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Original Article

OPTIMIZATION OF PROCESS PARAMETERS USING RESPONSE SURFACE METHODOLOGY FOR REMOVAL OF PHENOL BY NANO ZERO VALENT IRON IMPREGNATED CASHEW NUT SHELL

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ABSTRACT

Objective: The present research is an attempt to optimize the process parameters for phenol removal from aqueous solution using Nano zero-valent iron (NZVI) impregnated cashew nut shell (NZVI-CNS) by adopting statistical tool Response Surface Methodology-Box Behnken Design (RSM-BB).

Methods: Box Behnken Design (RSM-BB) design was used to explore the effect of variables on the removal of phenol. In RSM-BB method, high and low values were assigned for the five variables *viz.* initial pH, NZVI-CNS dosage, initial concentration, contact time and temperature. The preparation was carried out by simple liquid-phase reduction method, namely borohydride reduction method.

Results: The results of RSM-BB method showed the significant effect of pH (A), Dose (B), initial concentration (C), time (D), and temperature (E) on phenol removal from aqueous solution. The results of ANOVA and regression of the second order model showed that the linear effects of Dose (B) and Temperature and cross products effects of temperature and pH were more significant. All the critical variables having the greatest effect on the removal of phenol from Nano zero valent iron impregnated cashew nut shell.

Conclusion: Nano zero valent iron impregnated cashew nut shell successfully employed to remove phenol from aqueous solution. The factors optimized in the present work would helpful in phenol removal from aqueous solution.

Keywords: Cashew nut shell, Nano zerovalent iron, Box Behnken Design, Response Surface Methodology.

INTRODUCTION

Phenol, considered as a priority contaminant by the U. S. Environmental Protection Agency (US EPA, 1979), is a characteristic pollutant found in wastewaters and industrial effluents. The concentration of phenol in wastewater varies from 10 mgl^{-1} to 300 mgl^{-1} [1] but this can rise to 4.5 gl^{-1} in much polluted water [2]. Because of toxic and consequent health hazard of phenols, the World Health Organization (WHO) has set a limit level of 1 mg/l to regulate the phenol concentration in drinking water [3], Derivatives of phenol have been recognized as most persistent chemicals in the environment. The industrial use of phenol over the past decades had led to severe environmental pollution [4]. Different methods developed for the removal of phenol have been proposed. Those methods commonly used include adsorption by activated carbons, ion exchange, and chemical oxidation by ozone and biological treatment processes [5-7]. Biochemical oxidation and wet chemical oxidation [8], methods have suffered from some disadvantages such as long reaction times, high cost and low efficiency. The literature survey reveals that the Nano zero valent iron particles (NZVI) are particularly attractive for remediation purposes due to their significant surface area to weight ratio leading to a greater density of reactive sites and heavy metal removal capacity [9-10]. Previously dechlorination efficiency for chlorophenols in continuous column mode was studied with ZVI immobilized in silica. For better impregnation sonication was carried out, by finally reducing it through sodium borohydrate [11].

The focus of the current study involves, NZVI impregnated with cashew nut shell used as adsorbent. The effect of various experimental parameters such as solution pH, NZVI-CNS dose, contact time, initial concentration and temperature has been investigated by the statistical tool Response Surface Methodology-Box Behnken Design (RSM-BB).

MATERIALS AND METHODS

Preparation of nano scale zero-valent iron impregnated cashew nut shell

The preparation of adsorbent i.e. nano scale zerovalent iron impregnated with support material i.e. cashew nut shell was carried out by simple liquid-phase reduction process [18]. About1.0 g of CNS powder was first washed with water and then soaked in saturated $FeSO_4.7H_2O$ solution (6.5 g in 25 ml with 2 drops of concentrated H_2SO_4) for half an hour. After that, the soaked CNS along with the saturated $FeSO_4.7H_2O$ solution was sonicated in an ultrasonic bath (SONICS Vibra Cell, 750 Watts) for another half an hour. During sonication, the CNS particle gets broken down into small pieces. After sonication, 0.1 mol/l $NaBH_4$ was added slowly at ambient temperature, pressure and atmosphere. The ferrous ion impregnated into the CNS was reduced to ZVI as per the following reaction [12]

$$2Fe^{2+}{}_{(aq)} + BH_4^-{}_{(aq)} + 2H_2O + \text{sup port} \rightarrow 2Fe^0/\text{sup port}_{(s)} + BO_2^-{}_{(aq)} + 4H^+{}_{(aq)} + 2H_2(g) \quad (1)$$

The evolution of hydrogen gas was ceased and the water was decanted. The CNS system was washed with double distilled water followed by a wash with methanol to prevent the rust formation. The CNS system was dried and stored in an oxygen free nitrogen environment. The prepared material was termed as nano zero valent iron impregnated cashew nut shell (NZVI-CNS). The percentage removal of phenol was estimated by the following equation.

$$\%\ \text{Removal} = \frac{(C_o - C_e)*100}{C_o} \quad (2)$$

Where C_o (mg/l) and C_e (mg/l) is the initial and equilibrium concentration of phenol solution, respectively. Phenol concentration was determined quantitatively by a colorimetric method, using 4-aminoantipyrine as colour reagent. These analyses were performed according to the procedures described in Standard Method for the Estimation of Water and Wastewater [13].

Experimental design

Response Surface Methodology is a statistical experimental technique applied under appropriate experimental design to resolve multi-variable equations. Statistical analysis RSM was used to investigate the main effects of dependable variables on the

adsorption of phenol using cashew net shell impregnated with Nano zero valent iron particles. pH (A), Dose (B), initial Concentration(C), time(D), and temperature (E) were selected as independent variables. Box-Behnken (BB) was used for the experimental data and data were fitted to a second order polynomial model and regression coefficients obtained [14, 15,].

Design summary			
Study Type	Response Surface	Runs	46
Initial Design	Box-Behnken	Blocks	No Blocks
Design Model	Quadratic		

Table 1: Independent variables and their coded levels used in RSM studies for optimizing phenol removal

Factor	Name	Units	Low actual	High actual	Low coded	High coded	Mean	Std. dev.
A	pH		2	10	-1	1	6	2.359071
B	Dose	mg/l	0.5	2.5	-1	1	1.5	0.589768
C	Initial Conc	g/l	20	100	-1	1	60	23.59071
D	Time	min	10	50	-1	1	30	11.79536
E	Temperature	C	40	60	-1	1	50	5.897678

Table 2: Independent variables and their coded levels used in RSM

Std	Run	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Response 1	
		A: pH	B: Dose	C: Initial concentration	D: Time	E: Temp	Actual	Predicted
			mg/l	g/l	min	C	%	
46	1	6	1.5	60	30	50	98.12	96.88
14	2	10	1.5	20	30	50	49.32	49.63
11	3	6	0.5	60	30	60	74.61	72.88
13	4	2	1.5	20	30	50	59.63	66.57
7	5	6	1.5	20	50	50	69.39	73.39
36	6	10	1.5	60	30	60	44.87	50.12
22	7	6	2.5	20	30	50	61.03	63.36
43	8	6	1.5	60	30	50	96.98	96.88
38	9	6	2.5	60	10	50	68.28	64.07
20	10	6	1.5	60	50	60	61.09	62.78
26	11	10	1.5	60	10	50	47.20	48.97
15	12	2	1.5	100	30	50	71.03	75.47
2	13	10	0.5	60	30	50	58.61	55.72
30	14	6	1.5	100	30	40	82.55	81.16
3	15	2	2.5	60	30	50	67.08	66.06
28	16	10	1.5	60	50	50	49.57	47.59
25	17	2	1.5	60	10	50	61.29	61.68
27	18	2	1.5	60	50	50	74.43	71.07
40	19	6	2.5	60	50	50	64.00	61.04
12	20	6	2.5	60	30	60	61.43	58.95
29	21	6	1.5	20	30	40	80.74	76.85
10	22	6	2.5	60	30	40	64.49	68.64
39	23	6	0.5	60	50	50	73.05	75.84
21	24	6	0.5	20	30	50	72.97	71.05
18	25	6	1.5	60	50	40	88.12	86.44
17	26	6	1.5	60	10	40	60.22	62.28
33	27	2	1.5	60	30	40	76.23	71.73
5	28	6	1.5	20	10	50	73.14	70.89
41	29	6	1.5	60	30	50	97.01	96.88
16	30	10	1.5	100	30	50	58.40	56.21
24	31	6	2.5	100	30	50	66.20	71.04
31	32	6	1.5	20	30	60	75.43	69.91
32	33	6	1.5	100	30	60	84.10	81.08
44	34	6	1.5	60	30	50	94.97	96.88
6	35	6	1.5	100	10	50	81.87	77.12
19	36	6	1.5	60	10	60	73.48	78.92
37	37	6	0.5	60	10	50	63.24	64.78
45	38	6	1.5	60	30	50	98.29	96.88
8	39	6	1.5	100	50	50	81.14	82.64
1	40	2	0.5	60	30	50	60.10	56.83
42	41	6	1.5	60	30	50	95.92	96.88
34	42	10	1.5	60	30	40	48.54	48.91
9	43	6	0.5	60	30	40	65.32	70.22
4	44	10	2.5	60	30	50	31.62	30.98
35	45	2	1.5	60	30	60	63.12	63.50
23	46	6	0.5	100	30	50	78.27	78.86

Table 3: Analysis of Variance (ANOVA) for phenol removal

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob>F	
Model	10208.99	20	510.4495	29.69196	<0.0001	significant
A-Ph	1310.075	1	1310.075	76.20478	<0.0001	
B-Dose	240.5599	1	240.5599	13.99295	0.0010	
C-Initial Concentration	239.5537	1	239.5537	13.93442	0.0010	
D-Time	64.28077	1	64.28077	3.7391	0.0646	
E-Temperature	49.2804	1	49.2804	2.866555	0.1029	
AB	288.4905	1	288.4905	16.78099	0.0004	
AC	1.3456	1	1.3456	0.078271	0.7820	
AD	28.998	1	28.998	1.686763	0.2059	
AE	22.2784	1	22.2784	1.295896	0.2658	
BC	0.004223	1	0.004223	0.000246	0.9876	
BD	49.63203	1	49.63203	2.887008	0.1017	
BE	38.13042	1	38.13042	2.21798	0.1489	
CD	2.280176	1	2.280176	0.132634	0.7188	
CE	11.76504	1	11.76504	0.684352	0.4159	
DE	405.8209	1	405.8209	23.60589	<0.0001	
A^2	6266.323	1	6266.323	364.501	<0.0001	
B^2	2731.333	1	2731.333	158.8769	<0.0001	
C^2	574.7193	1	574.7193	33.43042	<0.0001	
D^2	1420.212	1	1420.212	82.61127	<0.0001	
E^2	1158.367	1	1158.367	67.38018	<0.0001	
Residual	429.7877	25	17.19151			
Lack of Fit	421.6654	20	21.08327	12.97866	0.4978	not significant
Pure Error	8.122283	5	1.624457			
Cor Total	10638.78	45				

Table 4: Summary of regression analysis

Std. dev.	4.146264	R-squared	0.959602
Mean	70.14109	Adj R-Squared	0.927283
C. V. %	5.91132	Pred R-Squared	0.840362
PRESS	1698.358	Adeq Precision	23.52519

Equation-1

R1=96.88167-9.04874A-3.8775B+3.86938C+2.004382D-1.755E-8.4925AB-0.58AC-2.69249AD+2.36AE-0.03249BC-3.5225BD-3.08749BE+0.755013CD+1.71501CE-10.0725DE-26.7958 A2-17.6908B2-8.115C2-12.7567D2-11.5208E2

The data were subjected to Analysis of Variance (ANOVA) and 3D diagrams were built utilizing Design Expert, (Stat-ease version-7) program. Regression analysis from numerous model define that has more than 95% of variety in the information can be utilized as best fit quadratic model which is viewed as noteworthy. The ANOVA and F ratio test have been accomplished to justify the goodness of fit of the established mathematical models. The calculated values of F ratios for lack-of-fit have been equated to standard values of F ratios consequent to their degrees of freedom to find the suitability of the developed mathematical models [16, 17].

Calculations and statistics

A statistically significant difference between means was determined according to Student's t-test at a probability level of 0.05. The statistical analyses were performed by SPSS Inc., 2014.

RESULTS AND DISCUSSION

Various factors were standardised using Design of Experiment (DOE) suggested by Design Expert software. On the basis of various combinations, the reaction was formulated and analysis was performed and the results were tabulated in table-2. Several works were formulated with respect to RSM and different parameters were analysed [14-17].

The plot of experimental values of phenol removal versus those calculated from the above equation indicated a good fit. The results of analysis of variance (ANOVA) gave a coefficient of determination (R^2) of 0.9596; indicating the competence of the realistic model. The probability (P) of the regression model significance was 0.001 which is less than 0.05, implying that the model is significant. Therefore, the developed model could sufficiently characterize the actual relationship among the variables selected.

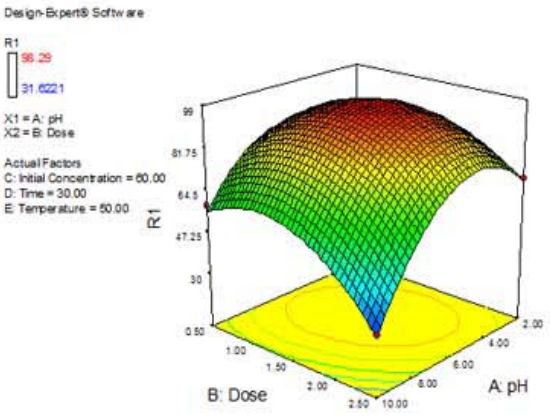
Based on the mathematical model given by equation the study of the effects of various parameters on phenol removal has been made so as to analyze the suitable parametric combinations.

Equation 2

R1=-419.75+19.29656 pH+82.70368 Dose+0.485639 Initial Concentration+4.941343 Time+12.70808 Temperature-2.12313 pH Dose-0.00362 pH Initial Concentration-0.0336pH Time+0.059 pH Temperature-0.00081 Dose Initial Concentration-0.17612 Dose Time-0.30875 Dose Temperature 0.000944 Initial Concentration Time 0.004288 Initial Concentration Temperature-0.05036 Time Temperature-1.67474 pH^2-17.6908 $Dose^2$-0.00507 Initial $Concentration^2$-0.03189 $Time^2$-0.11521$Temperature^2$.

The effects of each component on others were shown in the above graph. This result corroborated the validity and the effectiveness of this model. The maximum removal of phenol was observed at the pH 6, Dose of 1.5, Initial concentration of 60, with the maximum time of 30 minutes and with the temperature of 50°C and final removal was up to 96.88%.

According to Saeideh Adami and Ali Fakhr (2013) [19] adsorption capacity were reliant on the contact time, pH of the solution, adsorbent dosage and temperature. The determined amount of 4C2NP removed from the wastewater for nZVI and Pd-nZVI in the contact time with 10 min. The adsorption capacity of 4C2NP on Pd-nZVI is more than nZVI surfaces and the adsorption isotherms are incorporated by Langmuir equation. Similar results were reported by Mohammad Ali Zazouli et al (2014) [20] and Chandana Lakshmi et al. 2011 designed phenol degradation using *Ps.aeruginosa* using RSM-CCD and a second order polynomial regression model was explained in the experimental data with an R^2 value of 0.9669 based on which the maximum degradation of phenol that was estimated up to 80.45% within the range examined.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Actual Factors
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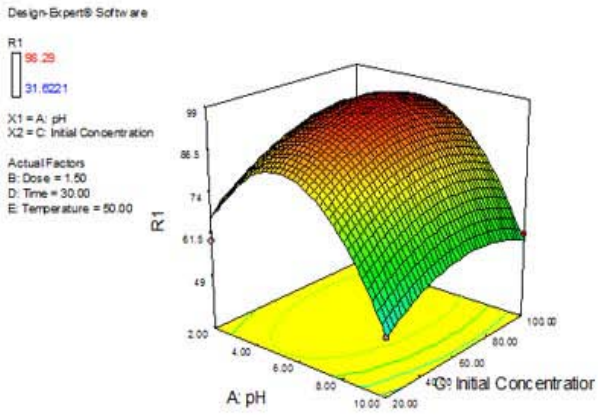
R1
B: Dose
A: pH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R1
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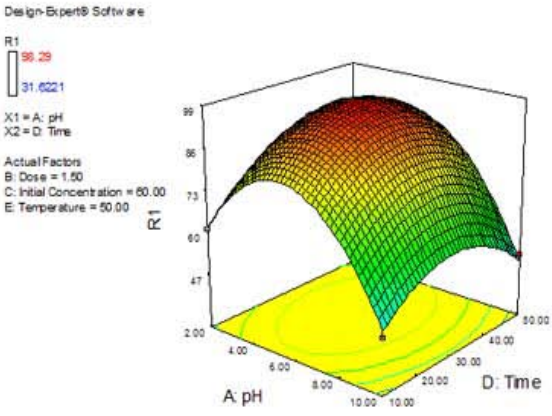
C: Initial Concentration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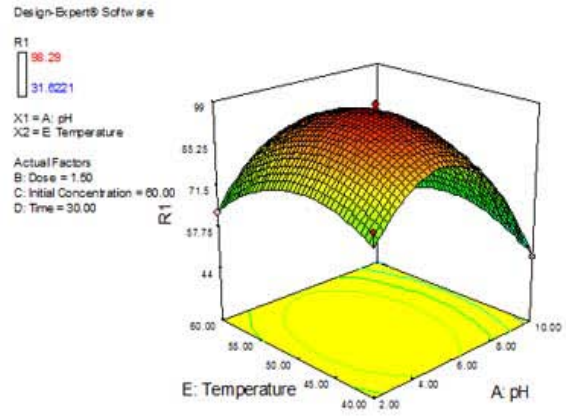
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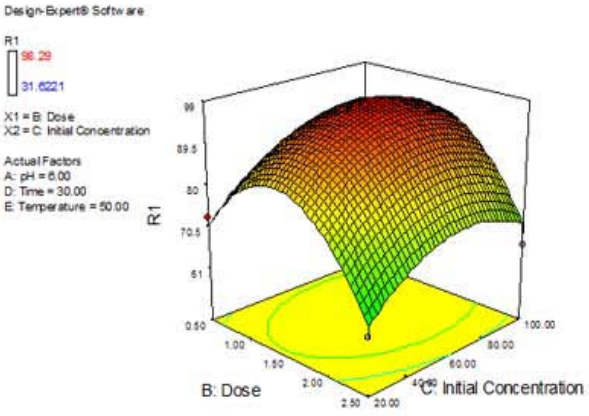
A: pH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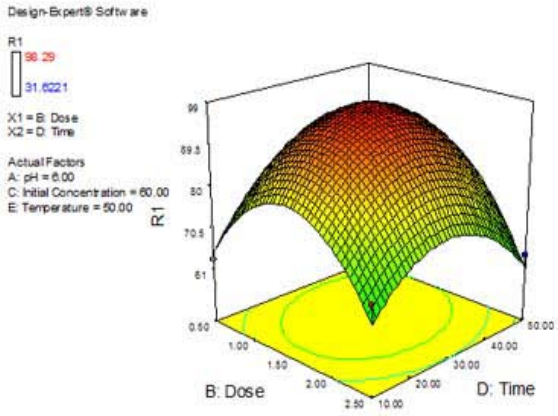
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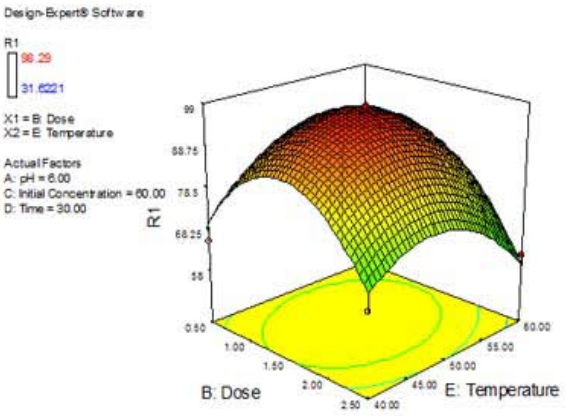
D: Time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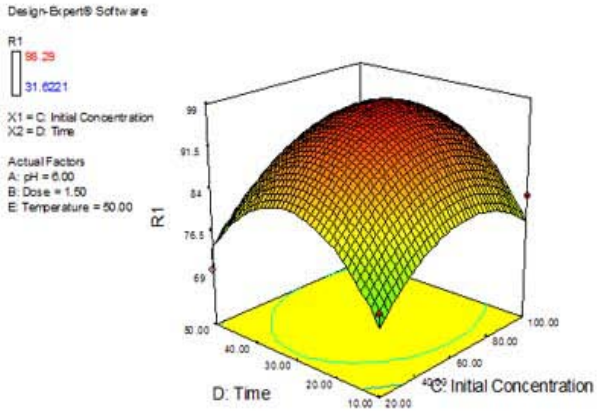
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R1
D: Time
C: Initial Concentration

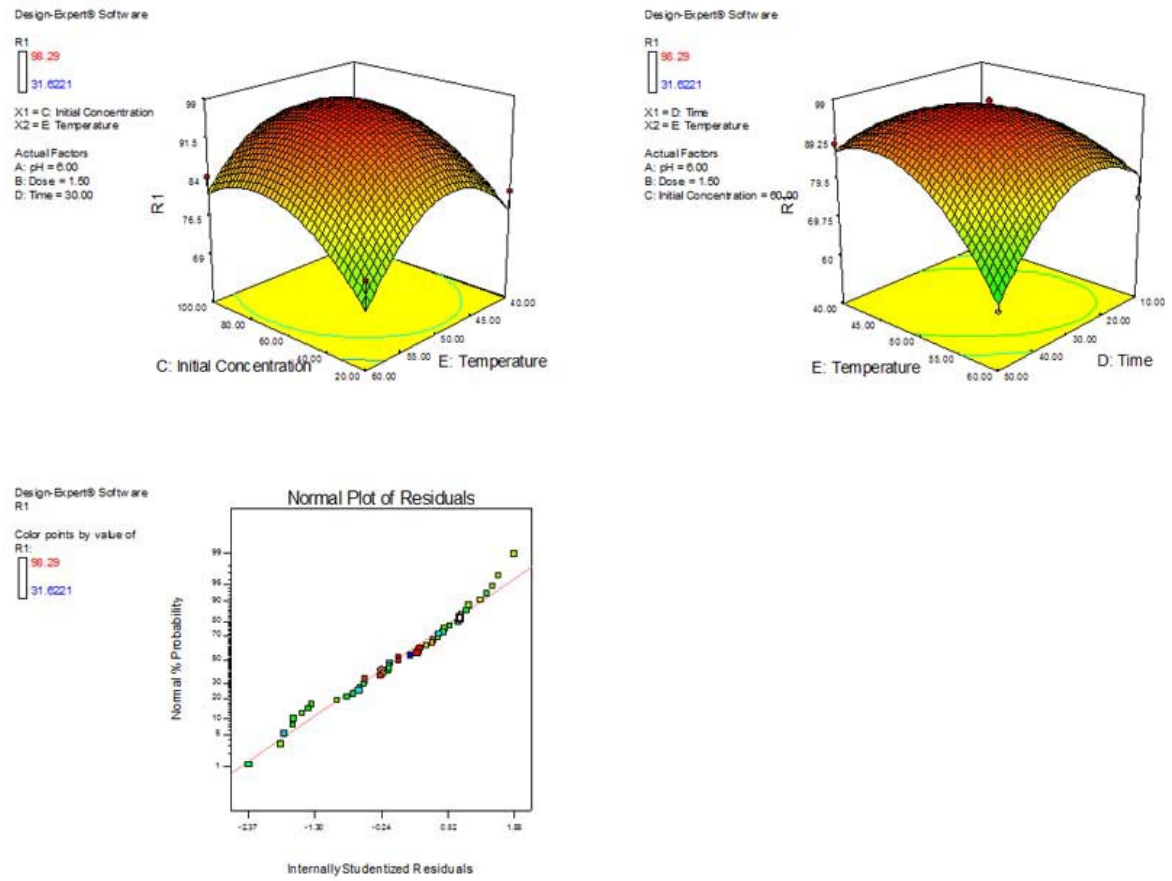

Fig. 1: Response surface graph for phenol removal by NZVI-CNS showing variable interactions with respect to different parameters

CONCLUSION

In summary the response surface methodology (RSM) was employed effectively for Optimization of process parameters using RSM for removal of phenol by Nano Zero valent Iron impregnated Cashew Nut Shell. All five nutritional parameters like pH (A), Dose (B), Initial Concentration (C), Time (D), and Temperature (E) had a significant effect on phenol removal. From the present study, it was observed that use of statistical optimization approach (RSM) had helped to identify the most significant operating factors and optimum levels.

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CONFLICT OF INTERESTS

The authors have declared that there is no conflict of interests

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