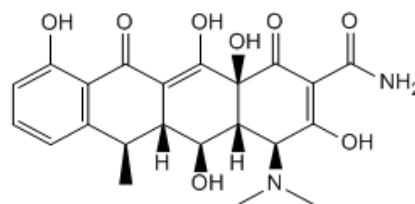


Fig. 1. Calibration curve for estimation of DOH.

DOH concentration [13-15]. A similar result was mentioned by Mohammed M. et al. [16].

The removal of DOH increases with time until reaching the equilibrium time at 90 min from that point, the removal rate of adsorption differentially decreases with times as shown in Tables 2 & 3 and Fig. 2 [17].

2-Effect of initial pH

pH is significant among the most parameters that impact on drug adsorption limit, It may replace the surface charge of the adsorbent, the degree of ionization of the adsorbent molecule and the range of separation of a useful collection of the effective destinations of the adsorbent [18]. The effect of pH on the adsorption of DOH on Al_2O_3 surface studied in range of initial pH (1.2 – 10) at 37.5°C for 90 min., the pH values of DOH were detected by adding the required amounts of 0.1 M HCl and NaOH. Table 4 and Fig. 3 show the effect of change initial pH. As appears in Fig. 3 the DOH absorption increases with an increase of pH.

3-Effect of Sample Volume

Table 5 and Fig. 4 are shown the effect of using different volumes of the DOH in the range (5-25 ml) on the adsorption. The dose of Al_2O_3 (0.1 gm), temperature 37.5°C and pH 6 for 90 min. was investigated and the results are shown that the adsorption increased with decreasing of the volume of DOH solution [19].

Adsorption Kinetics study

A kinetic study is essential in any adsorption process and assists in determining the sort of adsorption, the amplitude of adsorbent, reaction pathway and gives information about the rate and mechanism of adsorption, which is important for the effectiveness of the process. The study of adsorption kinetics is a key factor of designing a suitable adsorption process and measure the changes in the adsorption system with time to find a suitable kinetic model. In this study, various kinetic models were used (Elovich, Fractional power, Intra particle diffusion, First-order-pseudo and Second-order-pseudo) models. Linear regression method was used to determine the parameters of kinetic

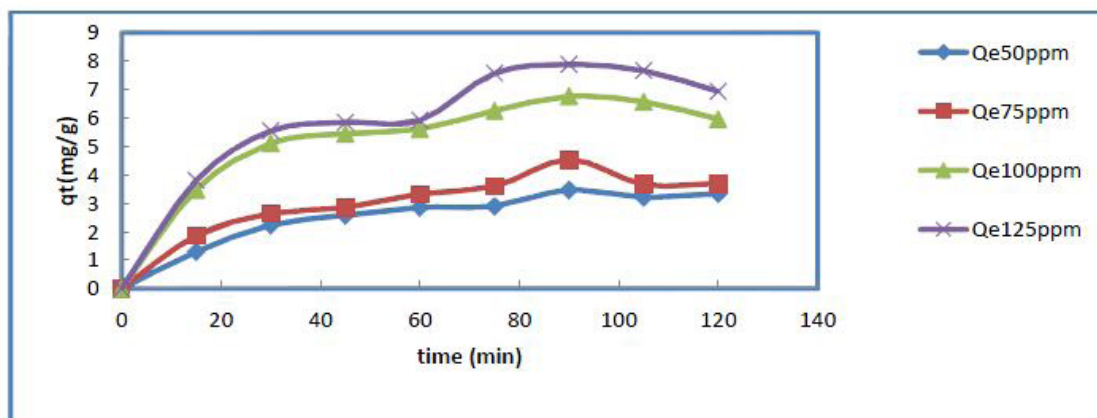


Fig. 2. Contact time effect on the adsorption of DOH.

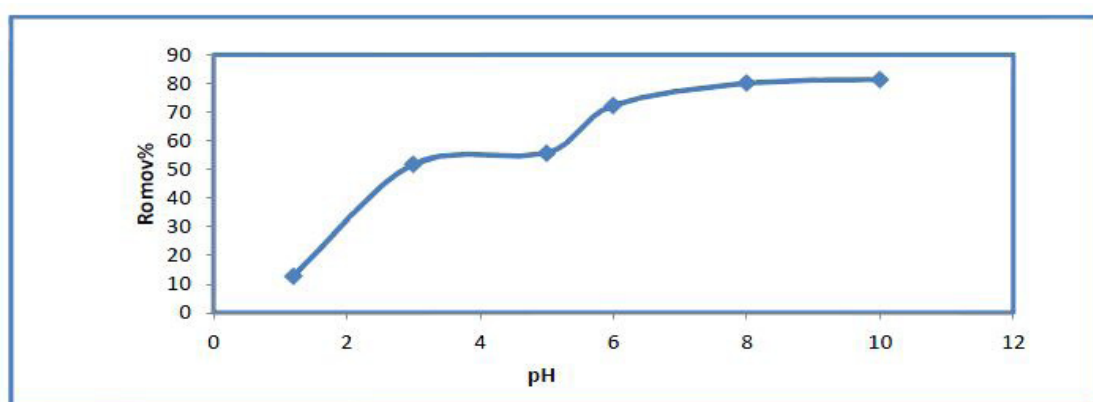


Fig. 3. pH effect on adsorption of DOH

models, the linear expression of these kinetic equations and the method of obtaining them were given in Table 6. The values of R^2 , χ^2 , NSD, ARE and the constants of various kinetic models are reported in Table 7.

The kinetics parameters of the (Pseudo-first-order and Pseudo-second-order) models are given in Table 7, in which the R^2 value for pseudo-second-order model was found greater than 0.916 and the theoretical q_e value for this model is closer to the experimental q_{exp} value than the pseudo-first order. In addition, as shown in Table 7, the χ^2 , NSD, ARE low for all concentrations' therefore, the pseudo-second-order kinetic model more suitable to describe adsorption of DOH in Al_2O_3 surfaces [22-26]. According to this model, the increase in DOH concentration from (50 – 125) $mg \cdot L^{-1}$ decreases the values of K_2 from 0.4 to 0.013 $g \cdot mg^{-1} \cdot h^{-1}$ as shown in Fig. 5. The reason for the lower rates of adsorption at high

initial concentration can be explained by the high rivalry for the adsorption surface sites. From this, we can conclude that the adsorption was chemical adsorption many studies kinds of research proved the validity of the pseudo-second-order model for the kinetic of DOH adsorption [16-29].

Elovich model is one of the helpful models for describing activated chemical adsorption. This model has recently been applied successfully to processes of pollutants removal in aqueous solution as shown in Table 8, the value of α , β increased as the initial concentration increased and the R^2 more than 0.91. That's means the reaction is homogeneous and adsorption type is chemical, so that the results are identical to Elovich model (Fig. 6). The Fractional power model has shown in Fig. 7 and Table 8 the values of ν were less than 1 and the R^2 was greater than 0.96 indicating that the parameter fit also into the fractional model. In the intra particle diffusion model based on

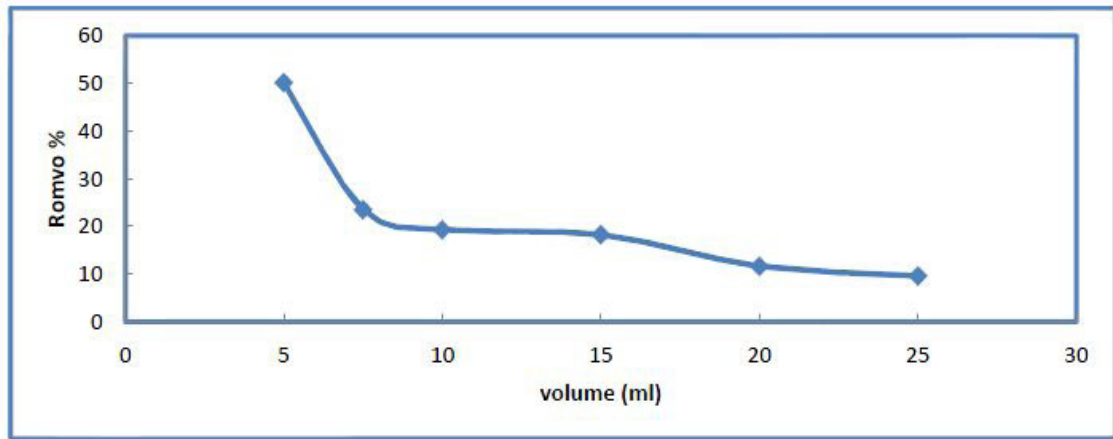


Fig. 4. Effect of sample volume on adsorption of DOH by the adsorbent

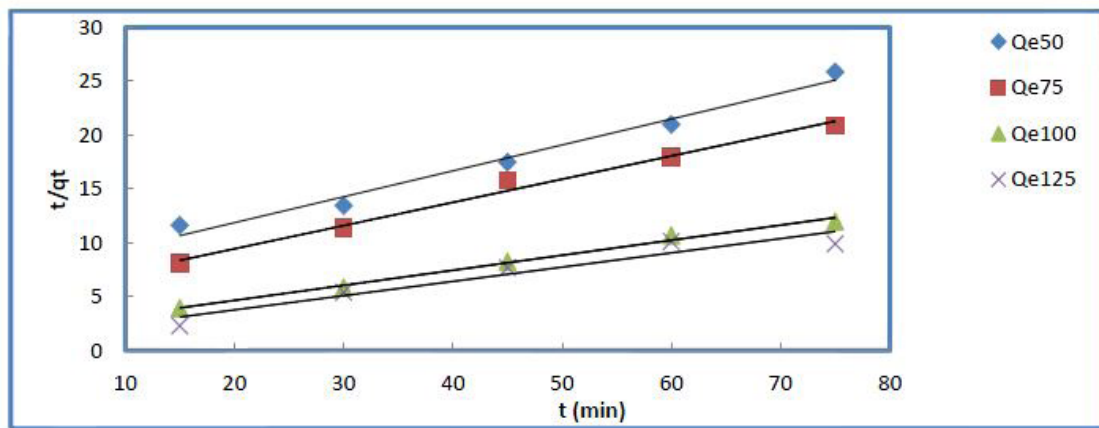


Fig. 5. Pseudo-second-order kinetic model of DOH by the adsorbent

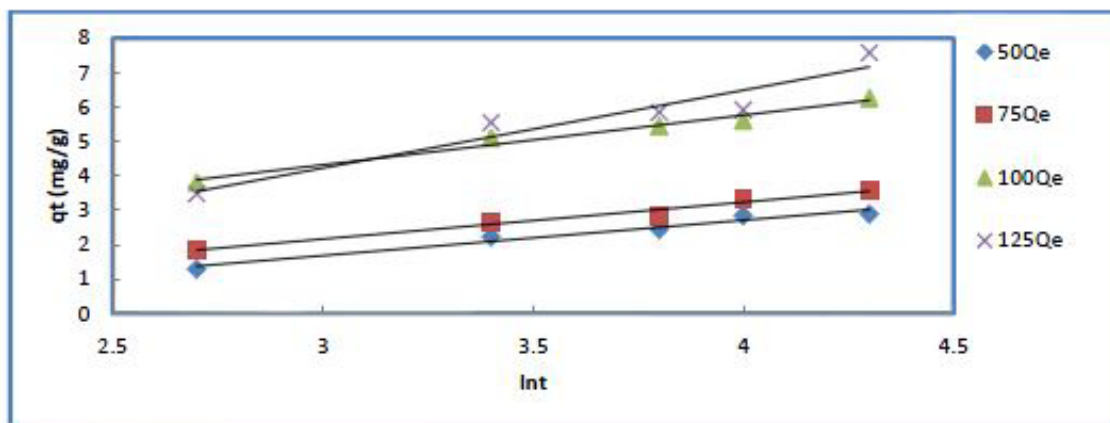


Fig. 6. Elovich kinetic model of DOH by the adsorbent

TABLE 7. Parameters of the pseudo-first-order and pseudo-second-order model at various initial DOH concentrations

Kinetic model equation	Parameters	C_0 (mg. L ⁻¹)			
		50	75	100	125
Pseudo-first-order kinetic model	$q_{e,exp}$ (mg. g ⁻¹)	3.472	4.536	6.768	7.890
	$q_{e,cal}$ (mg. g ⁻¹)	6.612	3.36	4.46	11.02
	k_1 (1min ⁻¹)	0.053	0.016	0.024	0.039
	R^2	0.808	0.983	0.9144	0.725
	$Chi X^2$	2.8397	0.3048	0.78706	1.2416
	NSD	84.257	27.6043	44.3582	55.7135
	ARE	56.794	6.096	15.7412	24.832

TABLE 8. Parameters of the Elovich, Fractional power and intra particle diffusion model at various initial DOH concentrations

Kinetic model equation	Parameters	C_0 (mg. L ⁻¹)			
		50	75	100	125
Elovich	β (gmg ⁻¹)	1.02	1.06	1.44	2.26
	α (mgg ⁻¹ min ⁻¹)	0.24	0.34	0.68	0.14
	R^2	0.96	0.97	0.97	0.91
Fractional power	ν	0.515	0.405	0.29	0.44
	K (mg g ⁻¹ min ^{ν-1})	0.34	0.63	1.7	1.08
	R^2	0.93	0.97	0.96	0.93
Intra particle diffusion model	k_{id} (mgg ⁻¹ min ^{0.5})	0.33	0.35	0.46	0.72
	C	0.207	0.56	2.23	0.95
	R^2	0.91	0.98	0.93	0.88

TABLE 9. Comparison of K_2 with other adsorbents in literature

Adsorbents	Contact time	K_2	Ref.
Rice straw	24h	0.026	29
NaY zeolite	24h	0.034	16
Graphene-like layered molybdenum disulfide	8h	0.0051	28
Graphene nanosheet	230 min	3.5×10^{-4}	32
Aluminum Oxide	90 min	0.4079	Present study

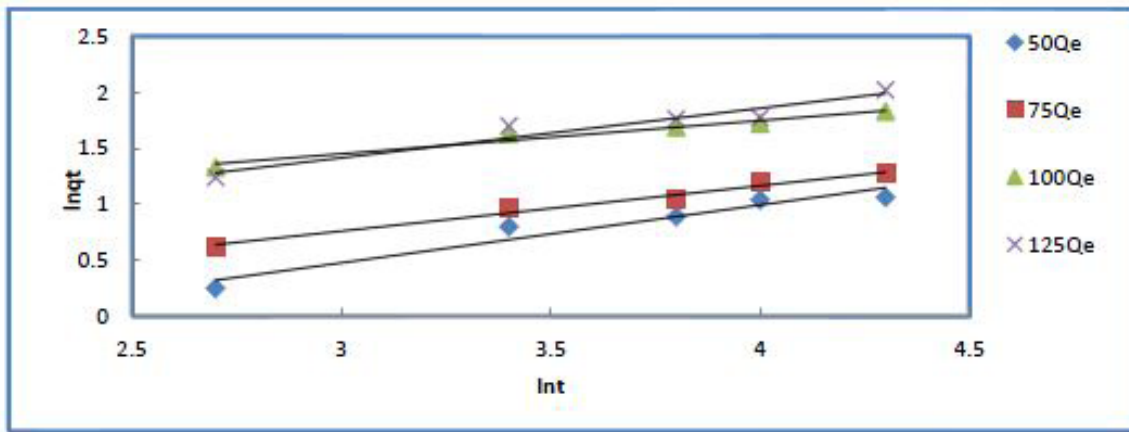


Fig. 7. Fractional power kinetic model of DOH by the adsorbent

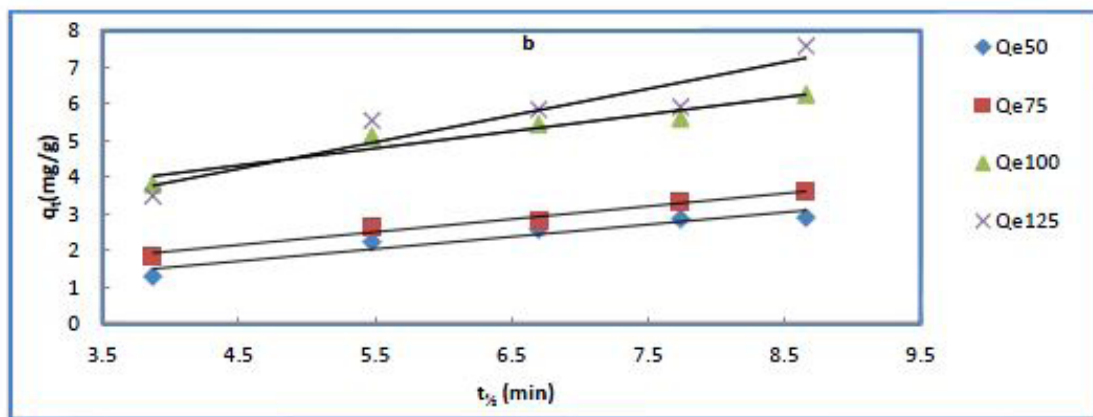
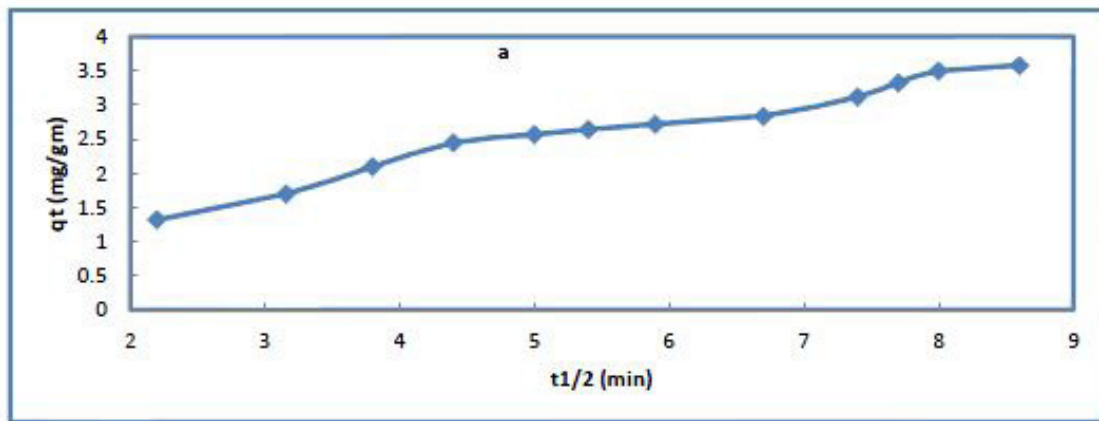


Fig. 8. Intra particle diffusion model mode of DOH by the adsorbent

the theory proposed by Weber and Morris was employed to identify the diffusion mechanism. In Fig. 8a we can be observed the small value of C_i and that indicates that the boundary layer has a less important effect on the diffusion mechanism of DOH adsorption on the Al_2O_3 as shown in Table 8 and Fig. 8b [25-27]. The intra particle diffusion plot between $t^{1/2}$ and qt for the removal of DOH by Al_2O_3 was divided into three stages this result is similar to the result of adsorption of DOH in rice straw [30]. The intra-particle diffusion plot shows that the adsorption occurs in 3 steps, the first is the faster sorption of DOH on the available external surface of Al_2O_3 , the second part was refer to the intra particle diffusion and at the last equilibrium stage, intra particle diffusion incept start slow because of the lower concentrations of DOH and less sorption site and intra particle diffusion was not the only rate limiting mechanism in the adsorption process and it was one of the rate-limiting steps in the adsorption process, as is evident from the Fig. 8b [31].

Comparison of Al_2O_3 with Differently Reported Adsorbents for DOH Removal

A comparative report has been studied for the adsorption of DOH at various adsorbents surfaces showed the adsorption process was kinetically fastest than the previously research values for other adsorbents. The fast kinetic of the adsorption obtained because DOH is a member of the tetracycline antibiotics which adsorb strongly to Al_2O_3 and the surface reaction reinforce structural transformation of DOH and that similar to the adsorption of tetracycline in Al_2O_3 surface [32]. All reported literature in Table 9 shown that the pseudo-second-order kinetic model was the best modeling.

Conclusion

The main objective of the research is to study the adsorption kinetics of DOH on aluminum oxide. A different kinetic model had studied pseudo-first-order, the pseudo-second-order, Elovich, Fractional power and intraparticle diffusion kinetic models, It was found that the kinetic model of the pseudo-second-order, Elovich, and Fractional power are effective in the adsorption reaction. As noted from intra-particle diffusion models result that the boundary layer has a less important effect on the diffusion mechanism of the adsorption process and it was one of the rate-limiting steps in the adsorption of DOH on aluminum oxide.

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