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Research Article

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Application of response surface methodology for removal of congo red dye by nano zerovalent iron impregnated cashew nut shell

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ABSTRACT

In the present study statistical tool Response Surface Methodology – Central composite Design (RSM-CCD) were applied to optimize process parameters for the removal of dye Congo red using Nano zero-valent iron (NZVI) impregnated cashew nut shell (NZVI-CNS). Central composite Design (RSM-CCD) design was used to optimize the effect of process variables on the removal of Congo red dye. The NZVI-CNS prepared by simple liquid-phase reduction method, namely, borohydride reduction method. The results of RSM-CCD method showed the significant effect of pH (A), Dose (B), initial concentration (C), time (D), and temperature (E) on Congo red dye removal from aqueous solution. The results of ANOVA and regression of second order model showed that the linear effects of Dose (B) and Temperature (E) were more significant. All the critical variables having greatest effect on the removal of Congo red dye from Nano zerovalent iron impregnated cashew nut shell. Thus the obtained nano zerovalent iron impregnated cashew nut shell successfully employed to remove Congo red dye from aqueous solution. The factors optimized in the present work would helpful in Congo red removal from aqueous solution.

Keywords: Cashew nut shell, nano zerovalent iron, Congo red, Response Surface Methodology - Central composite Design

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INTRODUCTION

Dyes are recalcitrant molecules that cannot be removed as easily. Synthetic dyes are used in industries like textile, paper, plastic, cosmetic, and leather, pharmaceutical, food. [1] Dyes are toxic and highly carcinogenic in nature. A major class of dye is azo dye includes mono, azo, diazo, triazo, and polyazo. They constitute about 60-70% of total dyes. [2]. Azo dye contains azo group of two nitrogen atoms (N=N). Azo dyes classified as direct, acid or basic. Congo red is direct anionic azo dyes. It is the known recalcitrant and carcinogenic compound. It is the common dye used in the paper industry for coloration of paper products. Therefore it is very important to remove the dyes from wastewater before disposal in to natural waters. Many methods are available for treatment which includes coagulation and flocculation [3], biological treatments [4), reverse osmosis [5], and adsorption [6].Among these separation technologies mentioned above, adsorption process offers flexibility and simple in design, convenience and ease of operation, and effective in the removal of heavy metal ions especially at lower metal ions concentration [7]. Nano Zero Valent Iron (NZVI) which is a promising technology is being used to successfully treat various dyes in aqueous solution such as reactive blue 13 [8], Congo red [9], Acid orange II [10], Basic yellow 33 etc.

The different methods were available for the preparation of ZVI such as sonochemical, chemical vapour condensation, thermal decomposition and chemical reduction. The main problem for using the ZVI is its accumulation in the effluent after the treatment. The main problem for using the ZVI is its accumulation in the effluent after the treatment. To overcome this problem, in the present study an attempt has been made to prepare the nanoscale zero-valent iron (NZVI) impregnated cashew nut shell (CNS) with the help of the sonication operation for

better impregnation. 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 – Central Composite Design (RSM-CCD)

EXPERIMENTAL SECTION

Materials and Methods

The preparation was carried out by simple liquid-phase reduction. About 1g of Cashew Nut Shell in powder form was first washed with water and then soaked in saturated $FeSO_4.7H_2O$ solution (6.5g 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 watt) for another half an hour. During sonication, the CNS particle gets broken down to 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 NZVI as per the following reaction (11).

$$Fe^{2+} + 2BH^{4-} \rightarrow Fe^{o} + 2B^{3+} + H_2 \quad (1)$$

The percentage removal of Congo red was estimated by the following equation

$$\%\,\mathrm{Re}\,moval = \frac{(C_o - C_e)X100}{C_o} \quad (2)$$

Where C_o (mg/L) and C_e (mg/L) is the initial and equilibrium concentration of Congo red solution, respectively. The concentration of Congo red in the experimental solution was determined from the calibration curve prepared by measuring absorbance of different determined concentrations of dye solutions at λ_{max} 497 nm using a UV-vis Spectrophotometer (Shimadzu, Japan).The pH of the solution was measured with a Hanna pH meter using combined glass electrode (Model HI 9025C , Singapore).

RESULTS AND DISCUSSION

Response Surface Methodology

Response Surface Methodology is a statistical experimental technique applied under appropriate experimental design to resolve multi-variable equations.

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

Factor	Name	Low Actual	High Actual	Low Coded	High Coded	Mean	Std. Dev.
A	pH	4	8	-1	1	6	1.861477
B	Initial concentration	20	100	-1	1	60	37.22954
C	Dose	1	3	-1	1	2	0.930739
D	Temperature	30	50	-1	1	40	9.307385
E	Time	10	50	-1	1	30	18.61477

Statistical analysis RSM was used to investigate the main effects of dependable variables on the adsorption of Congo red dye 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. Central composite design (CCD) was used for the experimental data and data were fitted to a second order polynomial model and regression coefficients obtained [12- 15].

Prominent factors were standardized 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 analyzed [12-15].

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

Std	Factor 1 A:pH	Factor 2 B: Initial Concen.	Factor 3 C:Dose	Factor 4 D:Temp	Factor 5 E:Time	Response (Actual)	Response (Predicted)
1	4	20	1	30	10	87.17	87.62
2	8	20	1	30	10	86.06	85.95
3	4	100	1	30	10	82.77	82.98
4	8	100	1	30	10	85.77	85.07
5	4	20	3	30	10	90.82	90.95
6	8	20	3	30	10	90.46	90.36
7	4	100	3	30	10	82.61	82.78
8	8	100	3	30	10	87.36	87.45
9	4	20	1	50	10	87.12	87.55
10	8	20	1	50	10	89.23	89.57
11	4	100	1	50	10	82.02	82.59
12	8	100	1	50	10	89.24	89.62
13	4	20	3	50	10	89.34	89.78
14	8	20	3	50	10	92.20	92.79
15	4	100	3	50	10	82.42	83.01
16	8	100	3	50	10	90.39	90.45
17	4	20	1	30	50	89.57	89.88
18	8	20	1	30	50	88.16	88.46
19	4	100	1	30	50	84.86	85.02
20	8	100	1	30	50	88.55	88.97
21	4	20	3	30	50	89.73	89.98
22	8	20	3	30	50	89.08	89.99
23	4	100	3	30	50	83.20	83.62
24	8	100	3	30	50	87.66	87.98
25	4	20	1	50	50	85.61	85.89
26	8	20	1	50	50	87.42	87.81
27	4	100	1	50	50	82.19	82.55
28	8	100	1	50	50	89.10	89.97
29	4	20	3	50	50	85.34	85.81
30	8	20	3	50	50	87.90	87.99
31	4	100	3	50	50	80.11	80.77
32	8	100	3	50	50	87.77	88.01
33	1.24317	60	2	40	30	73.05	73.55
34	10.7568	60	2	40	30	80.85	81.02
35	6	-35.1366	2	40	30	88.00	88.52
36	6	155.1366	2	40	30	80.24	80.74
37	6	60	0.37841	40	30	90.33	90.89
38	6	60	4.378414	40	30	91.90	91.99
39	6	60	2	16.21586	30	89.67	89.95
40	6	60	2	63.78414	30	88.56	88.91
41	6	60	2	40	-17.5683	89.84	89.98
42	6	60	2	40	77.56828	88.39	88.68
43	6	60	2	40	30	97.55	97.91
44	6	60	2	40	30	95.95	95.99
45	6	60	2	40	30	97.15	97.63
46	6	60	2	40	30	98.15	98.72
47	6	60	2	40	30	97.55	97.85
48	6	60	2	40	30	96.55	96.88
49	6	60	2	40	30	96.55	96.79
50	6	60	2	40	30	96.55	96.98

Table 3: Analysis of Variance (ANOVA) for congo red dye removal

ANOVA for Response Surface Quadratic Model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1326.754	20	66.33769	275.6158	< 0.0001	significant
A-pH	113.2452	1	113.2452	470.5041	< 0.0001	
B-Initial concentration	105.6513	1	105.6513	438.9535	< 0.0001	
C-Dose	5.392647	1	5.392647	22.40504	< 0.0001	
D-Temperature	1.909786	1	1.909786	7.934661	0.0086	
E-Time	3.433537	1	3.433537	14.26545	0.0007	
AB	49.67311	1	49.67311	206.3788	< 0.0001	
AC	1.544819	1	1.544819	6.41832	0.0170	
AD	22.32641	1	22.32641	92.76037	< 0.0001	
AE	0.062207	1	0.062207	0.258454	0.6150	
BC	9.564907	1	9.564907	39.73968	< 0.0001	
BD	1.694226	1	1.694226	7.039065	0.0128	
BE	3.421139	1	3.421139	14.21394	0.0007	
CD	0.622479	1	0.622479	2.586237	0.1186	
CE	13.62826	1	13.62826	56.62183	< 0.0001	
DE	18.46033	1	18.46033	76.69785	< 0.0001	
A^2	718.3359	1	718.3359	2984.498	< 0.0001	
B^2	301.3674	1	301.3674	1252.103	< 0.0001	
C^2	66.18721	1	66.18721	274.9905	< 0.0001	
D^2	116.0159	1	116.0159	482.0157	< 0.0001	
E^2	116.0159	1	116.0159	482.0157	< 0.0001	
Residual	6.979983	29	0.240689			
Lack of Fit	3.319855	22	0.150903	0.288601	0.9882	not significant
Pure Error	3.660127	7	0.522875			
Cor Total	1333.734	49				

Std. Dev.	0.490601	R-Squared	0.994767
Mean	88.3617	Adj R-Squared	0.991157
C.V. %	0.555219	Pred R-Squared	0.986429
PRESS	18.09993	Adeq Precision	76.06479

Equation

% Removal =+96.94 +1.62 A-1.56 B +0.35 C-0.21 D -0.28 E+1.25 A B +0.22 A C+0.84 A D -0.044 A E-0.55 B C+0.23 B D+0.33 B E-0.14 C D-0.65 C E-0.76 D E-3.60 A^2-2.33 B^2-1.09 C^2-1.44 D^2-1.44 E^2

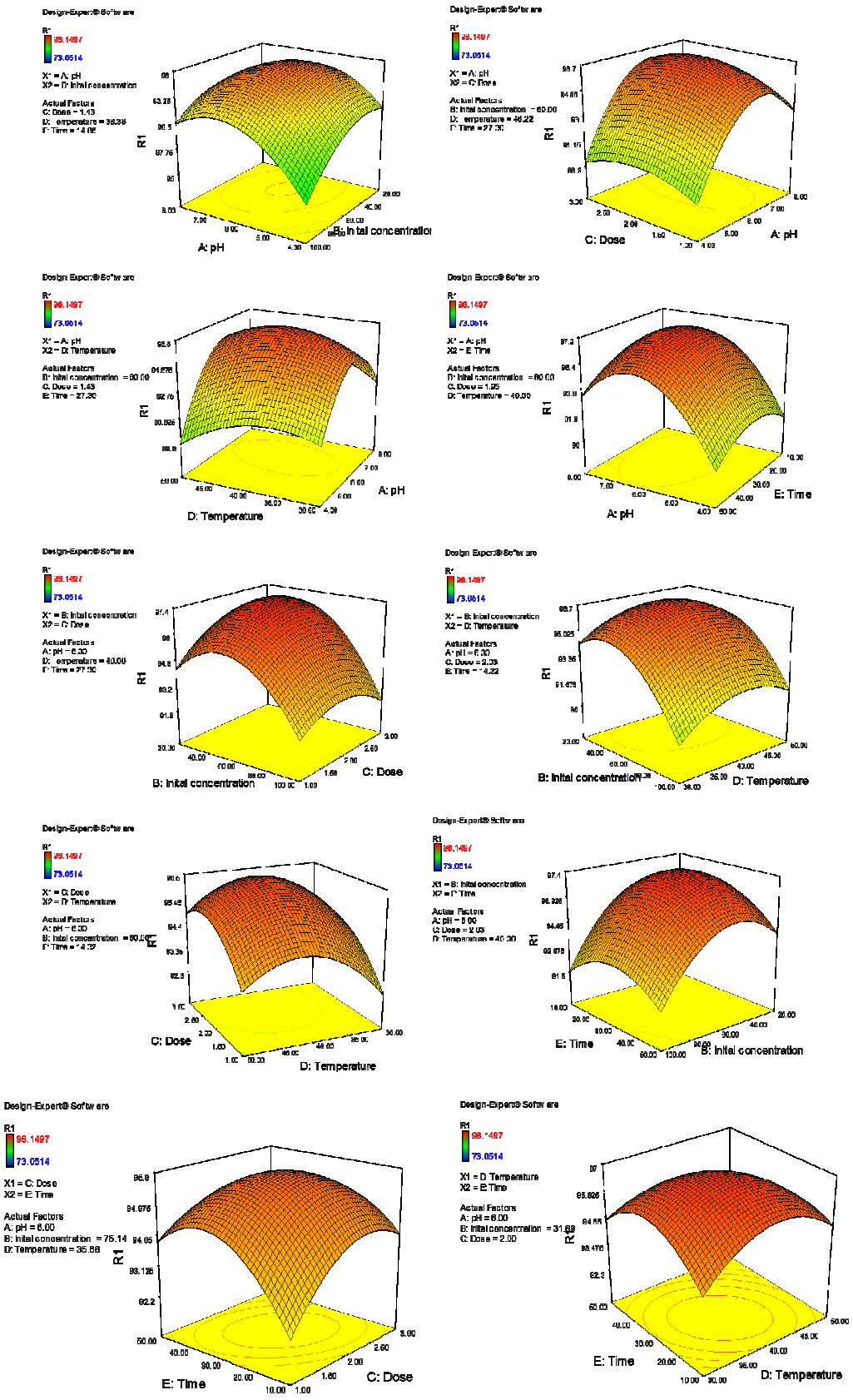

Fig. 1: Response surface graph for congo red dye removal by NZVI-CNS showing variable interactions with respect to different parameters

CONCLUSION

Adsorption of Congo red dye from an aqueous solution with a low-cost nano-adsorbent (NZVI-CNS) prepared from an agricultural waste was successfully applied for removal of congo red dye. Batch studies were performed to found out the influence of various process parameters such as pH, adsorbent dose, initial dye concentration, time, and temperature. Response surface central composite design methodology was used to find the interaction among the variables and to determine the optimum conditions towards the adsorption of congo red dye from the aqueous solution. The optimum values of pH, adsorbent dose, initial dye concentration, time, and temperature were found to be 6, 2 g/L, 40 mg/L, 30 min, and 40°C for complete removal of Congo red dye, respectively. The experimental values were in good agreement with predicted values, with R^2 is 0.9948.

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