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Design Expert Application in the Optimization of Cadmium (II) by Chitosan from Produced water

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ABSTRACT

Oil and gas industry generates by-products in large quantities and is known as produced water. It contains highly immiscible oil, grease, dissolved hydrocarbons, heavy metals, and other pollutants. Globally, produced water volume has increased and became the largest waste stream and requires remediation. Adsorption provides better removal efficiency for metals removal than any other techniques. The present study aimed to remove Cadmium (II) by using chitosan as an adsorbent. The response surface methodology (RSM) module in the software"Design-Expert® involving central composite design (CCD) was employed to optimize independent variables to achieve maximum ion removal. The effect of metal ion concentration, adsorbent dosage, contact time, and pH were analyzed empirically and successfully by RSM. Cd (II) in produced water represents a significant environmental and human health risk due to its high toxicity and bioaccumulation potential. Statistically significant quadratic polynomial for Cd (II) was obtained via regression analysis R2 (0.94). The highest removal efficiency, 89.45% was attained under the optimized conditions.

Keywords:
adsorption; adsorbent; cadmium; produced water; water treatment

1.Introduction

The processing of oil and gas produces a substantial amount of wastewater as a by-product in large amounts and is brought to the surface during production processes, commonly referred to as Produced water (PW) [1]. PW's main components are oil and grease (O&G), salts, heavy metals, radioactive materials, suspended solids, benzene, toluene, ethylbenzene, and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs), organic acids, and phenols [1, 2]. In 2014, the global PW volume was 202 billion barrels and was estimated to be approximately 340 billion barrels in 2020 [3]. Furthermore, almost 40% of PW is discharged untreated directly into water bodies contaminating surface and groundwater [4]. PW's chemical composition varies from well to well and depends on geological formation [5, 6]. Heavy metals are highly toxic, carcinogenic, and persistent in the environment. Even at trace levels, exposure to heavy metals is harmful to human beings [7]. Thus, removing undesirable metals is considered an essential task that is still threatening the environment. The permissible limit of cd(II) in drinking water is 0.02 mg/L and the excessive cd (II) ions damage the liver, kidney causes skin irritation and ulceration [8].

Numerous methods, such as chemical precipitation, adsorption, membrane filtration, electrochemical, and ion exchange, have been identified as effective methods for heavy metals removal [8-10]. Adsorption is the most flexible of these methods in terms of design and application, and it produces high-quality handled effluents in many situations. Appropriate desorption processes may regenerate adsorbents for several uses due to adsorption processes' reversible existence [11]. Many desorption processes have low operating costs, high efficiency, and are simple to use. As a result, the adsorption method is an essential technique for removing heavy metals from water/wastewater sources. According to previous research, adsorption can

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safely eliminate 80 percent of heavy metals from water and can possibly restore 100 percent of water [12]. Whereas, in PW, adsorption is utilized only as a unit process or polishing step in the PW treatment train. Natural polymers have drawn much interest due to their cost-effective and eco-friendly nature. Chitosan is a second-most abundant biopolymer in nature after cellulose and the deacetylation of chitin forms it, and it is linear alkali polysaccharide can be easily obtained from seafood processing wastes[13]. Chitosan is a competent adsorbent to remove heavy metals because it contains hydroxyl groups and amino acid compounds, which results in chelates formation when combining with heavy metals. It has surface reactivity and high adsorption capacity [14].
Response surface methodology (RSM), a mathematical and statistical technique used to improve, optimize, and develop different processes method, and independent variables have attracted significant attention[15]. This study aims to implement RSM to evaluate the ideal process conditions for Cd (II) adsorption in PW. The central composite design (CCD) in RSM is used to optimize Cd(II) by chitosan from synthetic PW for the first time. Optimum conditions were identified by varying independent variables such as adsorbent dose, contact time, initial concentration, and solution pH.

2. Materials and Method

2.1.Reagents

Chitosan and cadmium nitrate ($Cd(NO_3)_2.4H_2O$) were used as reagents in the present study.

2.2. Cadmium adsorption process

Stock solutions (1000mg/L) of Cd^{2+} was prepared by dissolving 2.103g in distilled water. The cadmium concentrations in the experimental solution was measured by atomic absorption spectrophotometer (AAS). 30 batch adsorption experiments were conducted using RSM in 100 mL Erlenmeyer flasks by varying contact time, initial pH, metal ion concentration and adsorbent dosage containing 50 mL Cd(II) the total volume of the solution on a temperature-controlled magnetic stirrer. The initial pH of the solution was controlled by adding 0.1 M NaOH and HCl solutions. Chemicals were of analytical grade. The amount of adsorbed Cd (II) ions (Qe) per gram of chitosan was calculated using Eq. 1:

$$\%MR = \frac{(Ci - Ce)}{Ci} * 100 \qquad (1)$$

2.3. Optimization and statistical analysis

The experiment was designed to model and test the effects of four independent variables on the response using RSM (A: pH, B: dose, C: contact time, and D: metal ion concentration) (R: metal removal percentage). CCD with total factorial was introduced. For the four independent variables, the CCD was centred on eight axial points, eight factorial points, and six replicates at the central point. Thus, a set of 30 experimental runs of sixteen fractional factor points, eight axial points and (1 * 1) central points centered on the ranges of independent variables. Contour plots were used to investigate the interactions between variables. The ranges of independent variables of each factor are shown in Table 1.

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Table 1. Independent variable ranges

Factor	Symbol	Unit	Independent variables ranges		
			-1	0	+1
pH	A	-	4	5.5	7
Adsorbent dose	B	g	0.5	1.5	3
Contact time	C	minutes	20	60	120
Concentration	D	mg/L	3	4	5

3. Results and Discussion

3.1 Model Development for Cd (II) Removal

In the present study, the interaction effects of independent variables such as metal ion concentration, contact time, pH, and adsorbent dose on the Cd(II) removal were investigated using a CCD matrix. To formulate the adsorption potential, a complete quadratic equation was determined after performing 30 experiments, each with three replicates. Table 2 shows the experimental design as well as the results

$$Cd(II) = +77.28 - 4.15A - 3.92B - 1.57C + 2.77D - 3.89AB - 0.8469AC + 3.91AD - 1.31BC - 1.14BD + 3.31CD - 14.23A^2 + 7.22B^2 + 2.37C^2 + 7.37D^2 \quad (2)$$

As a general rule, a high F value complemented by a low probability p-value (< 0.05) suggests a high significance of the regression model/parameters.

Table 3 represents the model fit summary for the Cd(II) removal. The obtained model significance can be calculated using the p-value, correlation of decision (R^2), and lack of fit test results. The model had p-values of less than 0.0001, indicating that they were important. The R^2 values were higher than 0.99 for Cd(II). Figure 1 shows the diagnostic plots of expected Vs real values for Cd(II) removal.

The supposition of normality was tested by plotting the normal percentage against the Studentized residuals, which was found to be satisfactory for Cd(II) illustrated in Figure 2. The data points is distributed roughly in the graphs along a straight line, indicating normal distribution.

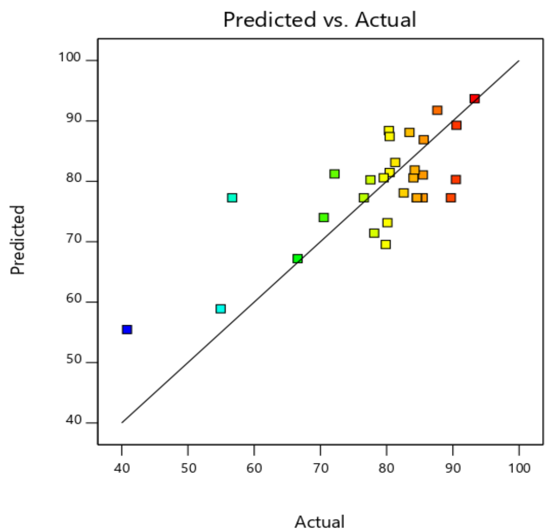

Figure 1. Diagnostic plots for predicted Vs. actual values for Cd(II) removal

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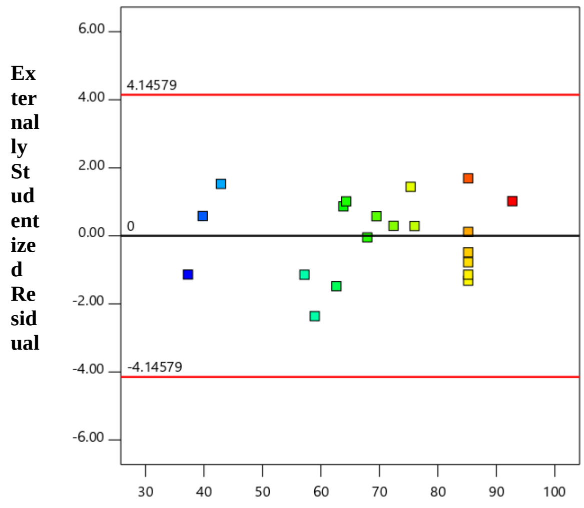

Figure 2**:** Diagnostics plots for residuals Vs. predicted values for Cd (II) removal

Table 3: Model fit summary for Cadmium removal

Source	**Sum of squares**	**df**	**Mean square**	**F, value**	**Prop>F/P-value**	**Remarks**
Cd (II) Model	6549.08	9	727.68	14.59	0.0009	Significant
A	163.70	1	163.70	12.10	0.0059	
B	137.49	1	137.49	10.16	0.0097	
C	698.56	1	698.56	51.64	< 0.0001	
D	2523.21	1	2523.21	105.33	<0.0001	
AB	148.35	1	148.35	10.97	0.0079	
BC	117.81	1	117.81	2.36	0.1682	
AD	78.56	1	78.56	167.28	<0.0001	
CD	268.42	1	268.42	8.07	0.0175	
A^2	773.13	1	773.13	55.47	< 0.0001	
B^2	504.45	1	504.45	31.33	0.0001	
C^2	1.81	1	1.81	0.1335	0.7224	
D^2	1.93	1	1.93	4.05	0.0793	
Residual	135.27	10	135.27			
Lack of Fit	2.92	3	0.73			non-significant

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Table 4. RSM model statistical parameters output table for Cadmium removal

Statistical Figures	Abbreviation	Cd (II)
Mean	Mean	64.54
Standard deviation	Std. Dev.	4.87
Coefficient of determination	R^2	0.9494
Adjusted – R^2	Adj. R^2	0.8843
Predicted – R^2	Pre. R^2	0.6276
Coefficient of variance	C.V.	8.94
Adequate precision	A. P	11.949
Predicted residual error sum of square	PRESS	2568.59

- **3-D surface plots**

The three-dimensional (3D) surface and contour plots of the quadratic models obtained from Equation (2) were used for the graphical representation of independent variables' effect on Cd(II) removal. As shown in Figure 3, the plots depicted the relationship between independent variables. Two independent variables were continuously varied for these graphs' responses, and the remaining variable was fixed. Correlations between the independent parameters were significant, so the response surface plots' peaks were prominent, as shown in Figures. All of the response plots had visible peaks, indicating that all of the design space variables had been given the best conditions for the best response.

- **Adsorbent dose effect on Cd(II) Removal**

The correlation between adsorbent dose of chitosan (g/L) and contact time at a fixed pH 6 is shown in Figure a. For Cd(II) removal the interaction between both parameters (adsorbent dose and contact time) was significant (p-value 0.0168) as presented in the plots. Additional active sites and a large surface area presence on the adsorbent surface result in increasing Cd(II) adsorption with an increase in adsorbent dose. The Cd(II) adsorption increased limited by increasing the dose from 0.5g to 3g/L. Similar results in line with the current study were reported by Qahtani [16] that the availability of the exchangeable site and surface area increases rapidly with increasing adsorbent dose until 4 g, which may be attributed to the greater availability of the exchangeable site and surface area. Sukurti et al. [17], reported that the above optimal value due to the inter-particle interaction reduces the adsorbent's total surface area and does not induce a drastic shift in adsorption.

- **pH Effect on Cd(II) Removal**

Figure b depicts the relationship between pH and adsorbent dose after 60 minutes of contact time (fixed); and the plot's peaks were prominent. The Cd(II) removal percentage gradually increased with an increase in pH, by increasing the aqueous solution's pH and adsorbent dose until specific values of both factors. Between the two variables, there was a significant interaction (pH and adsorbent dose), where the p-values of both parameters' interaction was found to be significant (p-value 0.0079) for Cd(II) removal. The Cd(II) adsorption depends highly on pH. It was observed at pH 4.0, Cd(II) removal efficiency was 45.12% and it increased even further when the

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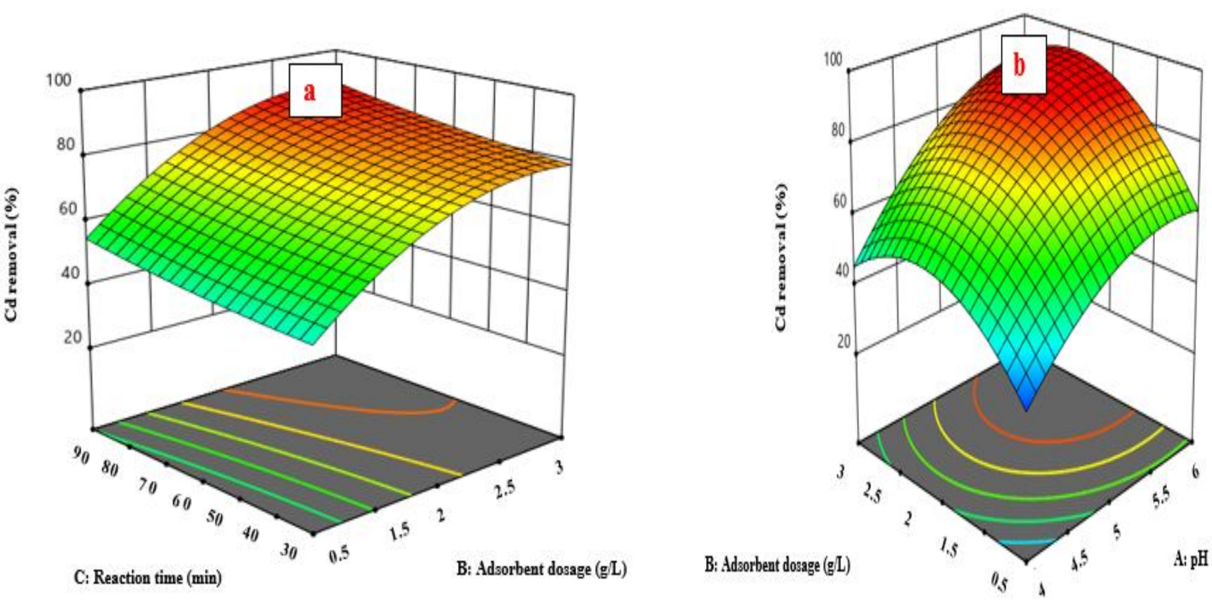
pH was raised from 4.0 to 6. The maximum removal of Cd(II) was obtained at pH 6, which showed that near-neutral pH was more suitable for adsorption in PW. Redha et al., [18] obtained maximum removal efficiency above pH 5. Elwakeel et al. [19] reported that the precipitation of cadmium hydroxide complexes by OH ions at higher pH inhibits cadmium adsorption. Previous studies reported that the optimal pH for cadmium ion adsorption was discovered to be between 3 and 7 [20]. The maximum removal was achieved at pH 6 in this study, and the optimum operating parameters which vary depending on the wastewater characteristics.

- **Contact time Effect on Cd(II) Removal**

At constant parameters, the effect of contact time and initial metal ion concentration on Cd(II) removal is shown in Figure C. The plots showed that increasing the amount of both parameters up to a certain value improved Cd(II) removal efficiency. By raising the reaction time from 30 to 90 minutes, the removal percentage was raised marginally. Due to the availability of large surface areas and new sites on the adsorbent surface, these findings indicated that the initial adsorption rate was very rapid [21]. Because of the difficulty of accessing the remaining empty sites, the removal of Cd(II) ions may be slowed due to repulsive forces. However, some studies found that as contact time increased, adsorption increased as well, but that no uptake occurred after optimal values due to a lack of adsorption sites for the adsorbent material [18, 21, 22].

- **Initial metal ion concentration Effect on Cd(II) Removal**

At constant parameters, the effect of metal ion concentration and pH on Cd(II) removal is shown in Figure D. When metal ion concentration increased, the metal removal percentage decreased because the lower concentration metal ions interact with the functional group and binding sites on the adsorbent's surface. Thus the percentage adsorption was 80.12 % at pH 6 and 4mg/L than those at higher metal ion concentrations. A higher concentration adsorption percentage decreased due to lack of sufficient surface area to accommodate more metal ions and saturation of adsorption sites. The optimum predicted maximum responses are presented in Table 3. The maximum removal percentages for Cd(II) was predicted to be 91%.



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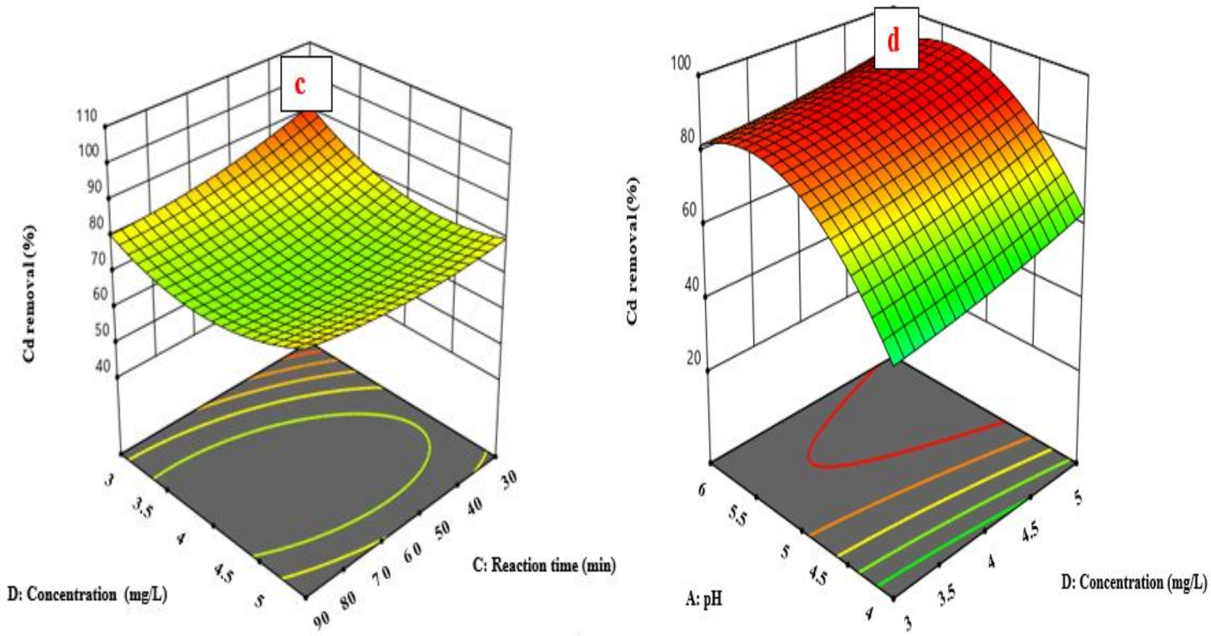

Figure 3. Combined effect of process variables (a) adsorbent dose and contact time, (b) pH and adsorbent dosage, (c) contact time and concentration (d) concentration and pH on Cd(II) removal

Table 3: The optimum predicted maximum responses and desirability for Cadmium removal.

Metal	Initial concentration	Contact time	Adsorbent dose	pH	Removal % Predicted Experimental		Desirability
Cd(II)	4	80.45	2.56	5.5	91.23	89.56	0.987

4. Conclusion

In the present study, the remediation of Cd (II) by chitosan was investigated systematically. Based on literature four operating parameters, the experimental design, consisting of 20 runs, was developed by CCD/RSM. Optimum values of independent variables for the current study were observed, such as 4 mg/L, 7.1, and 80.45 min, 5.5 pH, and 2.56 g/L of adsorbent dose, respectively. The maximum COD (89.45) removal were achieved under tested operating conditions. A satisfactory agreement was confirmed between experimental data and predicted data (obtained from the quadratic regression models). The high values of the coefficient of determination ($R^2 > 0.94$) by the analysis of variance verified the adequacy of the selected model. The findings of this study indicate an excellent efficiency of chitosan for the remediation of heavy metals in PW. The study recommends that it would be advantageous to conduct a continuous flow study for the assessment of field applications of eco-friendly adsorbent for the treatment of produced water.

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