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Catechol removal using MWCNTs from synthetic solutions: modeling, equilibrium and kinetics

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Abstract

The analyses of optimization, modeling, equilibrium and kinetics of catechol removal on Multiwall Carbon Nanotube (MWCNT) have been studied. The optimization process was performed using Response Surface Methodology (RSM). The optimum amount conditions were pH 4.5, initial catechol concentration 87 mg/l, MWCNTs 237 mg and contact time 22 min. Under this condition, the optimum adsorption percentage of catechol was obtained about 90. The kinetic and isotherm studies on the obtained optimum condition represented that the pseudo-first order and Freundlich equilibrium are more fitted with experimental data than other models.

Keywords:Catechol, Adsorption, Optimization, Equilibrium, Kinetic

1. Introduction

Phenolic compounds are used as a particular antiseptic because of its toxicity and deleterious characteristics. However they influence environment and aqueous ecosystems due to defective treatment systems or lack of them. Generally, these compounds are readily absorbed from live tissue such as the gastrointestinal tract which causes hemolysis and degenerates the renal tubes. Additionally they are produced by chemical, pharmaceutical, dye, rubbers, photographic, cosmetics and oil wastewater industries [1, 2]. Among phenolic compounds, catechol is more toxic than its other compounds and may cause cancer and neurodegenerative diseases [3].

Catechol compounds have been treated successfully using physicochemical and biological methods [4, 5]. Nevertheless, adsorption technique has been proposed as a considerable method because of its lower cost, reliability in operation, high efficiency, environmentally friendly technology and easy to operate [6-8].

Today because of the increasing interest of Carbon Nanotubes (CNTs), they are utilized intensively to remove various pollutants. According to literatures, there is an especially significant CNTs usage for removing metals, organic and inorganics from aqueous solutions [9, 10].

Several parameters affect adsorption that some of them have negative and others have positive effect on the removal efficiency in the adsorption process. Thus, parameter optimization is desired. The response surface

methodology (RSM) is a new method based on the statistical techniques for experimental design, model development, evaluation of parameters and optimization of conditions [11]. Other advantages include savings in experimental time, number of tests required and manpower [12]. The central composite design (CCD) is a design widely used for estimating second order response surfaces [13]. The main objective of CCD is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications.
There is no information available in the literature regarding the optimization of catechol removal using MWCNTs. The aim of present study was to investigate the optimization and modeling of catechol removal on MWCNT. The effects of different parameters such as initial catechol concentration, pH, adsorbent dose and contact time were optimized using RSM based on CCD. Additionally, isotherm and kinetic models of catechol removal on MWCNTs were obtained in the optimum condition.

2. **Experimental**

2.1.*Catechol and MWCNT*

The catechol was prepared from Merck in analytical grad and used without any purification in thepresent study. And also, the MWCNT (with purity >95%) was obtained from the US research nanomaterial company and its characteristics have been represented in Table 1. Additionally, Fig. 1 displays the Scanning Electron Microscopy (SEM) images of the prepared MWCNTs.

Table 1: The MWCNTs characteristics

characteristic	unit	value
Specific surface area (BET)	m^2/g	>270
Length	µm	10-40
Diameter	nm	10– 30
Thermal conductivity	S/m	1500

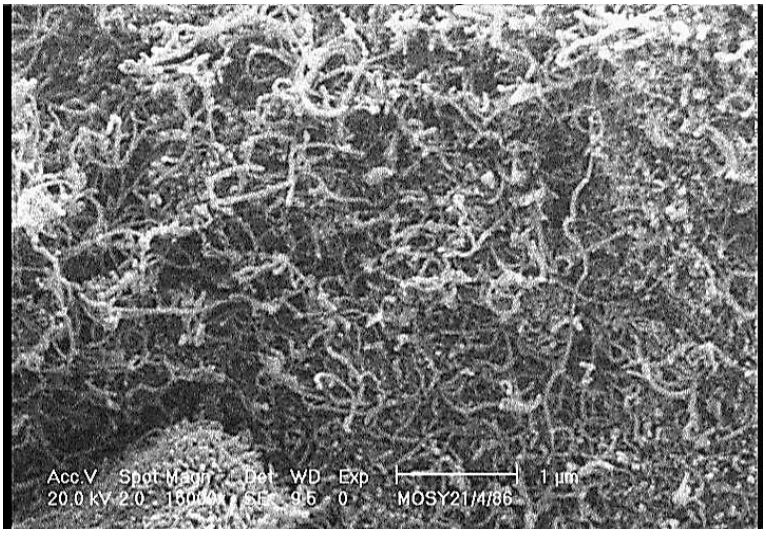

Fig 1: SEM images of the MWCNTs

2.2 *Batch Adsorption Experiments*

A shaker (INNOVA 4340, USA) with 100 rpm was used to prepare suitable agitate condition throughout the study. At the end of predetermined time intervals, the MWCNTs were separated and then the solution catechol concentration was determined. All experiments were carried out twice. Catechol concentration was measured

using an UV-spectrophotometer at λ_{max}270 nm (Rayleigh UV 9200, China). Adsorption efficiency was calculated based on the following equation:

$$\text{Adsorption efficiency } \% = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1)$$

where C_0 is initial concentration and C_f is final concentration of catechol (mg/l) in the solution.

2.3 *Experiments Design*

In order to build empirical model, the RSM was used as a collection of mathematical and statistical techniques [10]. This method provided a careful design of experiments to optimize the response. And also, CCD was widely utilized to fit a polynomial model. This method can provide some performance such as modeling and minimizing the number of experiments. Regard to CCD method, total number of test was estimated by $2k + n_\alpha + n_0$ equation, where k is the number of independent variables, n_α is axial points and n_0 center points. In this study a 16 (2^4) factorial design, 8 (2×4) axial points with 6 central points was selected. The CCD levels of the main variables has been considered in five level including –α, -1, 0, +1 and +α. The alpha (significance level) was set equal 2. The design experiment details are represented in Table 2.

Table 2: Variable factors with their levels

Factors	Symbol	α=-2	-1	0	+1	α=+2
Contact time (min)	A	1	8.25	15	22.75	30
Initial pH	B	3	4.25	5	6.75	8
Catechol concentration (mg/L)	C	50	87.5	125	162.5	200
MWCNTs dosage	D	50	112.5	175	237.5	300

3. **Results and discussion**

3.1. *Statistical Analysis*

According to the CCD, a total of 30 runs were designed. According to Table 3, the CCD experimental design and response have been shown. In addition, the ANOVA for the predicted response surface has been presented in Table 4. A low probability value (p-value< 0.0001) cause the model to be significant with regard to p-value< 0.05. The "R^2" of 0.93 is in reasonable agreement with the "Adj R^2" of 0.90. Accordingly, the response surface model for predicting catechol removal percentage was considered reasonable. Also, the coefficient of the variation (CV %) is the value of the reproducibility of the model and should not be more than 10%. In this study the CV was 6.01%, as a result, the experimental data is reliable and of high precision.

The adequacy of the obtained model evaluated by predicted versus actual values plot thatwas showed in the Fig. 2.The final regression of catechol removal percentage in terms of coded factors is represented as follows equation.

Catechol Removal (%) = 67.24 + 1.96 A - 1.38 B + 1.66 C + 13.31 D - 0.21 AB + 0.71 AC + 1.10 AD + 0.87 BD - 1.38 CD (2)

3.2.*Effect of Main Factors*

Fig. 3 illustrates the 2-D and 3-D plots of catechol removal using MWCNTs.Fig.3 a, represents the interaction between pH and adsorption time. Although, the pH has considerable effect on adsorption, but it is clear that the time is more effective. Accordingly, a maximize efficiency about >74% was determined when catechol concentration and MWCNTs were set 87 mg/L and 207 mg, respectively. Optimal zone is found in lower acidic

pH and upper adsorption time, so that the adsorption efficiency has arrived to more than 75% at pH below than 5 and upper 20 min of time. Significant catechol removal at lower acidic pH may be due to charging of the surface of MWCNTs with protons and consequently more adsorption has been resulted [15]. Chio and Abramson have been reported that with changing the medium pH, possibly an involvement of the phenolic OH group is occurred [16]. As a result, it could be changed in the pK_a of the phenolic OH group and finally coming into existence a positive charge in the side chain. This positive charge may be responsible for better catechol removal. Pan and Xing reported when the medium pH increase it can leads to increasing in solubility, ionization, and hydrophilicity properties, and consequently, adsorption of organic matter on CNTs is decreased [17].

Table 3: Experimental plan based on CCD and the results

Run	Time	pH	Conc	Dosage	Catechol Removal%
1	22.75	4.25	162.5	112.5	59.5
2	8.25	6.75	87.5	112.5	50.99
3	15.5	5.5	50	175	61
4	8.25	4.25	162.5	112.5	57.65
5	22.75	6.75	87.5	237.5	83
6	15.5	5.5	125	175	71.25
7	8.25	4.25	162.5	237.5	79.55
8	15.5	5.5	125	300	87.34
9	15.5	5.5	125	175	67
10	15.5	5.5	125	50	37
11	22.75	6.75	162.5	112.5	55.55
12	8.25	4.25	87.5	112.5	52.25
13	22.75	6.75	162.5	237.5	86.67
14	15.5	5.5	125	175	72
15	8.25	6.75	162.5	112.5	56.67
16	8.25	6.75	162.5	237.5	77.11
17	22.75	4.25	87.5	237.5	82.28
18	15.5	8	125	175	55.95
19	15.5	3	125	175	67.5
20	15.5	5.5	125	175	73.65
21	22.75	4.25	162.5	237.5	84.33
22	22.75	4.25	87.5	112.5	54.44
23	1	5.5	125	175	57
24	15.5	5.5	125	175	70.01
25	8.25	4.25	87.5	237.5	80.08
26	8.25	6.75	87.5	237.5	81.4
27	30	5.5	125	175	71.11
28	15.5	5.5	125	175	67.388
29	15.5	5.5	200	175	68.99
30	22.75	6.75	87.5	112.5	48.66

Table 4: ANOVA

Source	Sum of Squares	df	Mean Square	F -Value	P- Value
Model	4525.13	9	502.79	30.76	< 0.0001
A-Time (min)	91.84	1	91.84	5.62	0.0279
B-pH	45.73	1	45.73	2.79	0.1099
C-Catecholconc. (mg/l)	66.36	1	66.36	4.06	0.0575
D-Dosage (mg/l)	4250.41	1	4250.41	260.08	< 0.0001
AB	0.68	1	0.68	0.04	0.8399
AC	8.13	1	8.13	0.49	0.4886
AD	19.25	1	19.25	1.17	0.2907
BD	12.09	1	12.09	0.73	0.3999
CD	30.60	1	30.60	1.87	0.1863
Residual	326.84	20	16.34		
Std. Dev.	4.0		R-Squared		0.93
Mean	67.24		Adj R-Squared		0.90
C.V. %	6.01		Pred R-Squared		0.87

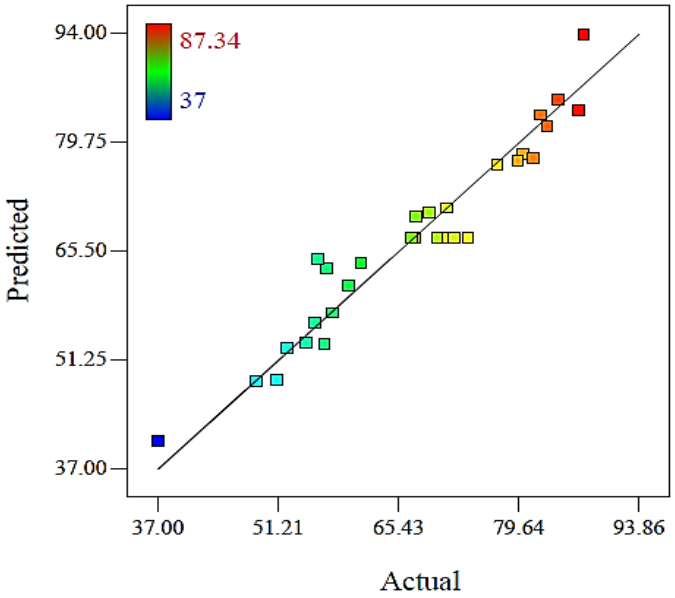

Fig 2: Predicted vs. actual plot of catechol removal data

In Fig. 3b, the effect of pH and MWCNTs on catechol removal is observed. This result was obtained with initial catechol concentration about 78 mg/L and time 22 min. Three is a cumulative adsorption potential with increase of MWCNTs dosage. However, it can be found that the change in pH has been impressed in narrow variation percentage. These results demonstrate that the adsorption of catechol is very dose-depended to MWCNTs. The interaction between time and MWCNTs dosage on adsorption is illustrated in Fig. 3 c, when pH and catechol were set in 5.5 and 87.5 mg/L, respectively. There is similar pattern of catechol removal in Fig. 3b. MWCNTs

dosage more impress on the adsorption of catechol rather than time and pH. Remarkable adsorption rate was acquired with higher dosage of MWCNTs. With regard to equation 1, it is seen that the dosage (D code) has greater numerical coefficient (13.31) than others. This fact can demonstrate higher impressing effect on catechol removal efficiency.

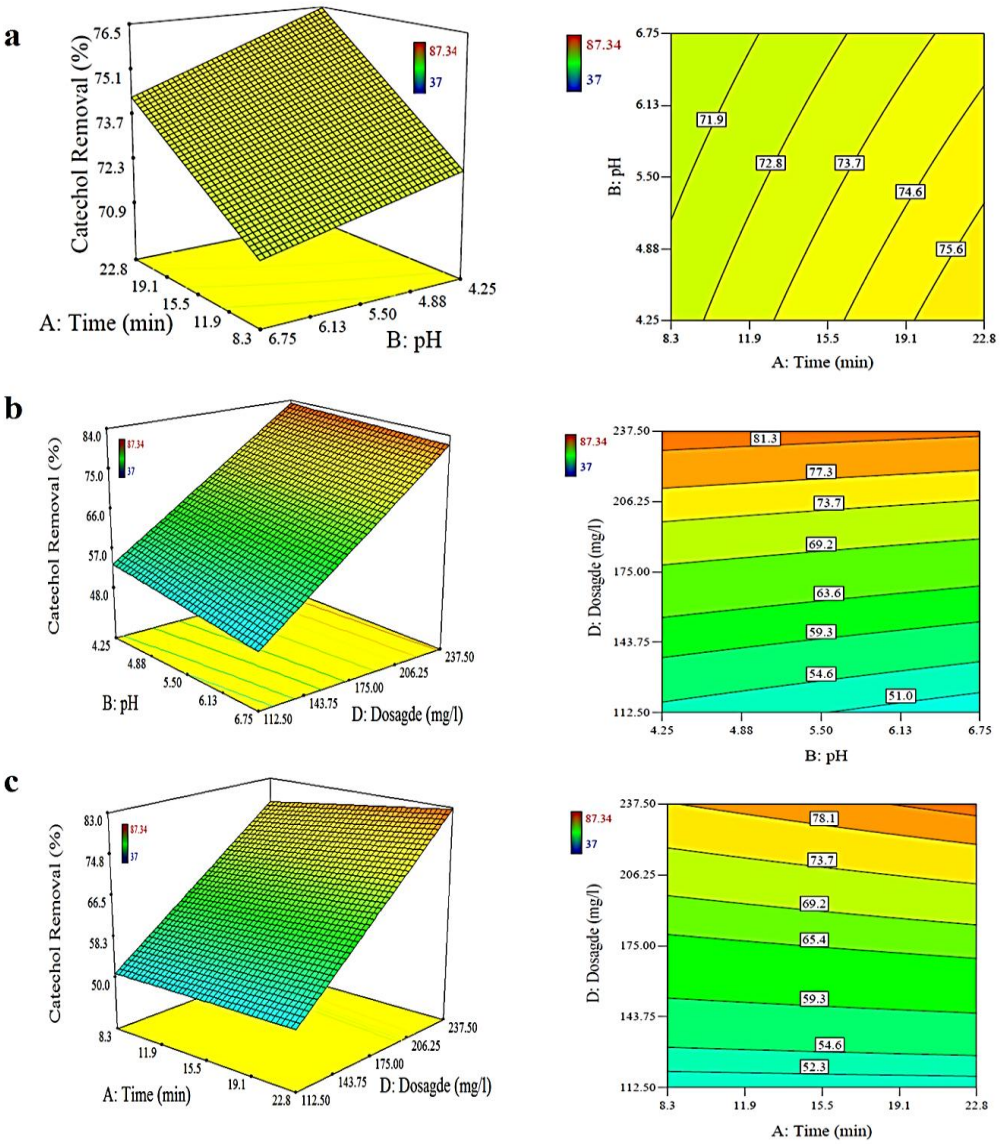

Fig 3: The 2-D and 3-D and contour plots of catechol removal using MWCNTs

3.3. *Optimization and Verification*

To achieve maximize performance, the desired goal for operational parameters was taken in "within the range", while the catechol removal efficiency was targeted in "maximize". Then, the optimal working conditions were obtained including pH 4.5, catechol concentration 87 mg/L, MWCNTs dose 237 mg, and 22 min of contact time. Under optimum condition, regard to the predicated, a verification test at actual condition was performed. Table 5, represents the result of verification run versus predicted value. Accordingly, it is clear that the result of verification test is confirmed the predicted value with 95% confidence interval (CI).

Table 5: Verification test result at certain condition

Response	Target	Correlation Predicted (%)	Confirmation Experiment (%)	95% CI Low	95% CI High
Catechol removal (%)	Maximize	85.2	90	79.5	90.84

3.4. *Kinetics of Adsorption*

In order to investigate the change in the concentration of catechol onto MWCNTs with shaking time, the kinetic data was subjected to three most popular kinetic models encompass interaparticle diffusion (Morris–Weber), pseudo-first/second-order kinetics. The linear form of these models is as follows[15]:

Interaparticle diffusion $q_t=K_{id}(t)^{0.5}+C$ (3)

Here q_t is the sorbed concentration of catechol at time't'. At among k_{id} is the interaparticle diffusion constant kinetic.

Psedudo first-order $\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$(4)

Psedudo second-order $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$ (5)

where q_e is the capacity of adsorption at equilibrium conditions (mg/g), k_1 (L/min)andk_2 (mg/g.min) are the pseudo-first/second order constants. As seen in Fig.4 the kinetic models are shown. According to it, the pseudo-first order with R^2 0.99 offers the best fit with the adsorption experimental data. Similarity, Shakir et al. reported that catechol adsorption onto organophilic-bentonite was more fitted withthe pseudo-first order kinetic[18].

3.5. *The isotherm Studies*

The Langmuir, Freundlich, and Dubinin–Radushkevick (D–R) isotherm models were considered to estimate the amount of adsorbed catechol per specific amount of MWCNTs. The linear form of these models was also used as following equations[15]:

Langmuir $\frac{C_e}{q_e} = \frac{1}{q_m . K_L} + \frac{1}{q_m}C_e$(6)

whereq_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L), and q_m is the maximum amount of metal ions required to form a monolayer (mg/g). The Langmuir constants, K_L and monolayer sorption capacity, q_m were calculated from the slope and intercept of the plot between C_e/q_e and C_e.

The linear Freundlich equation is:

$log(q_e) = log(K_F) + \frac{1}{n}log(C_e)$ (7)

where K_F and n are constants of Freundlich isotherm incorporating adsorption capacity (mg/g) and intensity, while C_e and q_e are the remaining concentration of adsorbate after equilibrium (mg/l) and the amount adsorbed at equilibrium (mg/g), respectively. The slope and the intercept correspond to (1/n) and K_F, respectively.

The linear D-R equation is:

$\ln(q_e) = \ln(q_m) - \beta\varepsilon^2$ (8)

where q_e is the amount of catechol adsorbed per unit dosage of the adsorbent (mg/g), q_m the monolayer capacity, and β, is the activity coefficient related to mean sorption energy and ε is the Polanyi potential described as

$\varepsilon = RT\ln\left[1 + \left(\frac{1}{C_e}\right)\right]$ (9)

Referring to R^2 value of models, better conformity between Freundlich isotherm (0.97) and experimental data can be seen. Moreover, based on the Langmuir and Dubinin–Radushkevick analyses, the maximum adsorption capacity (q_m) about 116 and 73.69 mg/g were obtained. there are plots, and more details for isotherm models in

the Fig.5. This higher potential adsorption catechol is related to unique properties of carbon base of MWCNTs. Chirdon et al. demonstrated by using a adsorbant material that include alcohols, amines, and carboxylic acids at structure can adsorb molecules containing catechol groups successfully[19]. Also, due to -COOH, -OH, and -OH2 surface functional groups catechol have strongly immobilized on the underlying CNT surface [2].

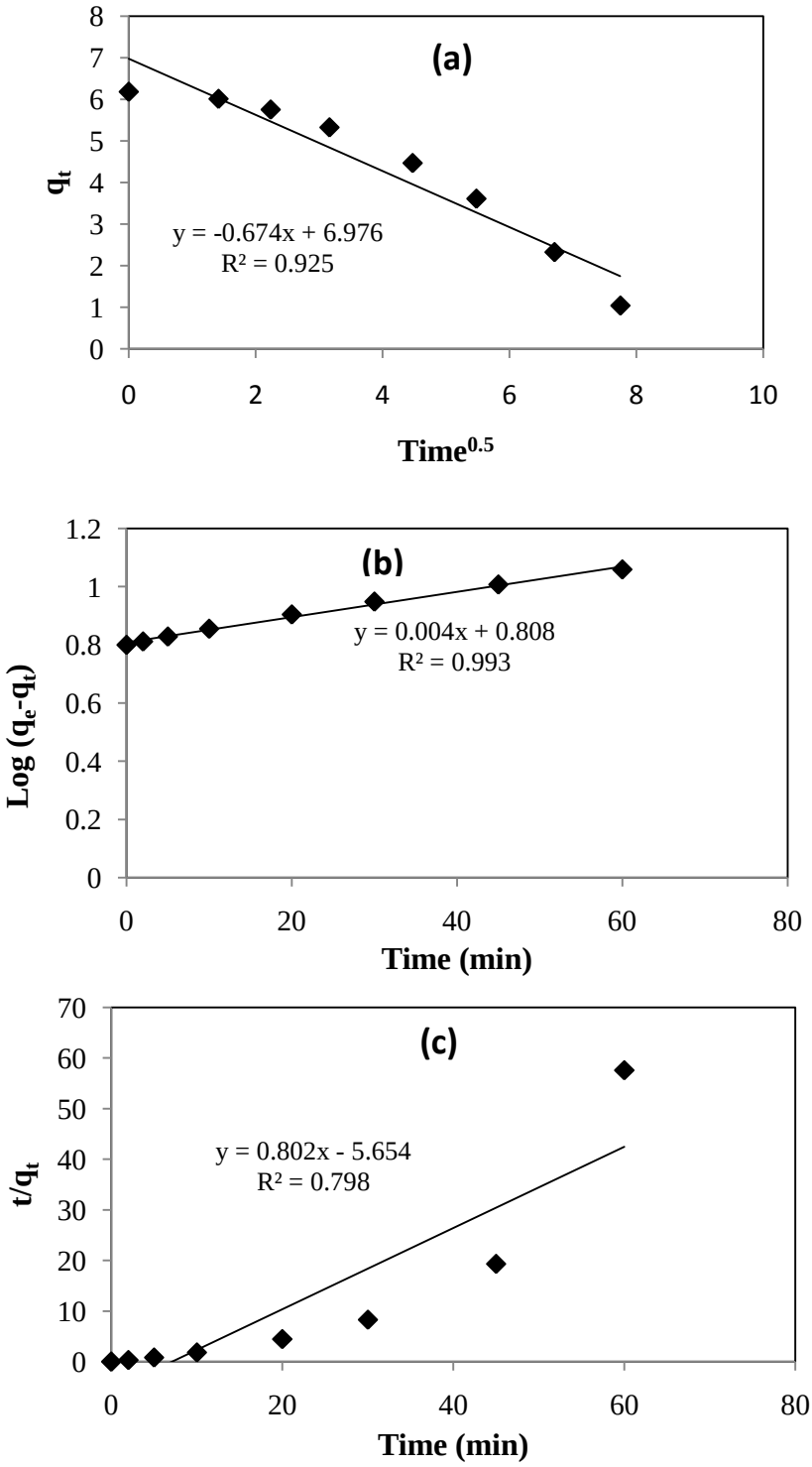

Fig 4: kinetic plots(a) interaparticle diffusion (b) pseudo-first (c) second-order.

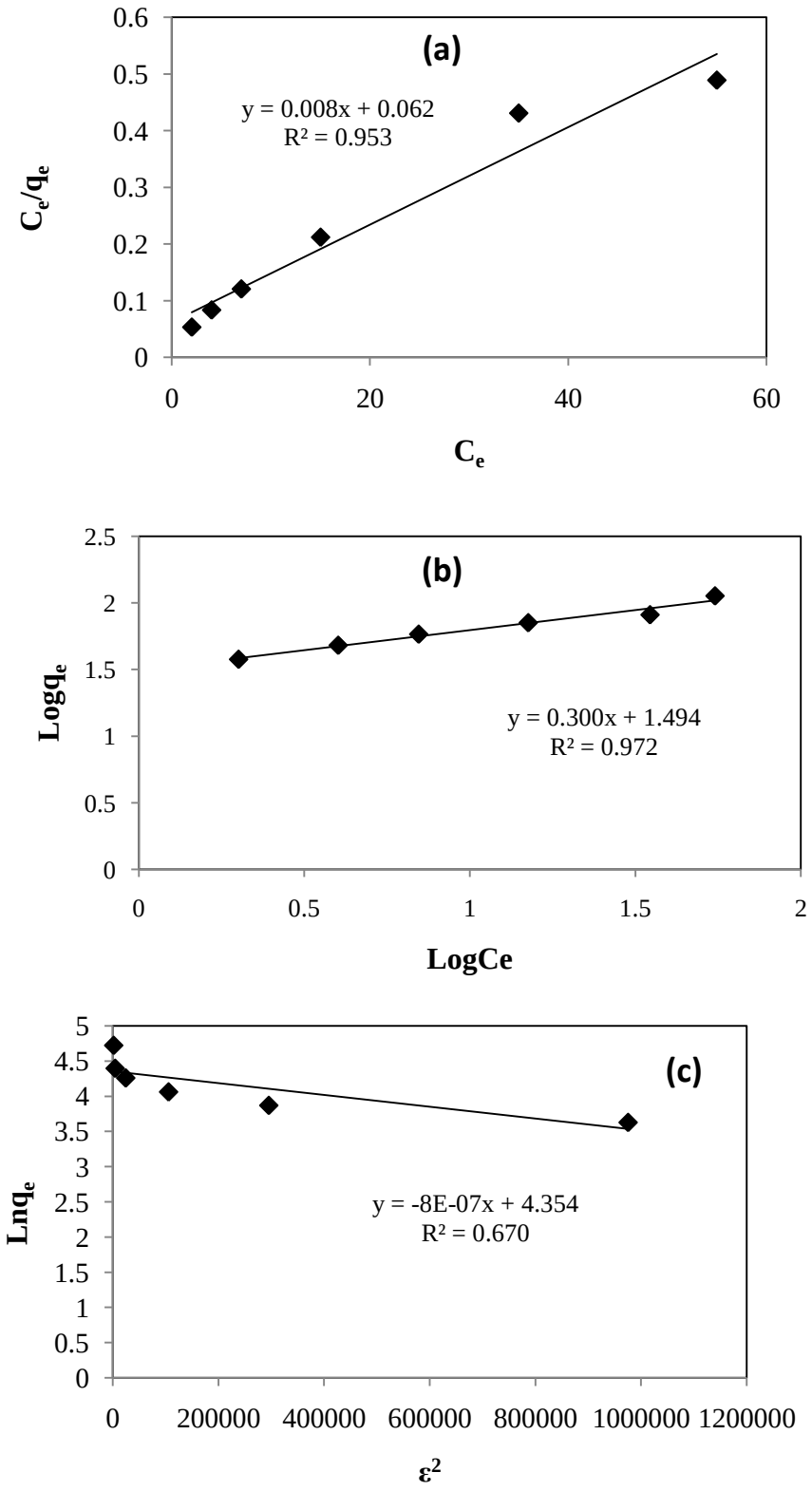

Fig 5: Isotherm plot (a)The Langmuir (b) Freundlich (c) Dubinin–Radushkevick(D–R).

Conclusion

MWCNTs was investigated for catechol removal from aqueous solution. RSM based on CCD were considered for experimental design and optimization catechol removal. The optimum amounts condition was pH 4.5, initial catechol concentration 87 mg/l, MWCNTs 237 mg and contact time 22 min. The maximize catechol removal was 85.2 %. The kinetic and isotherm studies fitted with the Pseudo-first and Freundlich models, respectively.

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