**AAP SAMPLE CHAPTER**

**Chapter # (i.e. 3)**

**Statistical Modeling for Adsorption of Congo Red onto Modified Bentonite**

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**ABSTRACT**

Abstract should be within 250 words.

**3.1 INTRODUCTION**

Synthetic dye stuff from various industries like textile, leather, plastic and paper pollute water bodies and act as an eco-toxic hazard contributing to serious environmental problem. Azo dyes like Congo red (CR) has been known to cause allergic reactions, various toxic effects on human & aquatics [1-5] and must be removed before they discharge into water streams.

Dyes have complex structure and resistant to various degradation methods posing technological challenge for many decades. Compared to several conventional methods of separation like oxidation, membrane separation, precipitation, coagulation and electro dialysis for color de contamination, Adsorption is proven to be most popular process due to its simplicity, high efficiency, easy recovery and reusability of the adsorbent, [6, 7]. Numerous adsorbents have been developed so far, and activated carbon is most popular among all, due to its high adsorption capacity. But it is expensive and non-economical to regenerate [8, 9]. This led to search for alternative materials which are cost effective and can replace activated carbon. In recent years extensive research is carried out for low cost adsorbents. Various naturally occurring materials and industrial waste materials were tested. Among all, Bentonite is proven to be a promising material for adsorption process in its pure and modified form [9-11].

In this work raw bentonite was modified by interacting with Acid solution to synthesize a new absorbent (Modified Bentonite) to remove Congo red dye from aqueous solution. The objective of the present work is to develop a successful model for CR removal onto modified Bentonite with the help of statistical tools.

**3.2 EXPERIMENTAL METHODS AND MATERIALS**

**3.2.1 Adsorbent**

The Bentonite was activated by adding concentrated H2SO4 (1:1 w/v) with constant stirring. The material was kept in a hot air oven at 110°C for 12 hours. This material was washed with distilled water and was soaked in 2% NaHCO3 solution overnight to remove the residual acid. Then the material was washed with distilled-water, until the pH of the adsorbent reached slightly above 7. Finally, it was dried in a hot air oven at 1100C for 4 hours. The particle size was determined by sieving the dried material and it is 125µm. The sieved adsorbent was stored in an airtight container for further experiment.

**3.2.2 Adsorbate**

Congo red is the first synthetic azodye produced that is capable of dyeing cotton directly. A stock solution of the dye with a concentration of 1000 mg L-1 was prepared with Millipore water and it is diluted to get the working solutions. Adsorbent dosage was measured accurately with an analytical balance (SHIMADZU - AX200). PH of the solution is measured with a digital pH meter (ELICO-L1 612) and varied by using 0.1 N HC1 and 0.1 N NaOH Solutions. Solution with added adsorbent is agitated with Remimake Temperature Controlled Orbital Shaker (REMI - CIS 24 BL). At the end the samples were collected and centrifuged to remove the suspended solid particles using REMI C 24 centrifuge. The clear liquid was collected and analyzed with UV-Visible Spectrophotometer (SYSTRONICS-117) at a wavelength of 498 nm.

All determinations were performed in triplicate per experiment. The amount of CR adsorbed onto modified bentonite was measured in terms of uptake, qt (mg of CR adsorbed per one gram of adsorbent) and percent removal %R which are calculated using the following equations:

 (1)

 (2)

Where C0 is the initial CR concentration (mg/1), Ct is the concentration of CR at a time t,

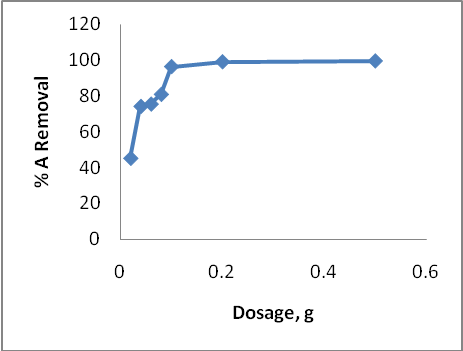
(mg/L), V is the volume of dye solution (L) and m is the mass (g) of the adsorbent.

**3.3 RESULTS AND DISCUSSION**

**3.3.1 Effect of Operating Parameters**

***3.3.1.1 Effect of Amount of Adsorbent***

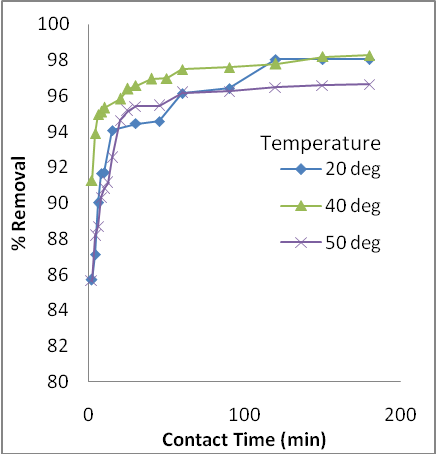
The amount of dye uptake prominently depends on the surface area available. Experiments were conducted to examine the extent of its dependence and fix the optimum dosage. Different amounts of adsorbent were added to 50 ml of 100 mg/L solution at 30°Cand the results were displayed in Figure 3.1. Dye removal percent increased with increasing amount of adsorbent from 0.02 to 0.1 g and slowed down up to 0.2 g. The further increase in the amount of adsorbent did not affect the removal significantly. Hence 0.1 g is taken to be the optimum dosage and used in further studies.



**FIGURE 3.1** The effect of adsorbent dosage on the color removal. (Source: Reprinted with permission from Ref. [22]. © 2012 Elsevier.

***3.3.1.2 Effect of Contact Time***

Experiments were conducted by adding 0.1 g adsorbent to 50 ml of 100 mg/L solution and agitated at fixed temperature. Samples withdrawn at different time intervals and were analyzed. This was repeated at temperatures (20, 40 & 500C) and the results were shown in Figure 3.2.



**FIGURE 3.2** Effect of agitation time and temperature on the adsorption. (Source: Reprinted with permission from Ref. [18]. © 2017 CRC Press.

Adsorption was rapid in the beginning up to first 50 min and thereafter it is stabilized.Finally, it attained equilibrium at 180 min. There is no considerable change in % adsorption at different temperatures, but it is slightly less at 50°C (96%) compared to other temperatures (98%).

***3.3.1.3 Effect of pH***

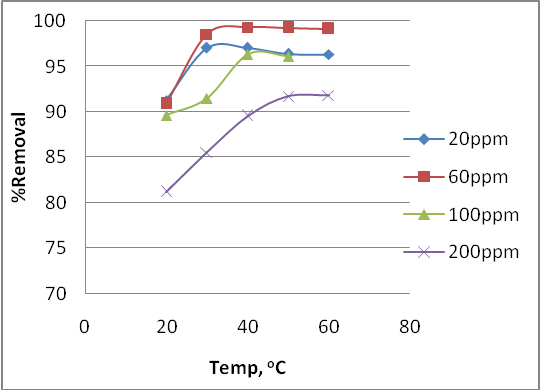
Effect of pH in the range of 2 - 12 was examined with 100 mg/L solution. The equilibrium dye uptake at these conditions are determined and tabulated (Table 3.1). There is a slight decrease in uptakewithpH. The insignificant change may be due to retention of H+ or OH**-**of clay fraction made the solution tend to neutral. Similar results were observed in case of Congo red removal with modified-bentonite [7] and adsorption of Ni, Zn and Pb onto bentonite [12].

**TABLE 3.1** Effect of pH on the Adsorption Capacity of Modified Bentonite

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| pH | 2 | 4 | 6 | 8 | 10 | 12 |
| uptake | 49.99 | 49.74 | 46.32 | 47.03 | 48.41 | 47.61 |

***3.3.1.4 Effect of Temperature***

The effect of temperature on adsorption of CR onto MB was presented in Figure 3.3. % removal increased with increase in solution temperature from 20oC to 50oC. This shows that the process is endothermic in nature.



**FIGURE 3.3** The effect of solution temperature on adsorption.

The increase in percentage removal at higher temperature may be due to a greater kinetic energy acquired, resulting in an easier diffusion from the bulk solution onto the surface of MB.

**3.3.2 Statistical Modeling and Analysis**

The factors that influence the sorption process are effluent concentration (Co), dosage(Do), temperature (T), pH, time & speed of agitation. The agitation speed is fixed at 150 rpm. Equilibrium time can beestimated from equilibrium studiesand is taken a 4hrs.The negligible influence of pH is observed in parameter studies. Based on these facts first three parameters (Co, Do & T) are considered for process modeling.Univariativeanalysis is very tedious with innumerable experiments. It also suffers with the disadvantage of overlooking the influence of interactions. Statistical design of experiments provides better prospects of analyzing individual parameters as well as their interactions. In general 2 factorial methods are used to eliminate parameters that have negligible influence[13]. In this case was replaced by parameter study presented in section3.1. A standard RSM design called central composite design requires a minimum number of experiments and is widely used in experimental studies [14].

Generally, the CCD consists of 2p axial runs and pc center runs along with 2P factorial runs[15].The axial points facilitate rotatability, ensuring constant variance of the model prediction at all points equidistant from the design center [16]. Replicates of the test at the center provide an independent estimate of the experimental error and hence are very important. The recommended number of tests at the centre is six to three variables [17]. Total number of runs (Nr) required in totality are estimated as:

 (3)

Response surface methodology was applied to the experimental data using statistical software, Design-expert 8.0.7.1 (trial version). Statistical terms and their definitions used in the Design-expert software are well defined elsewhere [18].The details of experimental domain and the levels of each factor are given in the Table 3.2. Experiments were conducted according to the design matrix generatedand the measured responses were presented in Table 3.3.

**TABLE 3.2** Experimental Range and Levels of Independent Variables

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Variables** | **Code** | **Symbol** | **- α** | **-1** | **0** | **1** | **+α** |
| Initial Concentration, mg/L | A | Co | 20 | 218.64 | 510 | 801.36 | 1000 |
| Dosage, g | B | Do | 0.01 | 0.109 | 0.255 | 0.401 | 0.5 |
| Temperature, oC | C | T | 20 | 26.08 | 35 | 43.92 | 50 |

**TABLE 3.3** Experimental Design Matrix

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Run** | **Concentration, mg/L** | **Dosage, g** | **Temperature, oC** | **Uptake,**  **mg/g** |
| 1 | 510.00 | 0.500 | 35.00 | 49.5185 |
| 2 | 510.00 | 0.010 | 35.00 | 424.691 |
| 3 | 801.36 | 0.109 | 43.92 | 281.609 |
| 4 | 510.00 | 0.255 | 35.00 | 85.3098 |
| 5 | 510.00 | 0.255 | 35.00 | 84.7756 |
| 6 | 20.00 | 0.255 | 35.00 | 3.36538 |
| 7 | 218.64 | 0.109 | 43.92 | 74.6764 |
| 8 | 510.00 | 0.255 | 50.00 | 84.8943 |
| 9 | 218.64 | 0.401 | 26.08 | 26.3385 |
| 10 | 510.00 | 0.255 | 35.00 | 85.292 |
| 11 | 510.00 | 0.255 | 20.00 | 77.5938 |
| 12 | 1000.00 | 0.255 | 35.00 | 159.182 |
| 13 | 801.36 | 0.109 | 26.08 | 161.098 |
| 14 | 801.36 | 0.401 | 26.08 | 88.2989 |
| 15 | 801.36 | 0.401 | 43.92 | 91.7675 |
| 16 | 510.00 | 0.255 | 35.00 | 85.7597 |
| 17 | 218.64 | 0.401 | 43.92 | 26.6857 |
| 18 | 218.64 | 0.109 | 26.08 | 63.7337 |
| 19 | 510.00 | 0.255 | 35.00 | 85.2802 |
| 20 | 510.00 | 0.255 | 35.00 | 84.8528 |

Various models were tested with the experimental data to obtain the regression equations. And the model adequacy was tested with sequential F-test, lack-of-fit test and otheradequacy measures were used for selecting the best model [19, 20].Analyzing the measured responses, the fit summary output indicated that the quadratic polynomial model was significant for the present system. General form of the quadratic model is

 (4)

Where q is CR uptake, b0 = constant coefficient,,­,, are the interaction coefficients of linear, quadratic and second order terms respectively. n is the number of factor and is the error [21,22].



The uptake of CR varied from 3.36 (minimum) to 424.69 mg/g (maximum) in the present study. Theratio of minimum to maximum uptake of congo red removal was 126.39, which was greater than 10 suggesting that transformationwas required in the present system. Since CR removalin the present investigationrepresented right skewness with non-zero positive values, a naturallog transformation was applied to the experimental data.

Sequential model Sum of Squares (Table 3.4) , Lack of Fit Tests (Table 3.5) and Model Summary Statistics ( Table 3.6) were carried out to check the adequacy of the model for CR removal by the MB. p values for the regressions were lower than 0.01 (see Table 3.4) suggesting a model of quadratic. The model summary statistics (Table 3.6) indicates higher regression coefficient (R2 = 0.9284) for the quadratic model with the minimum standard deviation (0.36).

**TABLE 3.4** Sequential Model Sum of Squares

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Source** | **Sum of Squares** | **df** | **Mean Square** | **F Value** | **p-value**  **prob>F** | **Remarks** |
| Mean vs Total  Linear vs Mean  2FI vs Linear  Quadratic vs 2FI  Cubic vs Quadratic  Residual  Total | 373.65  13.07  0.082  3.64  1.18  0.11  391.74 | 1  3  3  3  4  6  20 | 373.65  4.36  0.027  1.21  0.30  0.019  19.59 | 13.90  0.072  9.36  15.68 | 0.0001  0.9737  0.0030  0.0025 | Suggested  Suggested  Aliased |

**TABLE 3.5** Lack of Fit Tests

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Source** | **Sum of Squares** | **Df** | **Mean Square** | **F Value** | **p-value**  **prob>F** | **Remarks** |
| Linear  2FI  Quadratic  Cubic  Pure Error | 5.01  4.93  1.30  0.11  8.809E-005 | 11  8  5  1  5 | 0.46  0.62  0.26  0.11  1.762E-005 | 25870.12  34986.21  14701.97  6412.41 | <0.0001  <0.0001  <0.0001  <0.0001 | Suggested  Suggested  Aliased |

**TABLE 3.6** Model Summary Statistics

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Source** | **Std.**  **Dev.** | **Adjusted**  **R-Squared** | **Predicted**  **R-Squared** | **R-Squared** | **Press** | **Remark** |
| Linear  2FI  Quadratic  Cubic | 0.56  0.62  0.36  0.14 | 0.7228  0.7273  0.9284  0.9937 | 0.6708  0.6015  0.8639  0.9802 | 0.4992  0.3394  0.4547  -0.3771 | 9.06  11.95  9.86  24.90 | Suggested  Suggested  Aliased |

The significance of the regression models and individual model coefficients and the lack of fit are tested using the same statistical package. The resulting ANOVAfor the reduced quadratic models summarizes the analysis of variance of each response and shows the significant model terms. Table 3.7 shows the ANOVA result for CR removal onto the MB, with a model F- value of 14.40 implying that the model is significant (at p < 0.05). In this case, A( Co), B( Do) are highly significant model terms, A2 and B2 are significant model terms, while model values greater than 0.10 indicated that the model terms were not significant.

The “Lack of Fit F-value” of 14701.97 implies it is significant. There is only a 0.01% chance that a “Lack of Fit F-value” this large could occur due to noise. The “Pred R-Squared” of 0.8639 is close to the “Adj R-Squared” of 0.9284 as one mightnormally expect.

The desirable signal to noise ratio in “Adeq Precision” measurement is greater than 4. For CR removal by MB a ratio of 16.132 indicates an adequate signal. This model can be used to navigate the design space.

**TABLE 3.7** Analysis of Variance Table

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Source** | **Sum of Squares** | **Df** | **Mean Square** | **F – Value** | **p-value**  **Prob>F** | **Remarks** |
| Model  A-Co  B-Do  C-T  AB  AC  BC  A^2  B^2  C^2  Residual  Lack of Fit  Pure Error  Cor Total | 16.79  9.16  3.85  0.062  4.521 x 10-3  0.023  0.055  2.56  0.75  7.281 x 10-3  1.30  1.30  8.809 x 10-5 18.09 | 9  1  1  1  1  1  1  1  1  1  10  5  5  19 | 1.87  9.16  3.85  0.062  4.521x10-3  0.023  0.055  2.56  0.75  7.28x10-3  0.13  0.26  1.762x10-5 | 14.40  70.73  29.71  0.48  0.035  0.17  0.43  19.73  5.77  0.056  14701.97 | 0.0001  <0.0001  0.0003  0.5049  0.8555  0.6848  0.5281  0.0013  0.0372  0.8174  <0.0001 | Significant  significant |

The final mathematical model in terms of the actual factors as determined by Design- expert software is shown below:

In terms of coded factors:

 (5)

**3.4 CONCLUSION**

Bentonite was modified and used to remove Congo red from dye effluent water. It is proven to be an effective adsorbent. The equilibrium time required is determined as 4 hrs. Univariative parametric studies were conducted and ineffective variable (pH) was eliminated. Dye uptake increased with temperature indicating endothermic nature of the process. The effects of various parameters and their interactions were studied using Response surface methodology. Effluent concentration & Dosage were identified as most influential parameters and the second order effects of the same are also influencing the process. Statistical quadratic model was generated and its robustness was tested as per the standards given in the literature. 3D Response surface graphs and Contour plots were generated and analyzed.

**KEYWORDS**

congo red

modified bentonite

RSM

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