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Optimization Studies for 2-Chlorophenol Removal by Walnut Shell Activated Carbon (WAC) Using Taguchi's Experimental Design

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Abstract: *The statistical optimization of the process parameters involved in the adsorptive removal of 2-chlorophenol by walnut shell-activated carbon was carried out using Taguchi's experimental design. Taguchi's experimental design with an L_9 orthogonal array was employed for optimizing the effects of the four process parameters, namely: pH (6–10), temperature (30–50 °C), interaction time (60–180 min), and initial concentration of 2CP (50–150 mg/L) each varying at three different levels. The inputs from signal-to-noise ratio and variance analysis were considered to find the optimal conditions for removing and determining significant operating parameters. The orthogonal array was used for the design with the 'maxima are better' approach since better removal capacity was desirable. The pH of the 2-chlorophenol solution was observed to be the most influential factor according to the design. The result obtained from the experimental validation run agreed with the one predicted by Taguchi's design. From the results, it is evident that Taguchi's design for optimization is an efficient tool for optimizing the adsorption parameters involved with removing 2-chlorophenol.*

Keywords: *Adsorptive removal, 2-chlorophenol, walnut shell-activated carbon, Taguchi optimization, signal-to-noise ratio, Analysis of variance*

1. Introduction

2-chlorophenol (2CP) is an organochlorinated compound with a vast industrial application. Poor biodegradation and biomagnification of 2CP have led to the extensive pollution of the aquatic ecosystem [1, 2]. United States environmental protection agency (USEPA) and European Union (E.U.) have declared 2CP as a priority pollutant [3]. The international agency for research on cancer (IARC) of the world health organization has categorized 2-chlorophenol as a potential carcinogen [4]. Owing to the toxicity of 2CP, the USEPA has issued guidelines for maximum contaminant levels in effluents and drinking water as high as 2 and 0.1 µg/L, respectively [5].

Application of adsorption in the removal of 2CP is preferred due to the high-rate kinetics and simplicity in operation. Adsorption onto activated carbon has been interpreted as a robust method for

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2CP removal [6, 7]. Typically, the statistical optimization follows the "one-varying-factor" method, which is inferior owing to the amount of time required. Furthermore, they do not consider the parameters' relation and corresponding responses. Taguchi's experimental design is essentially a fractional factorial design approach and optimizes the process with a minimal number of experimental runs possible [8].

This study aims at optimizing the 2CP adsorption onto walnut shell activated carbon (WAC) by using Taguchi's design for optimization experiments.

2. Materials and Methods

2.1 Adsorbent and Adsorbates

The WAC was prepared from the waste walnut shells (collected from the dry fruit vendors of Rourkela city) via a thermochemical route. $ZnCl_2$ was used as the chemical activating agent for WAC preparation. The synthetic solutions of 2CP were prepared by mixing precisely weighed 2CP in the requisite volume of deionized water. Before every experimental run, the stock solution was freshly prepared. The pH of the 2CP solution was maintained by using either 0.1 M HCl or 0.1 M NaOH, as the case may be. All the chemicals used for this study were of analytical reagent grade and were procured from Thermo Fisher Scientific, India.

2.2 Analytical Methodology for 2CP Concentration Determination

After adsorption, the remnant concentration of 2CP was evaluated via UV-Vis spectrophotometric analysis (UV-1800 Shimadzu, Japan). The maximum absorbance of 2CP was observed at the wavelength of 273 nm. The calibration curve plot was drawn between the absorbance of samples versus their corresponding concentration. It was observed that the calibration curve was linear up to 100 mg/L concentration. Whenever necessary, the 2CP samples were diluted with deionized water to bring down the concentration of the solution into a linear range of calibration curve. The straight line equation obtained from the calibration curve was used for the evaluation of residual concentrations of the samples.

2.3 Taguchi's Method for Statistical Optimization of Process Parameters

Several researchers have used Taguchi's method for process optimization [9, 10, 11]. The literature has mentioned that the optimization of the process variables and the subsequent effects is in the minimum number of experimental runs. Furthermore, Taguchi's design provides the optimal conditions inside the boundary limits for each variable [12]. Taguchi's design tackles the individual factors through a very systematic approach to result in the maximum intended purpose [13]. The orthogonal array of parameters with their respective boundaries formulates the model quickly. The Analysis of variance (ANOVA) evaluates the significant parameters among the array of parameters considered for optimization. The signal-to-noise (S/N) ratio provides the basis for selecting the most influential parameter from the set of significant parameters adjudged by ANOVA. A higher S/N ratio is preferable for the optimal response since the deviations of predicted and desired values are at their lowest with higher ratios. In a broad sense, Taguchi's method comprises four distinct phases: designing the experimental combinations using the orthogonal array, conducting the experiments based on the orthogonal array, results from Analysis using ANOVA and S/N ratio, and validation of the optimized condition [9, 14, 15, 16].

2.3.1 Designing the Experimental Conditions

In this study, the process variables, namely; concentration of 2CP, pH, temperature, and contact time, were selected for optimizing the adsorption process. Three levels varied each parameter, and no second-order interactions were considered. Hence the total degree of freedom (DOF) for the design in this study is 8= 4[(3–1)]. Since the DOF of a 3-level parameter = (number of levels–1) and that of a second-order interaction = (number of parameters × DOF of the individual parameter), the secondary interactions were absent [16]. With a DOF of 8, an L_9 OA was chosen with only nine sets of experimental combinations. Minitab statistical software package [version 14.12.0.1, Minitab Inc., USA] was used for the experimental designing and subsequent Analysis of the model parameters. Tab 1 enlists the values of each process parameter at their three different levels.

TABLE 1. Targeted parameters and their levels of variation.

Parameter	Units	Symbol used	Levels		
			1	2	3
2CP concentration	mg/L	X_o	50	100	150
pH	---	pH	6	8	10
Temperature	ºC	T	30	40	50
Contact time	min	t	60	120	180

2.3.2 Conduction of Experiments Based on O.A.

The experiments were performed after each set of experiment combinations obtained from different parameters (enlisted in Tab 2). In 100 mL stoppered conical flasks, 50 mL of 2CP solution was taken, and the pH was maintained at the desired value using the buffers mentioned earlier. Accurately weighed adsorbent was then poured into the flasks and stoppered. Subsequently, these flasks were agitated at 130 rpm in an orbital shaker (Naanolab India, New Delhi) at the temperature mentioned in the O.A. After the contact time elapsed, the supernatant was sampled and centrifuged (Biogene, Biotechnologies Inc., India) at 9000 rpm for 10 minutes to separate WAC from the 2CP solution. The amount of 2CP adsorbed, q_t (mg/g), was evaluated by Eq. 1.

$$q_t=(X_o-X_t)(V/w) \tag{1}$$

Where X_o is the 2CP concentration (mg/L) before adsorption, V is the 2CP volume (L), X_t is the 2CP concentration (mg/L) at time t, and w is the WAC dose (g).

2.3.3 Experimental result analysis

The results from the conducted experimental runs were analyzed using the S/N ratio and ANOVA.

Signal-to-noise (S/N) ratio

The S/N ratio indicates the desirability degree for the prediction of Taguchi's design. Here, the signal depicts the mean value of the intended response. Besides, the noise represents the standard deviation of the outcome. In other words, the S/N ratio provides the necessary information for the deviation of output response from the desired value. Now, coming to the quality characteristics, the maxima-are-the-better approach was chosen since the maximum 2CP removal was desirable in this study. The signal-to-noise ratio (Z) with the maxima-are-the-better approach is represented by Eq. 2.

$$Z = -10\log\left[\frac{1}{n}\left(\sum_{i=1}^{n}\frac{1}{z_i^2}\right)\right] \tag{2}$$

Where n depicts, the number of experimental runs and z_i are the process variables for comparison related to the i^{th} experiment. Visual analysis is the key to identifying the most influential variable from an array of graphical portrayals of the effects caused by variables [17].

Analysis of Variance (ANOVA)

Process influencing parameters were evaluated from the array of parameters used for optimization using ANOVA [14]. ANOVA uses the statistical tool invented by Fisher to assess the significance and the effects of design parameters on optimal response. F value is the correlation of the mean of the squared deviations to those of squared errors. [9, 17].

3. Results and Discussions

The detailed batch adsorption studies of 2CP onto WAC has been communicated elsewhere for publication. Tab 2 depicts the O.A. used in this study, the adsorption capacity obtained with each combination, and their corresponding S/N ratio. It is evident from Tab 2 that due to the orthogonality of the design, the response effect of each variable at each level was different from the other.

Tab 3 represents the S/N ratio response matrix. Based on the intensity of the difference between maxima and minima values of S/N ratio, the process parameters were ranked to depict their influence. Fig. 1 is the graphical representation of the S/N ratio response of 2CP adsorption by WAC. The 2CP concentration followed an escalating trend through all three levels, which has returned enhanced adsorption capacity of WAC. The responses' pH and contact time have increased up to level 2, and they have shown a declining trend until level 3. On the contrary, the temperature response decreased from the beginning to level 2 and then escalated to level 3.

TABLE II. L_9 Orthogonal array and the corresponding adsorption capacities, S/N ratio.

Run	**pH**	t	X_o	T	$q_{t,WAC}$	**S/N Ratio**
1	6	60	50	30	22	31
2	6	120	100	40	27	34
3	6	180	150	50	38	38
4	8	60	100	50	29	41
5	8	120	150	30	106	113
6	8	180	50	40	29	29
7	10	60	150	40	19	27
8	10	120	50	50	5.2	12.9
9	10	180	100	30	16	20
Taguchi model predicted optimized combination of parameters						
	6	120	100	40	40	42

TABLE III. S/N ratio response matrix of different parameters for 2CP adsorption by WAC.

Process Parameters	Mean value of the S/N ratio				
	1	**2**	**3**	**Maxima-Minima difference**	**Ranking**
pH	26.42	53.82	12.33	41.49	1
t	21.65	45.87	25.18	24.22	4
X_o	17.89	23.28	53.67	35.78	2
T	46.59	21.33	22.46	25.26	3

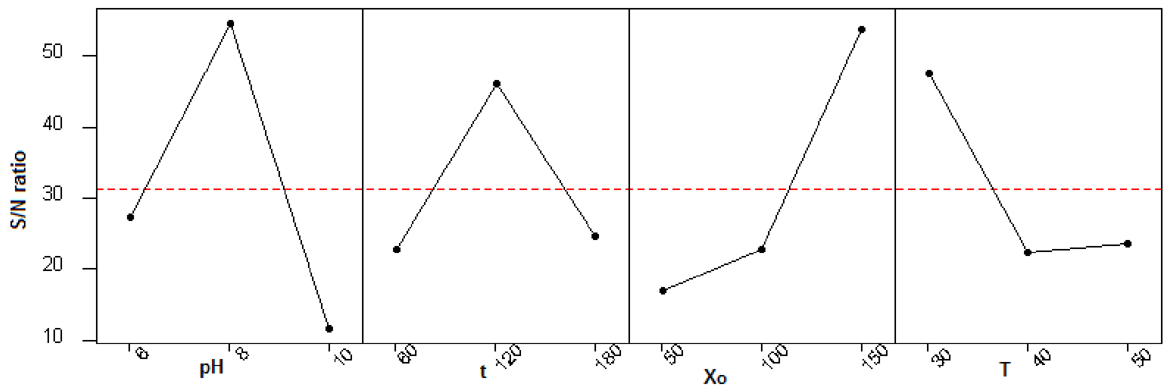

Fig 1. Graphical representation of S/N ratio for 2CP adsorption onto WAC.

The results for ANOVA are enlisted in Tab 4. Among the various parameters studied, pH was the parameter influencing the adsorption at maximum. The contribution of system pH for 2CP adsorption onto WAC had crossed 95%. On the contrary, the other parameters together have contributed to a meager 5% only.

TABLE IV. The ANOVA results based on the Fisher test and the sum of squares.

Parameters	DOF	Seq. Sum of squares	Adj. Sum of squares	Adj. Mean square	F (Denominator of F-test is zero.)	P
pH	2	2839.82	2839.82	1447.29	Very high	<0.0001
t	2	1054.48	1054.48	523.16	Very high	<0.0001
T	2	1233.27	1233.27	607.34	Very high	<0.0001
X_o	2	2407.67	2407.67	1205.17	Very high	<0.0001
Error	0	0.00	0.00	0.00		
Total	8	7535.24				

The validation of the design predicted parameter combinations was confirmed by carrying out the experimental run. The outcome of the experimental run based on Taguchi's design is enlisted in Tab 5. From Tab 5, it is evident that the implementation of Taguchi's design to optimize the process parameters to maximize the adsorption of 2CP by WAC was successful.

TABLE VI Outcomes of experimental validation run based on Taguchi's design.

pH	t	X_o	T	$q_{t,WAC}$	S/N Ratio
Taguchi model predicted optimized combination of parameters					
6	120	100	40	40	42
Result obtained from experimental run					
6	120	100	40	40.66	42±1

4. Conclusion

The orthogonal array based on Taguchi's design of experiments was proven to be a cost-effective approach with the involvement of a minimal number of experimental runs for the adsorption of 2CP. The L_9 OA matrix was constructed to investigate the effects of the process parameters of 2CP adsorption. Among the process parameters, the pH, contact time, temperature, and concentration of 2CP were considered for optimization. The S/N ratio response confirmed that the pH of the 2CP-WAC adsorption system was the most influential parameter. The ANOVA response based on F-test confirmed that all four parameters significantly contributed to the adsorption of 2CP onto WAC. The ANOVA responses have also confirmed that pH had the highest contribution towards the adsorption process among the set parameters considered. The design validation experiments have returned excellent responses with significantly minimal variation from design predicted values.

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