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Experimental Investigation and Statistical Modeling of the Cadmium Adsorption in Aqueous Solution using Activated Carbon from Waste Rubber Tire

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Abstract

Objectives: A universal low cost activated carbon adsorbent (WTAC) is prepared from waste tire are used to optimize the process parameters and maximize removal of cadmium from effluents. **Methods/Statistical Analysis:** Applying Response Surface Methodology (RSM), optimized the process parameters and interaction effects of adsorptive parameters on adsorption efficiency by regression and ANOVA analysis. **Findings:** Based on the statistical approach the experimental results were analyzed and the optimum process conditions are identified as pH:7.56, C_o: 3.57 mg/L, w:0.1 grams and T:315.94K. The square model (F = 614.52 and P = 0.00) and Linear (F = 1682.39 and P = 0.018) model terms highly significant effect than interactive (F = 24.39 and P = 0.27) model terms. Based on high 't'- and low 'P' value (< 0.05), both the linear terms and the squared terms, i.e., pH (x_1), C_o(x_2), w (x_3) and T (x_4), show significant effect; while in front of interaction effects, x_2x_4 are found to be significant effect and other interactions are to be insignificant on the percentage of Cd removal. Equilibrium data were well interpreted by Langmuir model, and the maximum amount of Cd deposited on the WTAC adsorbent surface is 2.59 mg/g at 313 K. The adsorption efficiency of CD onto *WTAC* adsorbent increases with increasing temperature of the solution. The variation of thermodynamic energy parameters (ΔG^o, ΔH^o and ΔS^o) with effluent temperature described that the adsorption process is endothermic, spontaneous at high temperatures and non-spontaneous at low temperatures. These condorder kinetics are feasible for a Cd adsorption process using *WTAC* adsorbent. **Application/Improvements:** *WTAC*, when utilized under the process conditions, may be a viable and effective treatment for Cd removal from industrial effluents.

Keywords: Adsorption Isotherms, Cadmium, Central Composite Design (CCD), Kinetics, Thermodynamic Studies, WTAC

1. Introduction

Cadmium, an element which is spread widely and found naturally, but a rare element. Cadmium exists as calcium sulphide occurs along with zinc. Cadmium is discharged into the environment almost due to the industrial processing of metals like zinc, aluminium, etc. The cadmium enters the food chain through the uptake of contaminated water and soil by the plants. Concentrations of cadmium in drinking water are less than 1μg/L or 1ppb (ATSDR 1999). The leachates from hazardous waste sites and industrial wastewaters seldom contaminate the groundwater with high levels of cadmium. 0.005 mg/L is set as the maximum cadmium (II) concentration in the domestic

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water supplies by the World Health Organization and the EU Directive[1,2]. The US Environmental Protection agency has set 2mg/L as the permissible discharge limit of Cadmium concentration to a waste waterbody. Indian standard code IS:10500 has set the maximum permissible limit of Cd in effluents while discharging them into the municipal sewers and surface waters as 2.0 and 1.0 mg/L respectively. Moreover, IS:10500 has set the maximum permissible limit of Cd in drinking water at 0.003mg/L. Cancer, malfunctions of human kidneys, damage of bones, and many other diseases[3]. Formation of stones in the kidney and calcium metabolism is caused due to the excessive intake of cadmium. From this study, it is evident that adsorption has been used by most of the researchers during the last few decades and it has proved to be a very efficient and economic process.

The new technology, adsorption has gained importance in the purification of all types of waters as it is environment friendly and a low cost technology[4]. Solid waste adsorbents are the most suitable adsorbents for the removal of toxic elements from wastewaters. Ongoing research to increase the effectiveness of low cost adsorbents converted into activated carbons from waste tires has been reported[5–11]. As a part of the best solution to pollution, the waste rubber tire can become an attractive source. Waste rubber tires are converted into activated carbon between 400– 700 °C in an inert gas to break down the cross-linkage between carbon atoms using a well-known process pyrolysis. Some of the properties of activated carbon produced from waste tires are affected by the temperature, heating rate, burn off, holding time and particle size[12–16]. The studies from the past literature reported the use of various materials from carbon and nanomaterials to remove pollutants from wastewaters[17–21]. The target of the present study is to make use of theoretical calculations to put more light onCd^{2+} adsorption produced from waste rubber tires.

This study aims at investigating the feasibility of WTAC adsorbent for cadmium removal from aqueous waters. CCD based on RSM was used to investigate the individual parameters like the initial Cd concentration, pH, Weight of the adsorbent, temperature and their interactions, which are considered as the most critical parameters affecting the removal of Cd^{2+} from aqueous solution. Design of complex experiments and analyzing the effects of independent variables on the system response can be done easily using an effective statistical tool, RSM. The aim of this study is the determination of optimum parameters within the operating conditions.

2. Materials and Methods

2.1 Synthetic Effluent Preparation

The Cd solution was prepared from Cd $(NO_3)_2$ (Merck-A.R. Grade). About 2.7442 g of Cadmium nitrate was weighed and a standard Cd effluent concentration of 1000 mg/l was prepared, and further working solutions of lower concentrations (2,4,6,8 and 10 ppm) were prepared as and when required. After adsorption, the final effluent solution was analyzed by atomic AAS of Perkin Elmer model-3100, a flame type AAS.

2.2 Batch Adsorption Experimental Studies

Metal investigation was completed in the batch process. The adsorption studies were completed in the exploratory conditions of various effective process parameters of pH 2-10, contact time 2-120 min, metal ion concentrations 2-10 mgL^{-1}, the weight of the adsorbent 0.025-0.15 g and the particle size of the adsorbent vary from 74 (100 mesh) -177 (200 mesh) μm. Agitation speed of 250 RPM was kept steady in the orbital shaker with the suitable time interims from 2-120 min. The mixed adsorbent solutions were filtered and analyzed for Cd^{+2} ion concentration in an Atomic Absorption Spectrophotometer. Batch experiments were conducted varies the temperature of the metal solution utilizing orbital shaker from 303 K-323K with equilibrium contact time of 70 min and analyzed by AAS to assess the thermodynamic parameters and study the feasibility of the process with temperature.

2.3 Cadmium Adsorption Capacity

The experiments were performed at different process variables for the WTAC adsorbent, the amount of Cd deposited onto WTAC surface utilizing the accompanying mathematical expression:

$$q = \frac{V(C_i - C_o)}{1000w}$$

where, q is the amount of Cd deposited on WTAC adsorbent *(mg/g)*, C_i is the initial solute concentration in the solution before adsorption *(mg/L)*, C_o is the final concentration of solute in the solution after adsorption *(mg/L)*, V is the volume of the metal solution *(L)* and w is the weight of the WTAC adsorbent.

3. Results and Discussions

3.1 Determination of Equilibrium Adsorption Process Time for WTAC Adsorbent

The adsorption process time is the key parameter for the selection of adsorbent for the adsorption process. The batch adsorption experiments were conducted for different cadmium concentrations from 2mg/L- 10 mg/l with the function of adsorption process time and removal efficiency of WTAC are demonstrated in Figure 1. The removal efficiency of Cadmium ions increases gradually with increasing adsorption process times and reaches equilibrium at around 70 min, at this point the maximum amount Cadmium is removed from the solution. The adsorption capacity proportionally increases with increasing with new active sites obtained on WTAC surface are depends on the thermal-chemical treatment process during the preparation of WTAC from waste rubber tires. The outcomes in the Figure 1. depicts that the adsorption efficiency, increased from 13.46 to 82.76 % at a contact time of 70 min with 2 mg/L metal concentration. At this optimum adsorption process time, the clump of the batch experiments was led to make sure that equilibrium is reached.

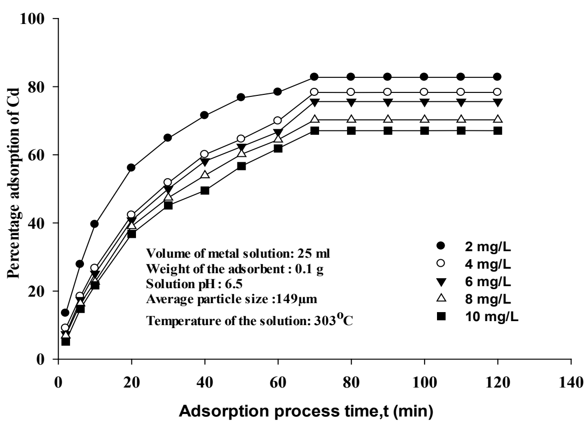

Figure 1. Effect of adsorption process time on % adsorption of Cd using WTAC as an adsorbent.

3.2 Influence of Hydrogen Ion Concentration (pH) on Cd^{+2} Binding

The variation of pH is highly effected on the adsorption process for removal of Cd^{+2} ions from waste water using WTAC as an adsorbent. This parameter is directly affected surface as well as the ionic strength between solute and adsorbate of different metal ions in the aqueous solution. The effect of pH on adsorption of Cd at constant temperature (303 K) for varying concentrations and time of adsorption 70 min is shown in Figure 2. It was observed that the pH of the solution varies from 1.0 to 3.0, the adsorption efficiency is very low because repulsion is taking place between solution and WTAC adsorbent. The adsorption efficiency is slowly increasing with pH (3.0 to 6.5) of the solution, because the effluent solution is exposed to the negative charges and strongly attracting the Cd^{+2} ions with the adsorbent surface. The solution pH value is increased 6.5 to 8.5; leads undergo hydrolysis process forming a precipitation of Cadmium hydroxide ($Cd(OH)_2$) and carbonate ($Cd(CO_3)_2$), dominate at high pH where as Cd^{2+} and aqueous sulfate species dominate at lower pH (<8). This subsequently leads to change the equilibrium conditions and the kinetics of the adsorption process. These studies were described that the potential of H^+ ions on the WTAC surfaces is not metal specific. The maximum adsorption efficiency 82.76% is obtained at pH 6.5.

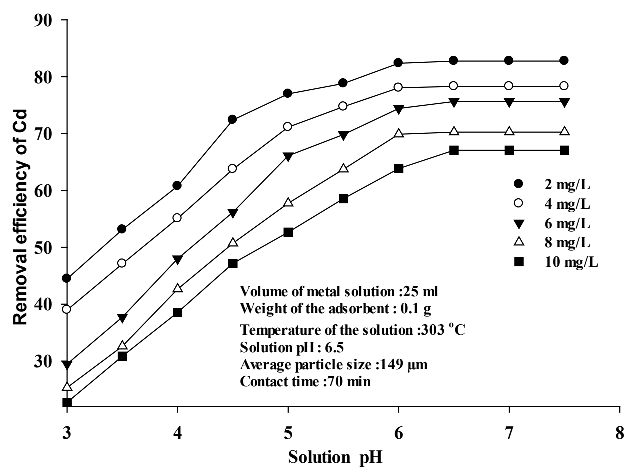

Figure 2. Effect of solution pH on the removal efficiency of CD using WTAC as an adsorbent.

3.3 Modeling of Isotherms

The isotherms are used to check the chemical interaction between adsorbent and adsorbate and strength of adsorption using WTAC adsorbent. The linear form of the Frendluich isotherm model is given by

$$\ln q_{eq} = \ln K_f + \frac{1}{n_f} \ln c_{eq}$$

From the Frendluich isotherm model, gives the straight line relationship with correlation coefficients decreases with increasing temperature, described that at lower temperatures this model fitted for the removal of Cd using WTAC adsorbent. The constants K_f and n_f are representing that effectiveness of adsorbent and the strength of adsorption in the adsorption process. Figure 3 shows that the n_f is increased from 1.61 to 1.83, while K_f increased from 0.804(mg/g)/(L/g)^n to 1.5 (mg/g)/(L/g)^n with increased temperature (303K - 323K) and solute concentration (2 mg/L – 10 mg/L). These outcomes revealed that the adsorption of Cd from solution using WTAC was favorable and this might be because of the chemical interactions between adsorbent and adsorbate. As the temperature increases, the constants K_f and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface.

The linearized Langmuir equation was applied to analyze the equilibrium experimental data. The equation is given as:

$$\frac{1}{q_{eq}} = \frac{1}{q_{max} K_L C_{eq}} + \frac{1}{q_{max}}$$

Based on experimental data for different solution temperatures the Figure 3. Yielding a straight line with R^2(0.999) indicating that the equilibrium experimental data is well executed with the Langmuir model. The value of Q_{max} increases with the solution temperature of 2.167 mg/g – 2.42mg/g. However, the WTAC would be an effective adsorbent for removing Cd from solution.

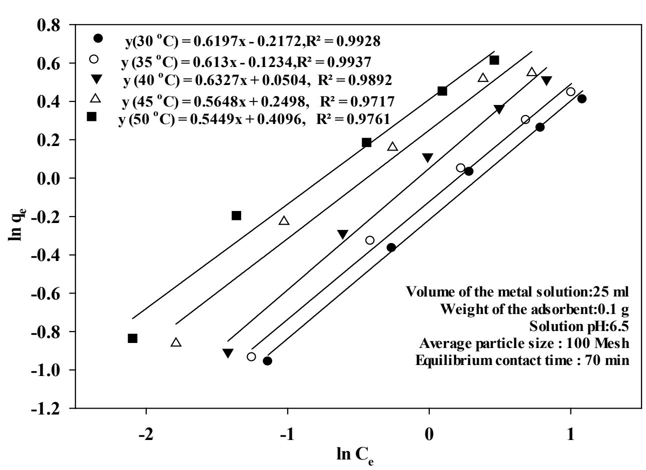

Figure 3. Frendluich isotherms at four different temperatures for removal of

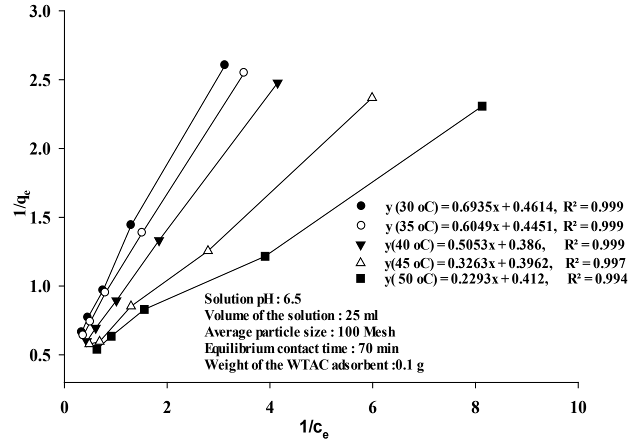

Figure 4. Langmuir isotherms at four different temperatures for the removal of Cd.

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3.4 Effect of Thermodynamic Energy Variables on Cadmium Adsorption

Based on the values of thermodynamic energy variables, like Enthalpy change (ΔH°), Entropy change (ΔS°), and Gibb's free energy (ΔG°) to verify the thermodynamic feasibility of an adsorption process. The experiments conducted for various temperatures (303K –323 K) with different solute concentrations (2 mg/L – 10 mg/L) of metal solutions are shown in Figure 5. It is found that the adsorption efficiency increases with increasing temperature. The Van't Hoff equation is described the thermodynamic parameters is given by using the following nonlinear equation,

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \text{ and } \ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

The relationship between ΔG^o and K is given by the following equation, $\Delta G^o = -RT\ln K$.

The Van't Hoff plot is drawn in Figure 6 from the present data. The values of ΔH^o, ΔS^o and ΔG^o for various initial concentrations of Cd at different temperatures are appearing in Table 1. The variation of thermodynamic energy parameters (ΔG^o, ΔH^o and ΔS^o) with effluent temperature described that the adsorption process is endothermic, spontaneous at high temperatures and non-spontaneous at low temperatures. Based on the experimental results, the WTAC adsorbent is efficient for the removal of Cd at higher temperatures. The positive value of ΔS^o, reflecting the high degree of disorder in the adsorbent/adsorbate interface that is formed during the transition.

Table 1. The values of isotherms constants for Cd adsorption using WTAC adsorbent (C_i : 2 – 10 mg/L, *w*: 0.1g, *d*: 149 µm, *T*:303-23 K, *pH*: 6.5 and *t*:70 min)

Isotherm model	Parameter	Solution temperature (K)				
		303	308	313	318	323
Freundlich	K_f (mg/g)/(L/g)^n	0.804	0.883	1.051	1.28	1.5
	n_f (L/g)	1.61	1.63	1.58	1.77	1.83
	R^2	0.992	0.993	0.989	0.971	0.976
Langmuir	q_{max} (mg/g)	2.167	2.24	2.59	2.52	2.42
	K_L (L/g)	0.660	0.735	0.763	1.21	1.79
	R^2	0.999	0.999	0.999	0.997	0.994

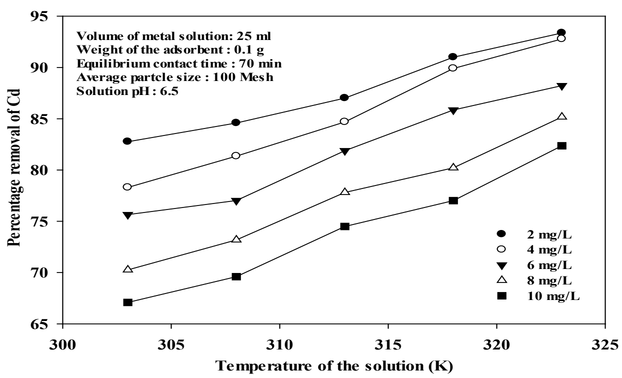

Figure 5. Effect of temperature on percentage removal of Cd onto WTAC adsorbent.

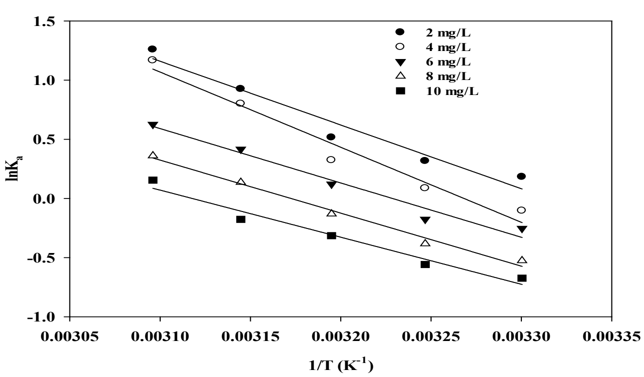

Figure 6. Plot for estimation of thermodynamic energy properties using Van't- Hoffrelation

3.5 Kinetic Modeling for Cd Adsorption on to WTAC Adsorbent

In order to investigate the rate controlling mechanism of adsorption process was concluded by the pseudo-first and second-order kinetic models were used for cadmium adsorption by treating with *WTAC*. The first-order kinetic model is generally expressed as

$$\ln(q_{eq} - q_t) = -k_f t + \ln q_{eq}$$

where, q_t(mg/g) is the amount of Cd deposited on the *WTAC* surface at time t, and k_f(min^{-1}) is the kinetic rate constant for adsorption process. The validity of the first order kinetic model for the adsorption of Cd using WTAC as adsorbent was evaluated separately at different initial concentration (2 – 10 mg/L) of Cd at optimum solution pH 6.5 and temperature is 303 K are represented in Figure 7. The Second-order kinetic model is expressed as

$$\frac{t}{q_t} = \frac{1}{q_{eq}} t + \frac{1}{k_s q_{eq}{}^2}$$

where, k_s (g mg^{-1} min^{-1}) is the second-order adsorption rate constant. The applicability of the second-order kinetic model is shown in Figure 8. It was identified that the adsorption experimental data is well correlated to the second-order kinetic equation with an R^2 value of 0.999. The adsorption kinetic constants were shown in Table 2. So, the chemical adsorption behavior may involve Wander Waals forces through the sharing of electrons between metal cations and adsorbent.

Table 2. Thermodynamic energy parameters for the adsorption of Cd using WTAC adsorbent

Initial concent-ration (mg/L)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	-ΔG°(kJ/mol)				
			30°C	35°C	40°C	45 °C	50 °C
2	44.77	0.148	0.074	0.81	1.55	2.29	3.03
4	41.19	0.131					
6	38.22	0.123					
8	37.28	0.118					
10	33.09	0.103					

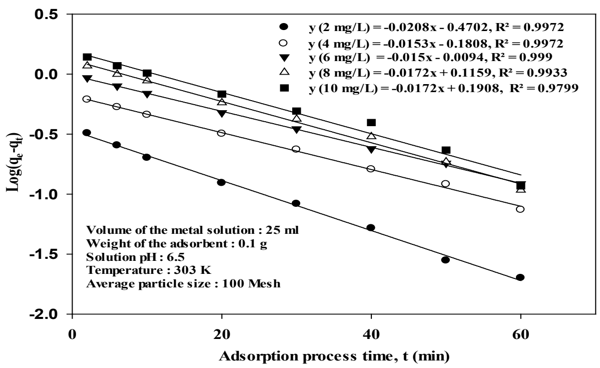

Figure 7. First order Kinetic model for adsorption of Cd on to WTAC as adsorbent.

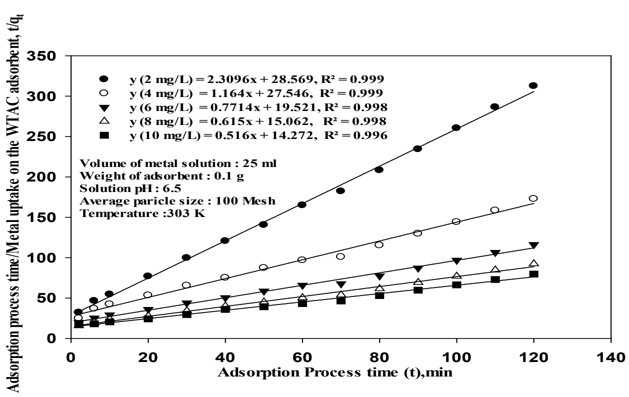

Figure 8. Second order Kinetic model for adsorption of Cd on to WTAC as adsorbent.

3.6 Optimization of Adsorption Process Parameters using Factorial Experimental Design

RSM is an efficient statistical method to reduce the number of experiments and optimize the process specifications of the adsorption process using *WTAC* as an adsorbent. Formulate the relationship between one or more response variables and a set of quantitative experimental variables or factors. Based on the independent and dependent variables in the adsorption process, RSM consists of design and experiments, response surface modeling through regression and optimization. The application of statistical experimental design techniques adopted in the adsorption process to attaining a high degree of metal removal, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs[22]. Among the varieties of factorial designs available, Central Composite Design (CCD) is the more viable design. It is held by adding two experimental points along each coordinate axis at opposite sides of the origin and at a length equal to the semi -diagonal of the hyper cube of the factorial design. The new acute values (low and high) for each parameter are summed in this model[23]. For a full factorial

$$\alpha = \left[2^{\frac{m}{4}} \right]$$

In this study four parameters: *pH*, C_o, *w*and *T* are considered and thus *m*= 4 and α = 2 from the above equation. Moreover, the total number of test points (N) in a CCD is ascertained from the accompanying mathematical statement:

$$N = 2^m + 2m + m_o$$

m_o is the number of central points. Thus, total number of experimental runs, N= 26 are considered and accordingly (m= 4; m_o = 2 and α= 2) from the above equation.

The response (*Y*) is the adsorption efficiency of cadmium. The response from CCD are subjected to a second-order multiple regression analysis to conclude the behavior of the system using the least squares regression methodology for obtaining the parameter reckoners of the numerical model[24].

$$Y = \alpha_o + \sum_{i=1}^{k} \alpha_i x_i + \sum_{i=1}^{k} \alpha_i x^2{}_i + \sum_{i<j} \sum^{k} \alpha_j x_i x_j + \in$$

where, Y is the response, α_o is the constant, α_i is the incline or straight impact of the data element x_i, α_{ii} and α_{ij} are the quadratic and linear interaction effect between the input factor x_i. The assessment of the coefficient of the regression equation is done using STATISTICA 6.0. The fit and significance of each term in the equation are tested by Analysis of variance (ANOVA). RSM is applied to examine the cumulative effects, individual effects and their interactions mutually.

3.6.1 Development Response Equation using CCD for Cd Adsorption Process

Central Composite Design (CCD) was used to develop a relation between the % removal and Process variables affecting the adsorption of cadmium from aqueous solution onto WTAC adsorbent. The complete experimental range and levels of independent variables are given in Table 3. CCD is applied to obtain an expression between the adsorption of cadmium from the Cd solution and the process variables investigated. The quadratic model suggested by the software was selected. Experiments were planning to obtain a quadratic model consisting of 26 trials and 1 replicate at the center point. The output data given by CCD (Based on the range of variables chosen) are shown in Table 4, along with the experimental and predicted values.

Table 3. Kinetic rate constants for Cd adsorption using WTAC adsorbent (C_i : 2 – 10 mg/L, *w*: 0.1g, *d*: 149 µm, *T*:303-23 K, *pH*: 6.5 and *t*:70 min)

C_i (mg/L)	Pseudo-first-order			Pseudo-Second-order		
	K_f(min-¹)	q_e (mg/g)	R^2	KS(g/ mg. min)	q_e (mg/g)	R^2
2	0.028	0.624	0.997	0.186	0.432	0.999
4	0.015	0.834	0.997	0.049	0.859	0.999
6	0.015	0.990	0.999	0.030	1.296	0.998
8	0.017	1.122	0.993	0.025	1.626	0.998
10	0.017	1.210	0.979	0.018	1.937	0.996

Table 4. Range of process variablesto be selected for the central composite design

Variable	Process parameter	Range of Process parameters				
		-2	-1	0	1	2
x_1	Solution pH	2	4	6	8	10
x_2	Initial Metal concentration (mg/L)	2	4	6	8	10
x_3	Adsorbent dosage (g)	0.05	0.075	0.1	0.125	0.15
x_4	Temperature (K)	303	308	313	318	323

The response model equation is performed by Regression analysis for the cadmium adsorption process. The coded values of variables in the equation represent adsorption efficiency (*Y*) as a function of pH (x_1), C_i (x_2), w(x_3) and T(x_4). The maximum adsorption efficiency of cadmium was found to be 82.24% at the optimal conditions suggested by the design. The information acquired was fitted to a second-order polynomial equation. Regression analyses, ANOVA and response surfaces were executed using the Design Expert Software (Version 8.0.7.1) subsequently.

The experimental data with multiple regression analysis was obtained from the following regression equation for the adsorption of Cadmium:

$$\% \text{ Removal efficiency } (Y) = -2491.99 + 20.24\,x_1 - 0.48\,x_2 + 3023.89\,x_3 + 14.77\,x_4 - 1.09x_1^2 - 0.38x_2^2 - 2150.67x_3^2 - 0.02\,x_4^2 + 0.05\,x_1x_2 + 3.60\,x_1x_3 - 0.01x_1x_4 + 21.95\,x_2x_3 - 8.42\,x_3x_4$$

where, x_1, x_2, x_3 *and* x_4 are the code values for the independent variables, x_1x_2, x_1x_3, x_1x_4, x_2x_3, x_2x_4, x_3x_4, x_1^2, x_2^2, x_3^2 and x_4^2 are the significant model terms for the adsorption of cadmium. The coefficients of the regression models calculated are listed in Table 5 for the adsorption of cadmium, which contains four linear, four square and five interaction terms. The efficiency of the model in predicting the % removal of adsorption was evaluated by the coefficient of determination (R^2), standard error, t-values, p-values and Fisher's 'F' test value. The R^2 value measures the fitness of adsorption process with variation between process parameters and their combinations. The probability value of greater than 0.0001, indicates the inaccuracy of any model are shown in Table 6. The model is statistically significant if the lowest *p*-value is less than 0.05 and the probability values less than 0.0001 shows 99% accuracy[25]. The interrelationship of the free variables and response can be clarified by the regression model as shown in Table 7. The model is best suited by determination of correlation R^2, 99.9% (0.999) value which is close to 1[26].

The observed and the predicted values of adsorption efficiencies are shown in Figure 8.

Table 5. Experimental design matrix and results for adsorption of cadmium onto WTAC adsorbent

Experiment runs	Independent variables				Observed value of % Adsorption of Cd	Predicted value of % Adsorption of Cd
	x1	x2	x3	x4		
1	-1	-1	-1	-1	62.38	61.98
2	-1	-1	-1	1	64.12	64.85
3	-1	-1	1	-1	66.73	67.11
4	-1	-1	1	1	68.17	67.87
5	-1	1	-1	-1	50.56	50.82
6	-1	1	-1	1	53.46	53.73
7	-1	1	1	-1	60.56	60.34
8	-1	1	1	1	61.14	61.14

9	1	-1	-1	-1	75.42	75.58
10	1	-1	-1	1	78.02	78.17
11	1	-1	1	-1	81.54	81.43
12	1	-1	1	1	82.24	81.92
13	1	1	-1	-1	65.17	65.17
14	1	1	-1	1	67.78	67.80
15	1	1	1	-1	75.44	75.41
16	1	1	1	1	76.13	75.93
17	-2	0	0	0	45.05	44.72
18	2	0	0	0	72.64	72.84
19	0	-2	0	0	78.67	78.56
20	0	2	0	0	61.47	61.45
21	0	0	-2	0	65.75	65.19
22	0	0	2	0	75.92	76.35
23	0	0	0	-2	74.54	74.45
24	0	0	0	2	76.76	76.76
25	0	0	0	0	76.17	76.15
26	0	0	0	0	76.17	76.15

Table 6. Optimized process parameters for adsorption of Cadmium on to WTAC adsorbent

Process parameters	Initial observed the limits of process parameters	Critical values of process parameters	Final observed the limits of process parameters
pH	2.0	7.56	10.00
Initial Concentration (mg/L)	2.0	3.57	10.00
Dosage (g)	0.05	0.1	0.15
Temperature (K)	308.0	315.94	318.00

The predicted value of % adsorption of Cadmium on WTAC adsorbent used CCD is: 82.24%

Table 7. **ANOVA** analysis of variance for removal of Cadmium using WTAC as an adsorbent

Variables	SS	DF	MS	F	P (Prob >F)
x_1	790.453	1	790.4532	4390.317	0.000000
x_1^2	361.921	1	361.9213	2010.175	0.000000
x_2	292.752	1	292.7521	1625.997	0.000000
x_2^2	45.264	1	45.2641	251.405	0.000000
x_3	124.546	1	124.5456	691.748	0.000000
x_3^2	34.690	1	34.6903	192.676	0.000000
x_4	3.979	1	3.9790	22.100	0.000649
x_4^2	0.693	1	0.6933	3.851	0.075506
x_1x_2	0.555	1	0.5550	3.083	0.106897
x_1x_3	0.518	1	0.5184	2.879	0.117805
x_1x_4	0.103	1	0.1027	0.570	0.466012
x_2x_3	19.272	1	19.2721	107.041	0.000001
x_2x_4	0.001	1	0.0012	0.007	0.936400
x_3x_4	5.908	1	5.9080	32.814	0.000133
Error	1.980	11	0.180		
Total SS	**2340.697**	**25**	**R^2 = .9991**	**R^2 (Adj) =.99808**	

DF:degree of freedom; SS: sum of squares; F: factor F; P: probability.

3.6.2 *Effect of Process Variables on % Removal of Cadmium using RSM*

Batch experiments were conducted for 26 optimized sample runs with different combinations of the process parameters to find the different adsorption efficiencies are used in statistical modeling. The influence of linear, square and interaction effects of process variables on the adsorption efficiency of Cd using *WTAC* is shown in (Table 7, Table 8). These results were demonstrated by means of Fisher's *F*-test and Student *t*-test. For all the parameters (Table 8), The square model (F = 614.52 and P = 0.00) and linear (F = 1682.39 and P = 0.018) model terms highly significant effect than interactive (F = 24.39 and P = 0.27) model terms of % cadmium removal. The Student *t*-test was used to signify the regression coefficients of the parameters with larger 't' and smaller '*P*' values[27]. From the Table.8, it is evident from the results that the squared effects of x_1^2,x_2^2 and x_3^2 variables for cadmium were also highly significant, because of their P-values were less than 0.05; the P values for pH (x_1), concentration (x_2), the weight of the adsorbent (x_3) and temperature of a solution were found to be 0.004, 0.9352, 0.00 and 0.055 respectively. From the *p*-values, the linear effects of x_1 andx_3, are significant(P<0.05) and are able to influence the %removal of cadmium[28]. The magnitude of t-value gives the positive or negative influence on the dependent variable. The coefficients of x_1, x_3 and x_4 showed the greatest linear positive effect and the negative effect by the other variable x_2 (Table 8) on cadmium removal. All the squared terms, x_1, x_2, x_3 *and* x_4 shows a negative influence on the adsorption of cadmium. The interaction effect between process variables of x_2x_3 (p = 0.000, t = 10.346) were found to be statistically significant and positive effect on % removal of cadmium, whereas the combination of x_3x_4 (p = 0.000 and t = -5.7254) significant and negative influence on the % adsorption of cadmium[29]. All other interactions are insignificant and negative influences on the % adsorption of cadmium.

Table 8. Regression coefficients and corresponding *t*- and *P*- values of the models

Adsorption parameter (Mean value)	Regression Coefficient	Standard Error	t-Value	p-Value
Constant	-2491.99	1077.929	-2.3118	0.041165
x1	20.24	5.734	3.5304	0.004712
x12	-1.09	0.024	-44.8350	0.000000
x2	-0.48	5.734	-0.0831	0.935281**
x22	-0.38	0.024	-15.8557	0.000000
x3	3023.89	459.036	6.5875	0.000039
x32	-2150.67	154.939	-13.8808	0.000000
x4	14.77	6.909	2.1381	0.055785
x42	-0.02	0.011	-1.9624	0.075506
x1x2	0.05	0.027	1.7558	0.106897**
x1x3	3.60	2.122	1.6968	0.117805**
x1x4	-0.01	0.018	-0.7552	0.466012***
x2x3	21.95	2.122	10.3460	0.000001
x2x4	0.00	0.018	0.0816	0.936400**
x3x4	-8.42	1.470	-5.7284	0.000133

**insignificant ($P \geq 0.05$)

Based on surface modeling equation, understanding the interaction effects of these variables on adsorption efficiency was depicted in Figure 9. The surface plots described the effect of process variables on the absorption capacity and determine the optimum level of each variable for maximum response. The contour plots are used to show the pictorial representation of the influence of process variables *pH*, C_i, *w* and *T* with their interactions on the adsorption efficiency of the Cd adsorption process. It represents the interactive effect of any two variables on the response variable, when the remaining variables kept constant. The shape of the surface plots indicates an interaction between the variables. The elliptical shape of the response surface curve indicates good interaction of two variables. Figure10is plotted between x_1 *and* x_4, x_3*and* x_4, x_2 *and* x_4, x_1 *and* x_3,x_1 *and* x_2 respectively. The response surface plot (Figure. 10) had a clear peak, which indicated that the optimum conditions fall inside the design boundary. The maximum adsorption efficiency of cadmium is indicated by the surface confined to the smallest curve of the plot with the other variable maintained at hold value[30–32].

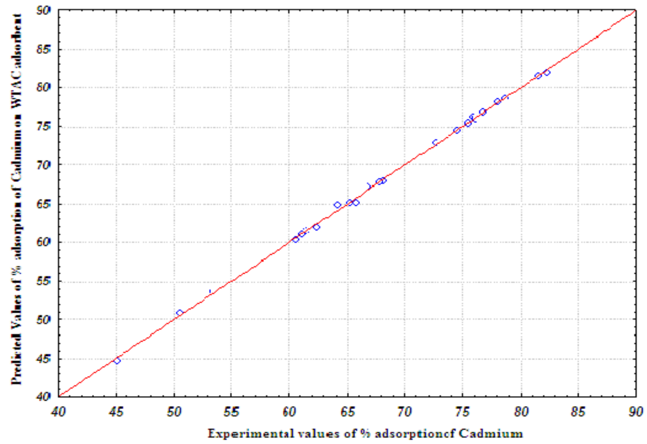

Figure 9. Correlation plot of experimental values Vs predicted values for the adsorption of cadmium.

3.6.3 *Optimization of Adsorption Process Parameters using Statistical Modeling*

The optimum adsorption process parameters obtained by using RSM for the adsorbent WTAC batch studies are pH 7.56, metal ion concentration 3.57 mg/L, adsorbent dosage 0.1g and temperature 315.94. The model approval has been characterized at optimum levels of the process variables, anticipated by the model to accomplish the maximum adsorption efficiency of 82.24 %.

4. Acknowledgement

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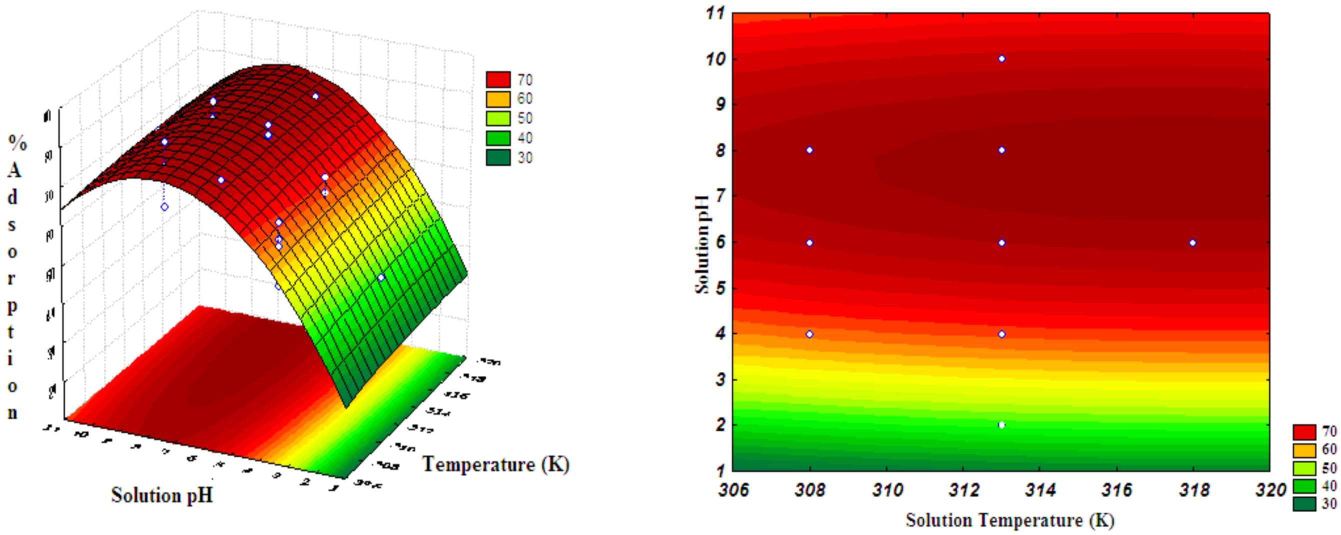
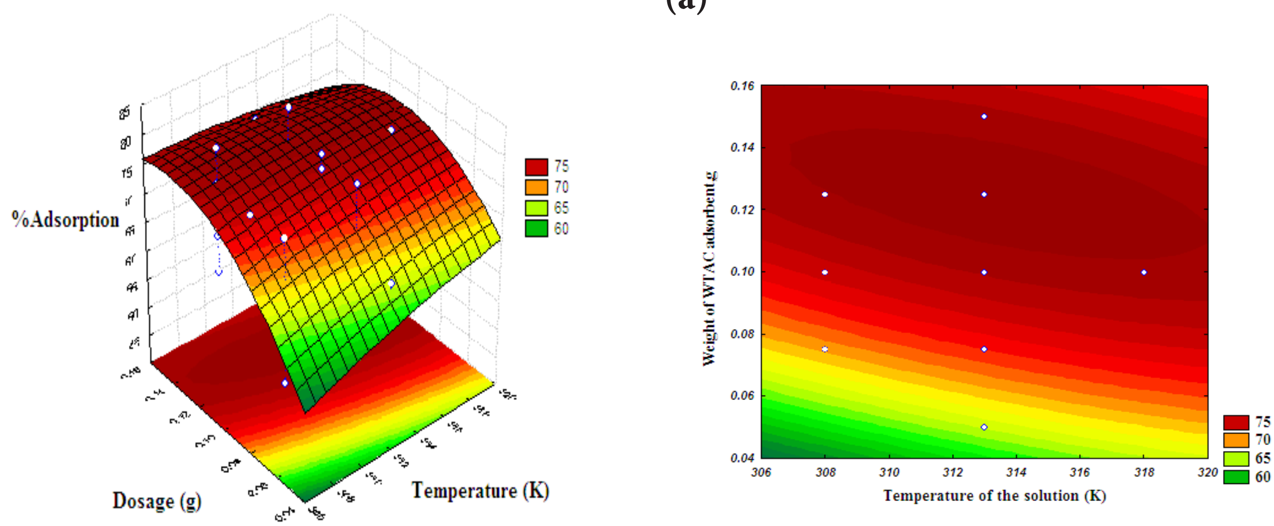
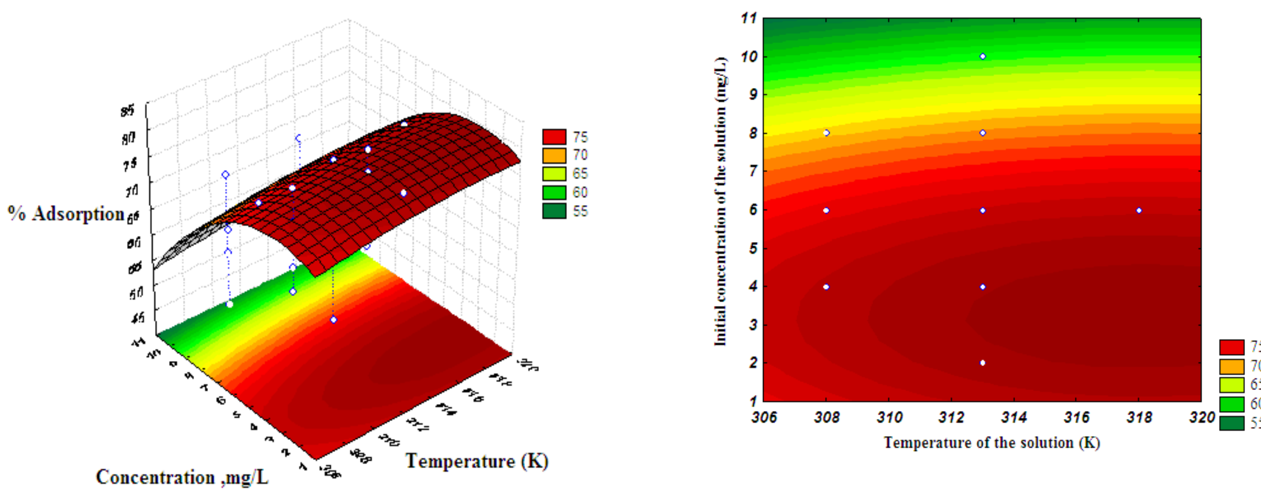

% Adsorption
Solution pH
Temperature (K)
70
60
50
40
30
Solution pH
Solution Temperature (K)
306
308
310
312
314
316
318
320

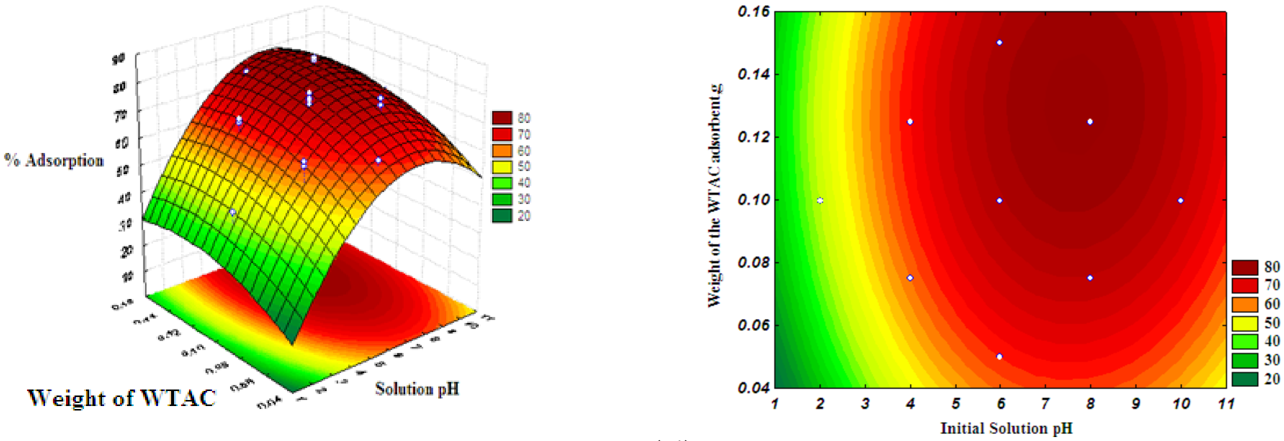
(a)


%Adsorption
Dosage (g)
Temperature (K)
75
70
65
60
Weight of WTAC adsorbent g
Temperature of the solution (K)
0.04
0.06
0.08
0.10
0.12
0.14
0.16

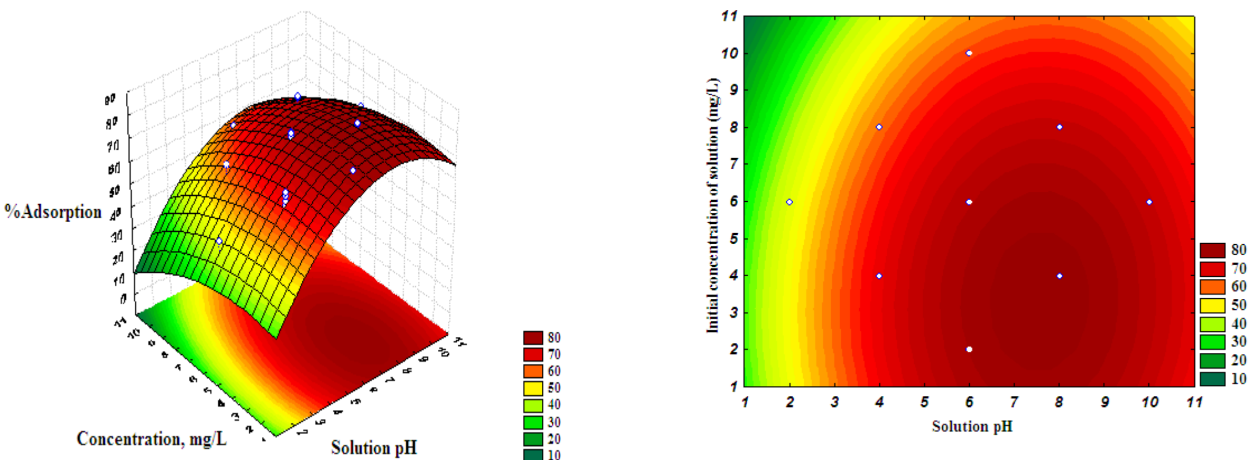
(b)


% Adsorption
Concentration ,mg/L
Temperature (K)
75
70
65
60
55
Initial concentration of the solution (mg/L)
Temperature of the solution (K)

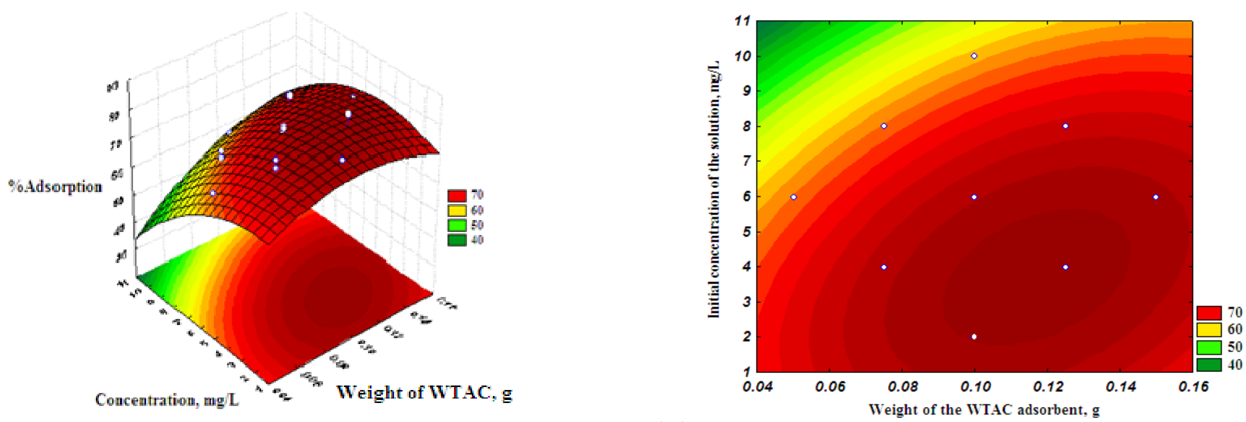
(c)



(d)



(e)



(f)

Figure 10. Response surface and contour plots showing ***(a)*** the effect of pH(x_1) VsSolution temperature(x_4) and their mutual interaction on % removal of cadmium, with constant of x_3 and x_2; ***(b)*** the effect of x_3, x_4 and their mutual interaction on % removal of Cd, with constant level of x_1 and x_2 ; ***(c)*** the effect of x_2, $x_4$and their mutual interaction on % removal of Cd, with constant level of x_1& x_3; ***(d)*** the effect of x_1, $x_3$and their mutual interaction on % removal of Cd, with constant level of x_2& x4; ***(e)*** the effect of x_1, $x_2$and their mutual interaction on % removal of Cd, with constant level of x_3& x_4; ***(f)*** the effect of x_2, $x_3$and their mutual interaction on % removal of Cd, with constant level of x_1& x_4.

5. Conclusions

- The maximum adsorption capacity of Cadmium onto the WTAC adsorbent was obtained at pH 6.5, equilibrium adsorption process time 70 min, Ci: 100 mg/L, w = 0.1 g and T: 303 K. The adsorption efficiency of Cd under these process conditions is 82.76%.
- Adsorption isothermal data were easily interpreted by a Langmuir model with maximum adsorption capacity of 2.167 mg/g at 303 K of Cd ions on WTAC and kinetic data were appropriately equipped with the second-order kinetic model.
- Consequences of thermodynamic investigations, properties of ΔHo, ΔGo and ΔSo are 44.77 KJ/mole, -0.074 KJ/mole and 0.148 KJ/mole. K, demonstrates that the variation of thermodynamic energy parameters (ΔGo, ΔHo and ΔSo) with effluent temperature described that the adsorption process is endothermic, spontaneous at high temperatures and non-spontaneous at low temperatures.
- Based on the experimental results, the WTAC adsorbent is efficient for the removal of Cd at higher temperatures.
- The positive value of ΔSo, reflecting the high degree of disorder in the solid/solution interface that is formed during the transition.
- The optimum adsorption conditions determined using RSM for the adsorbent WTAC batch studies are pH 7.56, metal ion concentration 3.57 mg/L, adsorbent dosage 0.1g and temperature 315.94. The model approval has been characterized at optimum levels of the process variables, anticipated by the model to accomplish the maximum % adsorption of 82.24%.
- Observations on contour plots, the cadmium adsorption process using WTAC adsorbent is highly influenced by pH, solute concentration in solution(ci) and mass of the adsorbent on adsorption efficiency.

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