

Removal Optimization of Chlorophenols on Newly Synthesized Polymeric Resin using Factorial Design Approach

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Abstract:

A total of 19 chlorinated phenols exist but in present study removal of only 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) along with phenol are optimized as these are the most likely to occur in drinking-water as possible by-products of disinfection. A new Schiff's base polymer has been synthesized by condensation of triflouroacetylacetone and amino-XAD resin. Synthesized resin was characterized by FT-IR spectroscopy and thermal analysis. Response Surface Methodology (RSM) was adapted to optimize removal of phenol, CP and DCP by synthesized resin. Eighteen runs design were performed with different levels of variables in order to optimize sorption parameters such as pH, concentration of adsorbate, agitation time and amount of polymeric resin. Values of R^2 and R^2_{adj} found were between 99.95% and 99.92%, indicated a good agreement between the predicted and observed values. Maximum removal obtained was 88.7%, 95.3% and 100% for phenol, CP and DCP respectively. Recovery of adsorbed chlorophenols was checked by different solvents and recovery was found to be quantitative (~99%) with methanol. The model was validated by performing sorption experiments at optimum conditions

Key Words; Schiff's base resin, Removal of chlorinated phenols, removal optimization, Response Surface Methodology, Factorial Design

1. Introduction:

Chlorophenols are a group of chemicals with chlorines attached to phenol. Chlorophenols have been used directly as pesticides or converted into pesticides. Chlorophenols, especially 4-chlorophenol are used as antiseptics.

Also small amounts of some chlorophenols, especially the mono- and dichlorophenols, may be produced when water is disinfected with chlorine. Chlorophenols are also produced during the bleaching of wood pulp in paper industries. Chlorophenols exposure to man includes chlorinated drinking water, breathing air contaminated by mono- and dichlorophenols as they are used as wood preservatives and pesticides.

According to one of the National Occupational Exposure Survey (NOES) from 1981-1983 it has been estimated that about 5,000 people in the United States are exposed to 4-chlorophenol,

2,4,5-trichlorophenol, or 2,4,6-trichlorophenol at work [1]. Chlorophenols are considered as health hazardous and the International Agency for Research on Cancer (IARC) has included the chlorophenols as possible carcinogenic to man. The Environmental Protection Agency (EPA) has determined that 2,4,6-trichlorophenol is a probable carcinogen [2].

Exposure to the mono- and dichlorophenols can cause severe skin injury include redness, swelling, scabbing, and scar formation [2].

Adsorption is considered as one of the most effective and simple approach to remove toxic pollutants from aqueous systems. Activated carbon is one of the most widely used adsorbents for this purpose. [3–7]. However, it is well recognized that activated carbon adsorption still suffers from costly regeneration, high attrition rate and is difficult to regenerate [8]. Polymeric adsorbents are widely applied in modern adsorption technology due to their physicochemical stability, large adsorption capacity, excellent selectivity and structural Diversity [9-11]

In Present study we aim in to synthesize a new schiff's base type polymeric and removal optimization of phenol, chlorophenols (CP) and dichlorophenols (DCP) onto modified resin using response surface methodology (RSM).

2. Experimental

2.1 Apparatus

Concentrations of phenols in aqueous solutions were determined by Hitachi 655 liquid chromatograph. The wavelength of UV detector was adjusted at 270 nm. The column ZORBX Eclipse XDB-C-18, 4.6×150 mm, 5 um was used. Elution order of phenols was as phenol, chlorophenols and dichlorophenols with 70:30 methanol: water solvent system.

ThermoNicolet FT-IR spectrometer was used to record the FT-IR spectra. Digital pH meter (Hanna 211, Germany) equipped with a combined glass calomel electrode was used for the pH measurements.

2.2 Reagents and Solutions

Analytical or equivalent reagent-grade chemicals were used to prepare all solutions. Solutions were prepared by dissolving appropriate amount of phenol, CP and DCP in small amount of methanol and volume was made up with de-ionized water. The working and reference solutions were prepared on daily basis by diluting of stock standard solution. Amberlite XAD-2 (bead size 200-400 mesh, pore diameter 90-50 Å and surface area 300-750 m² g⁻¹) was purchased from Fluka, Germany.

2.3 Synthesis of TFAA Coupled Amberlite XAD-2

Amberlite XAD-2 beads (5 g) were first washed with distilled water and then with methanol and were finally were dried in oven at 80 °C for 12 hrs. Tetra Flouroacetylacetone (TFAA) coupled XAD resin was synthesized in two steps; amino resin of Amberlite XAD-2 was prepared in first step followed by its coupling with triflouroacetylacetone (TFAA). Amberlite XAD-2 beads were nitrated with 10 cm³ of concentrated HNO₃ and 25cm³ of concentrated H₂SO₄ at 60°C. Thereafter, the reaction mixture was poured into an ice-water mixture and was washed thoroughly with de-ionized water. Nitrated resin then were treated with a reducing mixture of 40g of SnCl₂, 45 cm³ of concentrated HCl and 50 cm³ of ethanol for 12 h at 90 °C in N₂ atmosphere in order to convert nitro group into amino group. Amino resin and TFAA were mixed together refluxed at 90c for 8 h. The final product was washed and stored for further analysis.

2.4 Optimization of Phenol, CP and DCP Removal by Synthesized Resin

The retention of phenol and chlorophenols on synthesized resin was conducted by batch adsorption experiments in a thermostated shaker keeping the temperature of 25°C. Different

amounts of resin were agitated with solution containing different concentrations of phenols (pH 2-9) for a period of 10-180 min at 150 rpm. The residual concentration of analytes was analyzed HPLC. The % removal was calculated by eq. 1.

$$\% \text{ removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

Where C_o is the initial and C_e is equilibrium concentration ($\mu g/l$) of phenol, CP and DCP. All experiments were carried out in duplicate in order to minimize the error.

2.5 Mathematical and Statistical Procedure

Multi-variant sorption optimization was performed using Draper-Lin small composite design, RSM. The design contained eighteen batch experiments. Each experiment was performed at the different level of independent variables. The range and level of independent variables are summarized in Table 1.

Table 1. Factor	levels used in	n experimental	design for 1	removal of	Phenol, C	CP and DCF	' by]	ſFAA
modified XAD-	-2							

Independent variable	Coded levels					
		-1	0	+1		
Amount (mg)	$A(X_1)$	10	55	100		
Concentration (µg/L)	B (X ₂)	10	55.5	100		
рН	C (X ₃)	2	5.5	9		
Time (min)	D (X ₄)	10	95	180		

3. RESULTS AND DISCUSSIONS

3.1 Characterization of TFAA Modified XAD-2

3.1.1 FT-IR Spectroscopic Analysis

TFAA loaded Amberlite XAD-2 was characterized by FT-IR spectroscopy and thermo gravimetric analysis. Figure 1 shows the FT-IR spectra of plain XAD-2, nitrated XAD-2, amino XAD-2 and TFAA coupled XAD-2. Appearance of two peaks at 1545 cm⁻¹ and 1350 cm⁻¹ in nitrated resin and then their respective disappearance in amino resin confirms the conversion of Amberlite XAD-2 first into nitro and then into amino resin. The characteristic bands at 1687,1556, 1249, 1183 and 1106 cm⁻¹ can be attributed to the stretching vibration of C=O

(amide), N-H (bending, amide), C-N (aryl, stretching) and C-F vibrations respectively, confirmed the coupling of TFAA with amino XAD-2.

3.1.2 Thermo Gravimetric Analysis

Figure 2 shows the thermogravimetric (TG) curve of TFAA modified XAD-2. Modified resin showed a single step mass loss of 49.8% which corresponds to the weight of TFAA moiety of modified resin and two water molecules which again confirms the formation of modified resin. TG curve also shows that the modified resin is thermally stable.



Figure 1 FT-IR Spectra of; Red: Amberlite XAD-2 plain, Green: Nitrated XAD-2, Brown:



Figure 2 Thermogravimetric (TG) Curve of TFAA modified Amberlite XAD-2

3.2 Removal Optimization by Factorial Design

Most of the methods reported so far used the traditional or uni-variant sorption optimization in which one factor is optimized at a time keeping all other parameters at fixed values. In this type

of optimization methodology the effect of interaction terms cannot be studied which could lead to erroneous results. Another disadvantage of traditional sorption optimization is that it requires time and its cost is usually high. Response Surface Methodology (RSM) in other hand studies the effect of all parameters simultaneously on removal. RSM has advantages of results reliability because it considers interaction effects of parameters on each other. Time saving, cost and prediction of optimum response [12] are additional advantages of RSM. Draper-Lin composite design was used to correlate observed and predicted % removal of all three analytes from the aqueous solution. The design of 18 experiments is summarized in Table 2 with results of experimental and predicted values of the % removal for phenol, CP and DCP.

Figure 3a-c shows the plots of observed versus predicted values of percent removal of Phenol, CP and DCP respectively by modified resin. Values of R^2 and R^2_{adj} found were 99.91, 99.51%, 95.4, 95.5% and 99.92, 99.6 and 97.7% respectively for phenol, CP and DCP, indicating a close agreement between the predicted and observed values confirming the validity of m



Figure 3 The plot of observed versus predicted values of percent removal a) Phenol b) CP c)

DCP

Trial No. Phenol CP DCP Observed Fitted Observed Fitted Observed Fitted Value Value Value Value Value Value 34.4 1 12.2 12.0 35.4 34.4 35.4 2 15.6 15.6 37.2 38.2 37.2 38.2 3 69.0 35.0 35.4 68.9 69.0 68.9 4 24.2 24.2 60.3 61.3 60.3 61.3 5 18.8 18.6 36.2 35.2 36.2 35.2 40.7 6 25.3 25.7 40.7 40.8 40.8 7 10.1 9.9 7.5 6.8 7.5 6.8 8 32.3 32.7 88.5 88.6 88.5 88.6 9 23.3 24.0 45.7 49.8 45.7 49.8 10 58.3 58.1 94.5 93.5 94.5 93.5 11 29.4 29.5 77.2 73.3 77.2 73.3 12 88.7 87.7 95.3 95.3 100.0 100.0 20.4 63.0 13 20.4 62.0 63.0 62.0 14 35.4 35.8 31.9 31.8 31.9 31.8 15 51.5 51.9 65.2 65.3 65.2 65.3 77.9 16 65.5 65.9 77.9 78.0 78.0 41.0 65.0 64.7 17 42.1 65.0 64.7

Table: 2 Experimental design and results for the observed and estimated % removal of phenol,

 CP and DCP by modified Resin

18	42.2	41.0	65.0	64.7	65.0	64.7

3.3 Interpretation of Residual Graphs

In order to find out whether the linear model is appropriate for the data, residual plots were examined. The residual is the difference between the observed value of % removal and the predicted value. Figure 4a-c is residual plots of residuals on y- axis and the % removal on x-axis. Points in a residual plot (Fig. 4 a-c) are fairly randomly distributed around the horizontal axis with first two negative values followed by two positive values and again negative values and so on. This random pattern shows the appropriateness of a linear regression model.





Figure 4 Plot of the normal probability versus studentized residuals a) Phenol b) CP c) DCP

3.4 Student's t Test

In order to determine whether the calculated effects were significantly different from zero, Student's *t* test was employed. It was observed that for a 95% confidence level and eight degrees of freedom, the *t* value was equal to 3, 3, and 3.1 respectively for phenol, CP and DCP. The evaluations are illustrated by means of Pareto charts in Fig. 5a-c. The vertical line indicates the minimum statistically significant effect magnitude for a 95% confidence level. The values shown in the horizontal columns are Student's *t* test values for each effect. All the values presenting an absolute value higher than 2.3, which are located right of the line, are significant.





Figure 5 Pareto chart of statistical effects on the removal of a) phenol b) CP c) DCP

3.5 Recovery of Adsorbed Analytes

Desorption of adsorbed phenol, CP and DCP were tested by agitating modified resin after adsorption of analytes with different volumes of organic solvents such as methanol and ethanol. Recovery of all three analytes were found to be uantitative (~99%) with 5 mL of methanol.

4. Validation

The optimum sorption conditions determined from mathematical model were validated by conducting sorption experiment at optimum conditions predicted (Table 3). Table 3 shows a good agreement between the calculated and the predicted values for the removal of phenol, CP and DCP.

Conclusion:

Amberlite XAD-2 is successfully modified with TFAA. TFFA coupled XAD-2 was found to be thermally stable and was very useful for the removal of phenol, chlorophenolsand dichlorophenol. Correlation values of R^2 and $R^2_{adj.}$ showed the success of Draper-Lin composite design for prediction of the sorption parameters of arsenic onto modified resin. Residual plot analysis suggested that the linear equation is best fit and the sorption data can be interpreted satisfactorily by tested model.

P = Predicted

E = Experimental

Factors	Low	High	Optimum Value (P)		% Removal (P)			% Removal (E)			
			Phenol	СР	DCP	Phenol	СР	DCP	Phenol	СР	DCP
Amount	10	100	11	11	78	94.80	100	100	92.1	99.8	100
pН	2	9	4.8	4.4	2.0						
Con.	10	100	10	34	77						
Time	10	180	180	180	112						

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