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Statistical Analysis of the Removal of Acid Fuchsin Dye Using Zeolite 5A

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Abstract

Investigation of the adsorption of acid fuchsin dye (AFD) on Zeolite 5A is carried out using batch scale experiments according to statistical design. Adsorption isotherms, kinetics and thermodynamics were demonstrated. Results showed that the maximum removal efficiency was using zeolite at a temperature of 93.68751 mg/g. Experimental data was found to fit the Langmuir isotherm and pseudo second order kinetics with maximum removal of about 95%. Thermodynamic analysis showed an endothermic adsorption. Optimization was made for the most affecting operating variables and a model equation for the predicted efficiency was suggested.

Key words: Dyes, Adsorption, Design of experiments, Zeolite5A, Response Surface Methodology.

Introduction

One of the most important environmental problems is the presence of dyes in the waste water effluent of the textiles and dyestuff industries, paper printing, food, cosmetics, pharmaceutical and color photography. Dyes are considered synthetic aromatics containing various functional groups. These toxic substances are reported to be harmful to human being causing allergy, skin irritation, dermatitis, mutations and cancer [1]. Also they reflect sunlight entering the water, which interfere biological degradation of impurities in the water.

Adsorption has demonstrated to be an efficient operation and is economically feasibile as a wastewater treatment process compared to the other purification and separation methods. It has gained importance as a purification and separation process on an industrial application. Therefore, many adsorbents were used for such treatment [2], starting from activated carbons, [3, 4, 5], natural zeolite [6]; clays like kaolinite [7] or bentonite [8] to low cost types like, peanut hull [9], eggshell membrane [10], peat [11] and by microbial decolorization [12], photo degradation on fly ash [13] and many more.

Investigating the process parameters and modeling its response is of vital or essential part of a process analysis. The factorial experimental design method can be used for controlling the adsorption independent variables because its usage decreases the number of experiments, time and material resources by a simple statistical design of experiments. Dye concentration, time, temperature, adsorbent loading, mixing speed and initial pH are chosen as process parameters. Regression models are used in a constrained optimization to find optimum conditions for maximum de-colorization reduction efficiency of the reactive dye. Using classical method to optimize the parameters could be made by changing one variable but keeping all factors constant in the same time. This may be effective in some cases, but it needs extra time, material and large number of trials. Also, the combined effect of factors cannot be fixed and due to all these limitations, analysis and investigation can be efficiently made using statistical experimental design.

This paper describes the use of zeolite (5A) for removal of acid fuchsin dye (AFD) from aqueous solutions. The adsorption of AFD was investigated as a function of contact time, pH, temperature, dye concentration and zeolitet dose by using Response Surface Methodology (RSM) using Minitab software. The AFD has been absorbed by zeolite 5A from synthetic AFD-polluted wastewater. Isotherms, kinetics and thermodynamic studies had been performed to describe the process.

Experimental Work

Materials and Methods

Adsorbate

Acid Fuchsin dye (AFD) or 2-amino -5- [(4-amino-3-sulfophenyl) (4-imino3-sulfo-2,5 - cyclohexadien-1-ylidene) - methyl]-3-methylbenzenesulfonic acid is an organic dye (C.I. 42685) and has the formula $C_{20}H_{17}N_3Na_2O_9S_3$, Its structure is given in Figure 1, and XRD for AFD as shown in Figure 2. AFD, also called Acid Violet 19 or Fuchsin Acid or Rubin S, was obtained from the State Company for cotton textile industries located at Al-Khadimya in Baghdad. The concentration of the dye was measured with Shimadzu UV Spectrophotometer at wave length corresponding to the maximum absorbance for dye, 566 nm. According to the Lambert-Beer law, the absorbance was found to vary linearly with concentration and the calibration curve is shown in Figure 3.

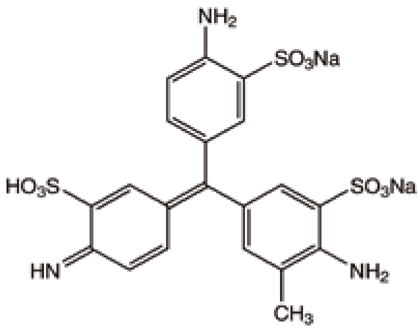

Fig. 1: AFD Chemical Structure

Adsorbent

Zeolite 5A was supplied by Al-Taji Refinery, North Refineries Company. Specifications are given in Table 1.

Table 1: Zeolite 5A Specifications

Appearane	Spherical shape and White
Pore size	5A
Cation	Ca
Bulk density	0.75-0.8 g/ml
Surface area	475 $m^{2/}g$
Partical size	16-20 mesh>90% 0.833-0.991 mm
Selective pore volume	11.1 % (v)
Abrasiveness %	0.8 max.

Procedure

The AFD adsorption on zeolite was determined by performing adsorption tests in 100 ml conical flasks where 50 ml of AFD solutions with different initial concentrations (25, 137.5 and 250 mg/l) in each flask. The pH of the solutions was gradually adjusted by adding small amounts of 0.1 M HCl or NaOH solution. Specified amount of zeolite was added to each flask and kept on a magnetic stirrer of 500 rpm at different temperatures (298-323 K) for duration up to180 min. Then the samples were filtered and the residual concentrations of AFD in centrifuge (Centrifuge PLC Series) were analyzed by a UV-Visible Spectrophotometer (Thermo, Electron Corporation) at maximum wave lengths of 566 nm. The uptake of AFD at equilibrium, qe (mg/g) was calculated by the following expression

$$qe = \frac{(Co - Ce)V}{W} \qquad \ldots(1)$$

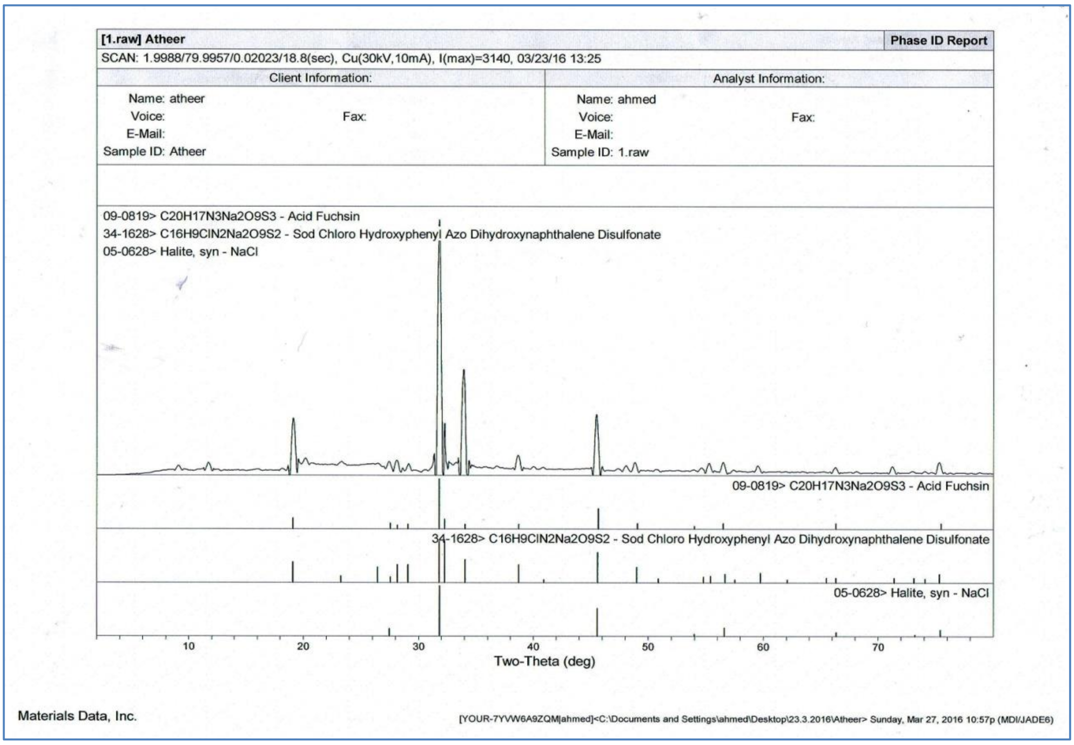

Fig. 2: X-ray diffraction of AFD

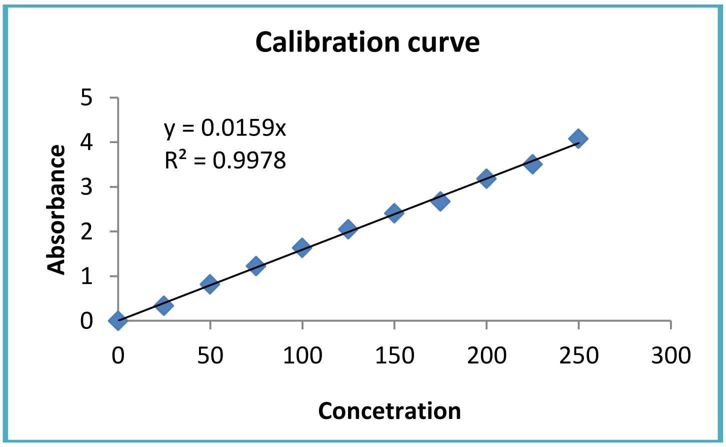

Fig. 3: Calibration curve for aqueous solution of AFD

Experimental Design Using CCD

A standard response surface methodology (RSM) design known as central composite design (CCD) was used to study the parameter for adsorption of AF dye on zeolite5A, and was used to create a set of designed experiments by MINITAB software (version 17). In this work, five independent variables were studied for the AFD adsorption; x_1= pH, x_2= temperature (C), and x_3= zeolite dosage (g), x_4=concentration of dye solution (ppm), x5, time (hr).

Following the experimental design shown in Table 2, a total of 52 experiments were carried out according to a 2^5 full factorial CCD, consisting of 32 factorial experiments (coded to the usual±1 notation), 10 axial experiments (on the axis at a distance of ±α from the center), and 10 replicates (at the center of the experimental domain). The variables were coded to the (-1, 1) for low and high level respectively. The axial points are located at (±α, 0, 0) (0, ±α, 0) and (0, 0, ±α). Here α is the distance of the axial point from center and makes the design rotatable. In this study, α value was fixed at 1 (rotatable). The AFD removal (Y), is the response correlated to the variables using a second degree polynomial equation as follows [14].

$$Y = \beta + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum\sum_{i<j=1}^{k} \beta_{ij} X_i X_j + \varepsilon \qquad \ldots(2)$$

$ß_o$ = constant coefficient, $ß_i$ =linear coefficients, $ß_{ii}$ =quadratic coefficients, $ß_{ij}$= interaction coefficients and X_i, X_j are the coded values of the variables. MINITAB (version 17) was used for the regression and graphical analysis of the data obtained. The reliability of the fitted model was justified through and the coefficient of R2, The p-value of less than 0.05 indicates that the model is significant for 95% probability [15]. It is desirable to indicate the influence of particular model terms that have significance on the response. Experimental operating conditions having the highest desirability were selected to be verified.

Results and Discussion

Adsorption Isotherms

The adsorption isotherm is the most important information, where the equilibrium amount adsorbed qe (mg/g) is related to the equilibrium concentration Ce (mg/L) indicating how adsorbate molecules are distributed between the liquid phase and solid phase as the process reaches equilibrium [16]. The adsorption process was performed at initial concentrations (25, 137.5, 250 ppm) and different temperatures (25-50 °C). Four most common isotherm equations namely, Langmuir, Freundlich, Temkin and Sips were tested in this work to describe equilibrium adsorption. Table 3 lists the four isotherms along with the constants of the linear plots at the range of temperature studied in this work.

Starting with Langmuir isotherm, KL (L/mg) is the Langmuir constant , which is related to the affinity, of binding sites. qm (mg/g) is the theoretical monolayer saturation capacity. For Freundlich isotherm, the constant KF represents the adsorption capacity and the exponent n for its strength. Using Temkin isotherm was for describing the adsorption behavior of the system which is assumed as heterogeneous surface and here B_1 is Temkin constant related to adsorption heat, and K_t (L/mol)is the constant of equilibrium binding corresponding to maximum binding energy. Finally, in the Sips isotherm qs (mg/g) as related to the maximum uptake and Ks (L/mg) is related to the energy of adsorption. Also, m could be a measure for the system heterogeneity.

Table 2: Design of Experiments

Run	Levels					AFD adsorption variables					AFD removal %	
	X1	X2	X3	X4	X5	pH	Temp.	Dosage.	Conc.	time	Exp.	Pred.
1	1	1	1	1	1	10	50	2	250	6	65.032	62.2842
2	-1	1	1	1	1	2	50	2	250	6	94.944	90.9318
3	1	-1	1	1	1	10	25	2	250	6	53.46	57.1122
4	-1	-1	1	1	1	2	25	2	250	6	83.547	84.8144
5	1	1	-1	1	1	10	50	0.5	250	6	53.2	58.3983
6	-1	1	-1	1	1	2	50	0.5	250	6	87.4216	84.3826
7	1	-1	-1	1	1	10	25	0.5	250	6	62.54	58.7121
8	-1	-1	-1	1	1	2	25	0.5	250	6	80	83.7511
9	1	1	1	-1	1	10	50	2	25	6	58.76	61.3694
10	-1	1	1	-1	1	2	50	2	25	6	65.541	61.3127
11	1	-1	1	-1	1	10	25	2	25	6	65.8	62.7085
12	-1	-1	1	-1	1	2	25	2	25	6	84.08	81.7221
13	1	1	-1	-1	1	10	50	0.5	25	6	56.4	60.4982
14	-1	1	-1	-1	1	2	50	0.5	25	6	67.28	68.6782
15	1	-1	-1	-1	1	10	25	0.5	25	6	53.44	58.2077
16	-1	-1	-1	-1	1	2	25	0.5	25	6	77.36	74.5579
17	1	1	1	1	-1	10	50	2	250	2	73.92	76.9649
18	-1	1	1	1	-1	2	50	2	250	2	89.614	90.4114
19	1	-1	1	1	-1	10	25	2	250	2	62.54	58.5847
20	-1	-1	1	1	-1	2	25	2	250	2	69.056	71.0858
21	1	1	-1	1	-1	10	50	0.5	250	2	72.64	77.2455
22	-1	1	-1	1	-1	2	50	0.5	250	2	92.7296	88.0286
23	1	-1	-1	1	-1	10	25	0.5	250	2	69.5596	64.3511
24	-1	-1	-1	1	-1	2	25	0.5	250	2	71.32	74.1889
25	1	1	1	-1	-1	10	50	2	25	2	74.6	72.3672
26	-1	1	1	-1	-1	2	50	2	25	2	80.36	77.1249
27	1	-1	1	-1	-1	10	25	2	25	2	56.4	51.3826
28	-1	-1	1	-1	-1	2	25	2	25	2	64.76	64.3105
29	1	1	-1	-1	-1	10	50	0.5	25	2	71.56	66.5469
30	-1	1	-1	-1	-1	2	50	0.5	25	2	62.74	68.6413
31	1	-1	-1	-1	-1	10	25	0.5	25	2	54.72	60.1637
32	-1	-1	-1	-1	-1	2	25	0.5	25	2	62.54	58.5847
33	-1	0	0	0	0	2	37.5	1.25	137.5	4	71.3	72.5731
34	1	0	0	0	0	10	37.5	1.25	137.5	4	60	57.6748
35	0	-1	0	0	0	6	25	1.25	137.5	4	56.9	54.9423
36	0	1	0	0	0	6	50	1.25	137.5	4	60.287	61.1926
37	0	0	-1	0	0	6	37.5	0.5	137.5	4	59.3	59.2030
38	0	0	1	0	0	6	37.5	2	137.5	4	63.6	62.6449
39	0	0	0	-1	0	6	37.5	1.25	25	4	60.35	59.0212
40	0	0	0	1	0	6	37.5	1.25	250	4	65.64	65.9167
41	0	0	0	0	-1	6	37.5	1.25	137.5	2	58.2	58.4343
42	0	0	0	0	1	6	37.5	1.25	137.5	6	59.003	57.7166
43	0	0	0	0	0	6	37.5	1.25	137.5	4	57.8	58.5699
44	0	0	0	0	0	6	37.5	1.25	137.5	4	58.9	58.5699
45	0	0	0	0	0	6	37.5	1.25	137.5	4	57.8	58.5699
46	0	0	0	0	0	6	37.5	1.25	137.5	4	58.9	58.5699
47	0	0	0	0	0	6	37.5	1.25	137.5	4	57.8	58.5699
48	0	0	0	0	0	6	37.5	1.25	137.5	4	58.9	58.5699
49	0	0	0	0	0	6	37.5	1.25	137.5	4	57.8	58.5699
50	0	0	0	0	0	6	37.5	1.25	137.5	4	58.9	58.5699
51	0	0	0	0	0	6	37.5	1.25	137.5	4	57.8	58.5699
52	0	0	0	0	0	6	37.5	1.25	137.5	4	56.89	58.5699

By examining Table 3, the results gave a different linearity calculated by the correlation coefficient (R^2) which ranges between 0.777 and 0.9985, so, based on R^2, the adsorption of AFD is best fitted in the Langmuir isotherm indicating the homogeneous nature of sample surface where each molecule had equal adsorption activation energy and monolayer coverage of AFD is

formed on the outer surface of zeolite [17]. But, Sips model got high values of R^2 which can predict the Langmuir suggested behavior with the help of Freundlich model taking into account the heterogeneity of the surface [18].
The values of (1/n) ranging between 0 and 1 in Freundlich isotherm is an indication of surface heterogeneity, and the closer to zero, the more heterogeneous is the surface. It is clear from Table 3 that all values of 1/n were greater than 1 confirming the non-heterogeneity of the surface of adsorbent.

Table 3: Isotherm parameters for removal AFD by zeolite

Langmuir constants $qe = \frac{q_L\ KLCe}{1 + KLCe}$	**kL (L/mg)**	**q*m(mg/g)***		**R^2**
25°C	0.000827	80.04595		0.9985
37.5°C	0.0012233	84.34346		0.9964
50°C	0.001581	93.68751		0.9954
Freundlich constants $qe = \mathrm{KF}\ Ce^{1/n}$	**log KF**	**1/n**		
25°C	-1.21826	1.028752		0.9686
37.5°C	-1.00971	1.01489		0.9873
50°C	-0.85318	1.02214		0.959
Temkin constants $qe = B_1\ lnK_t + B_1\ ln(Ce)$	**K_t**	**B_1**		
25°C	0.175	1.673943		0.791
37.5°C	0.246	1.824137		0.8507
50°C	0.3454	1.91042		0.777
Sips constants $qe = \frac{qs\ Ks\ Ce^{1/m}}{1 + Ks\ Ce^{1/m}}$	**q_s**	**Ks**	**m**	
25°C	8.94102	0.00551	0.84915	0.9953
37.5°C	10.3456	0.00797	0.8556	0.9976
50°C	12.9238	0.01008	0.8819	0.9948

Thermodynamic Analyses

Thermodynamic parameters were investigated referring to Vant Hoff 's equation. The distribution coefficient Kd is used to calculate the thermodynamic parameters ΔG, ΔH and ΔS the following equations

$$\Delta G = -RT ln(K_L) \qquad \ldots(3)$$

$$\ln(K_L) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad \ldots(4)$$

Plot of KL versus 1/T for the adsorption of AFD onto zeolite is given in Figure 4, while the thermodynamic parameters obtained are given in Table 4.
As shown in Table 4, the negative values of ΔG at different temperatures indicates the spontaneous nature of the adsorption process. Positive ΔH reveals endothermic adsorption, while the positive value of ΔS suggests the increased randomness at the solid/liquid interface during the adsorption of the dye onto silica. A similar trend has been reported for the adsorption of Congo red onto coir pith carbon and fly ash [19].

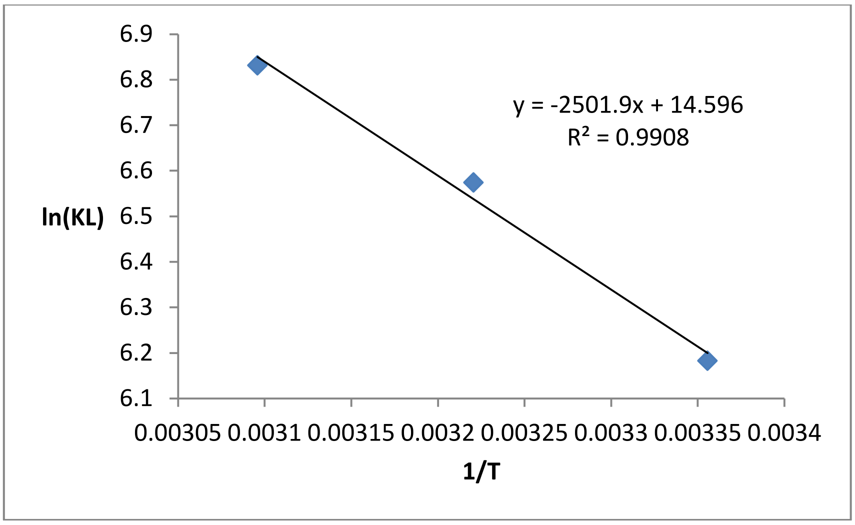

Fig. 4: Vant Hoft plot of AFD adsorption on zeolite

Table 4: The thermodynamic parameters of removal AFD by zeolite

ΔH° ($kJ.mol^{-1}$)	ΔS° ($kJ.mol^{-1}.K^{-1}$)	ΔG° ($kJ.mol^{-1}$)		
		298 °C	310.5 °C	323 °C
20.8008	0.121351	-15.3176	-16.971	-18.3438

Kinetics Analysis

In this section, the adsorption rate, is investigated. The pseudo first-order, pseudo second order and intra-particle diffusion models were adopted to the test experiment data.

Results, as shown in Table 5, indicate that the adsorption of AFD perfectly complies with pseudo 2nd order reaction based on the correlation coefficient. Similar results was reported for adsorption of malachite green dye by BSAC [20].

Table 5: kinetic constants for the removal of AFD on zeolite

Model	Constant	R^2
Pseudo-first order $ln(qe-qt)=lnqe-k_1t$	**k_1 (L min^{-1})**	**R^2**
	0.01624	0.9515
Pseudo-second order $\frac{t}{qe}=\frac{1}{k_2q_e^2}+\left(\frac{1}{qe}\right)t$	**k_2(g/mg min)**	
	0.001092	0.9805
Intra particle diffusion $qt=K_Dt^{1/2}$	**K_D (mg/g $min^{0.5}$)**	

Modeling Using Minitab Software

In this study, the relationship between the response and variable is examined by regression.

The predicted removal efficiency of AFD or the response of surface methodology (Y) is given in Equation 5.

$$Y=58.57-7.449x1+3.125X2+1.721X3+3.448\,X4-0.359X5+6.55\,X_1^2-0.5X_2^2+2.35X_3^2+3.9X_4^2-0.49X_5^2-0.236X1X2-0.666X1X3-2.172\,X1\,X4-3.8\,X1\,X5+1.371X2X3+1.628X2\,X4-3.302\,X2\,X5-1.525\,X3\,X4+1.042X3X5-0.921X4X5 \quad \ldots(5)$$

The predicted values versus the experimental values for AFD removal can be seen in Figure 5 results reveal that the developed model successfully captured the relation between the variables to the responses within the range of the studied variables.

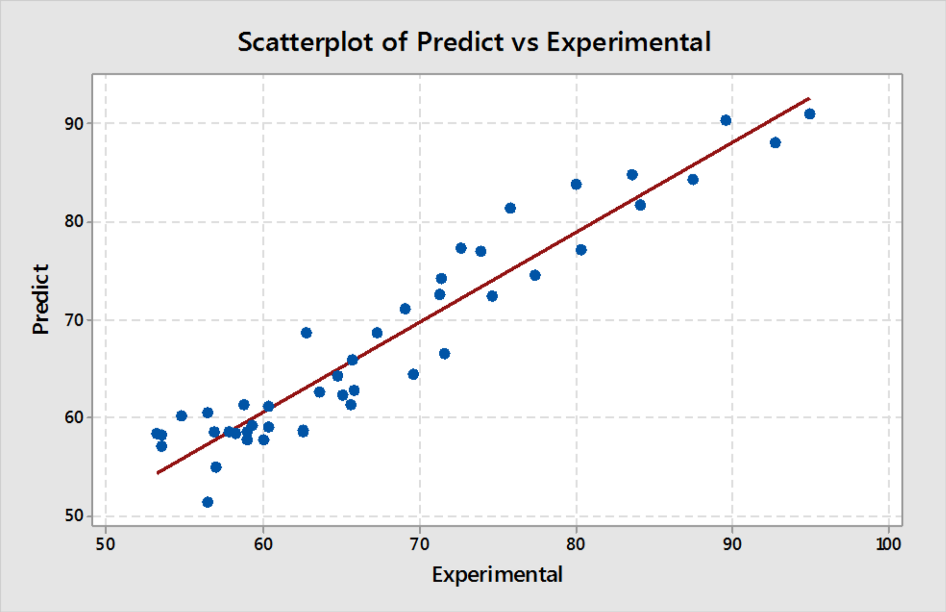

Fig. 5: Relationship between predicted and experimental data for AFD removal

As well as the application of the Equation 5 on the previous research for the same, dye and different adsorbent, as it is shown in the Table 6.

Table 6: Comparison of AFD removal onto various adsorbents based on eq. 5

Adsorbent	% Exp Removal	% Pred Removal	% Abs.Error	Ref.
zeolite 5A	94.944	90.9318	4.22	This study
polyaniline-Fe_2O_3 magnetic nano-composite	98.5	65.225	33.7	[21]
Laccase-Modified Zeolite	93	58.57	37	[22]
polyaniline–Fe_3O_4 magnetic nanocomposite	95.2	64.618	32.123	[23]
LTA-type zeolite	71.6	74.088	3.5	[24]
Carbon Alumina Composite pellet	84.48	59.675	29.36	[25]

Effects of Variables and their Interactions

A hypothesis was assumed that this relationship is statistically significant, for a p-value coefficient. This probability was set as 95 % of the observation is significant or 5% is rejected.

The Final equation is:

$$Y = 58.57 - 7.449x1 + 3.125X2 + 1.721X3 + 3.448\,X4 - 0.359X5 + 6.55\,X_1^2 - 2.172\,X1\,X4 - 3.8\,X1\,X5 + 1.628X2\,X4 - 3.302\,X2\,X5 - 1.525\,X3\,X4 \qquad \ldots(6)$$

It can be deduced from Table 7 that the effect of pH, temperature, zeolite dosage and concentration were more pronounced than time based on the F-values of 120.71 (pH), 21.25 (temperature), 6.44 (weight of adsorbent), 25.86 (concentration) and 0.28 (time).Only the quadratic effects of pH was meaningful having (F-value of 6.8).

The following important binary interactions were found as follows:

- pH (x1) and temperature (x2) with time (x5), where x1x5 got high F-value of 29.57 and low P-value of

0.000, x2x5 got high F-value of 22.32 and low P-value of 0.000.

- pH (x1), temperature (x2) and zeolite dosage (x3) with concentration (x4), where x1x4, x2x4 and x3x4 got high F-value of 9.66, 5.43 and 4.76 respectively, and low P-value of 0.004, 0.027 and 0.037, respectively. While the other the interaction of x1x2, x1x3, x2x3, x3x5 and x4x5 were of lesser degree of significance according to F-value obtained in Table 7.

Table 7: Analysis of variance (Response Surface Regression)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model					
X1	1	1886.66	1886.66	120.7	0.000
X2	1	332.06	332.06	21.25	0.000
X3	1	100.69	100.69	6.44	0.016
X4	1	404.15	404.15	25.86	0.000
X5	1	4.38	4.38	0.28	0.600
X1*x1	1	106.34	106.34	6.8	0.014
X2*x2	1	0.62	0.62	0.04	0.843
X3*x3	1	13.72	13.72	0.88	0.356
X4*x4	1	37.64	37.64	2.41	0.131
X5*x5	1	0.61	0.61	0.04	0.845
X1*x2	1	1.79	1.79	0.11	0.738
X1*x3	1	14.19	14.19	0.91	0.348
X1*x4	1	150.99	150.99	9.66	0.004
X1*x5	1	462.15	462.15	29.57	0.000
X2*x3	1	60.19	60.19	3.85	0.059
X2*x4	1	84.79	84.79	5.43	0.027
X2*x5	1	348.92	348.92	22.32	0.000
X3*x4	1	74.44	74.44	4.76	0.037
X3*x5	1	34.72	34.72	2.22	0.146
X4*x5	1	27.13	27.13	1.74	0.197
Error	31	484.52	15.63		
Lack-0f-Fit	22	480.07	21.82	44.13	0.000
Pure Error	9	4.45	0.49		
Total	51	5962.81			
Model Summary					
	R^2	R^2(adj)	S		
	91.87%	86.63%	3.95342		

Figure 6 is the surface plot showing the combined effect of both pH and concentration at (50 °C) using (2g) of zeolite after 6hours. From Figure 6 it can be seen an increase in the percentage AFD removal can be observed with decrease in pH from 10 to 2 as well as there is an increase in concentration from about 25 to 250 ppm. Decreasing the pH to acidic values offers higher tendency of zeolite surface to accept AFD molecules which contains protonated amine groups thus, increases its uptake. Zeolites are known to encourage acidic reaction and contain acidic sites of different grades depending on the type of zeolite. And as zeolite A is of low silica to alumina ratio i.e. of low acidity, the acidic media will enhance the reaction with the AFD. A similar trend was reported for adsorption of Azo Benzidine Reactive Dye onto Zno surface [26]. Also, the reason behind increasing the removal in higher concentration media is that a higher mass transfer gradient occurred which causes higher AFD diffusion inside the pores of zeolite. A similar trend was reported for adsorption of Basic fuchsin onto mussel shell biomass [27].

Figure 7 shows the combined effect of zeolite dosage and concentration for AFD removal. From this figure an increase in the percentage AFD removal can be observed with the increase in zeolite dosage from 0.5 to 2 g as well as there is increase in concentration from about 25 to 250 ppm, increasing the weight of adsorbent. This increase in the removal can be explained by the extra available surface area and open pores when the zeolite dosage in increased. Increasing concentration increases the flux of the AFD to be occupied by zeolite. A similar observation was reported for removal of dyes by low cost adsorbents [28].

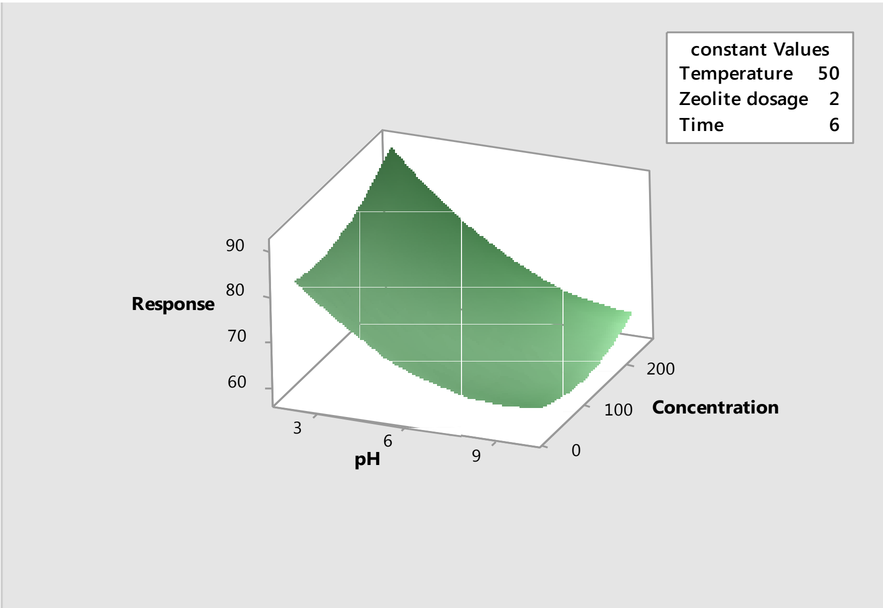

Fig. 6: Effect of pH and Concentration

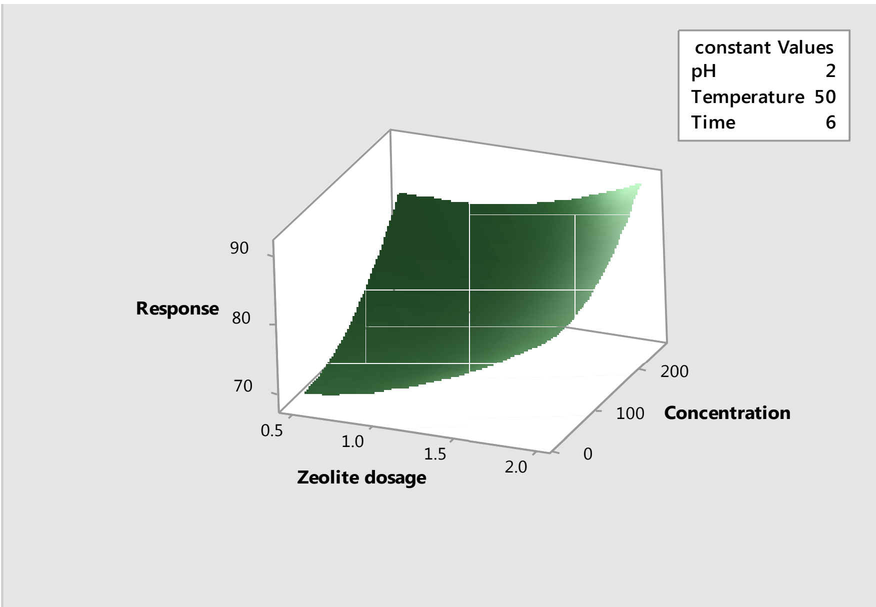

Fig. 7: Effect of Zeolite dosage and Concentration

The combined effect of concentration and temperature for AFD removal can be seen by the surface plot of Figure 8, where, an upsurge in the percentage AF dye removal can be observed with increase in temperature from 25 to 50 °C as well as increase in concentration, increasing the temperature. This increases the diffusion rate of the dye through the boundary layer to the pores of the zeolite particle. Also, increasing the concentration increases the viscosity of solution, causing to increase the resistance for diffusion in viscous media [29].

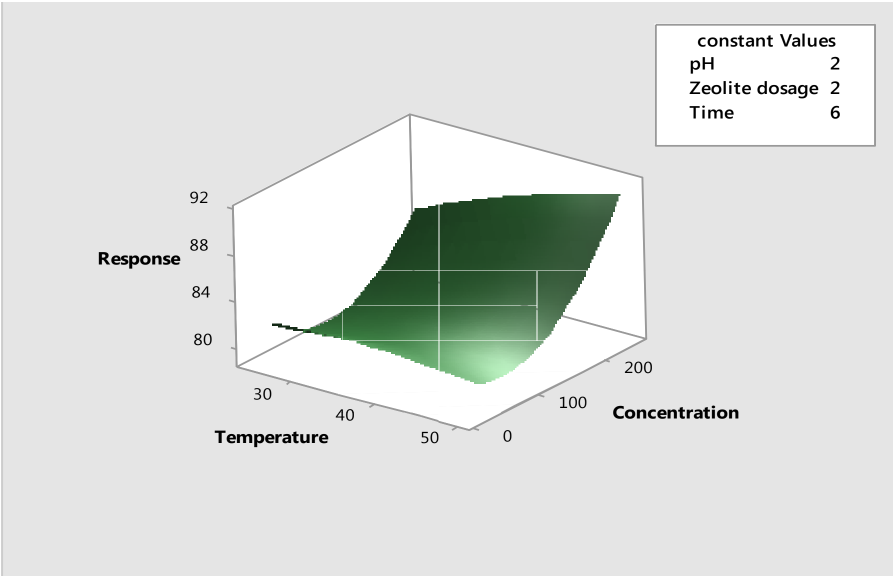

Fig. 8: Effect of temperature and Concentration

The effect of time and temperature for AFD removal is also cross related to each other. The degree of removal is increased gradually with time. The adsorbate needs time to diffuse from the bulk aqueous solution to the external surface then to the interior site of adsorbent, as shown in Figures 9 and 10 respectively. This relation is also found significant in similar work of [30] for adsorption of Reactive dye onto a novel activated carbon. Figure 10 Combined effect of pH and time for AFD removal

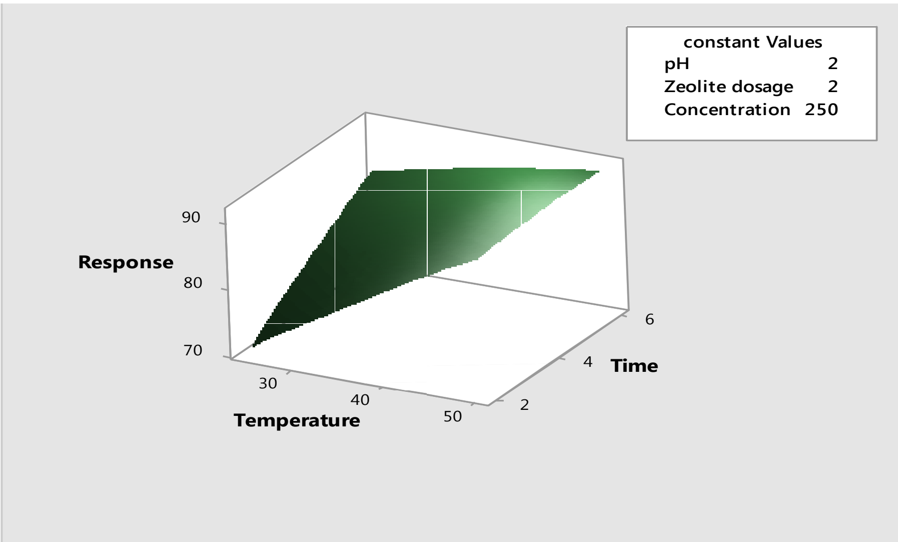

Fig. 9: Effect of temperature and time

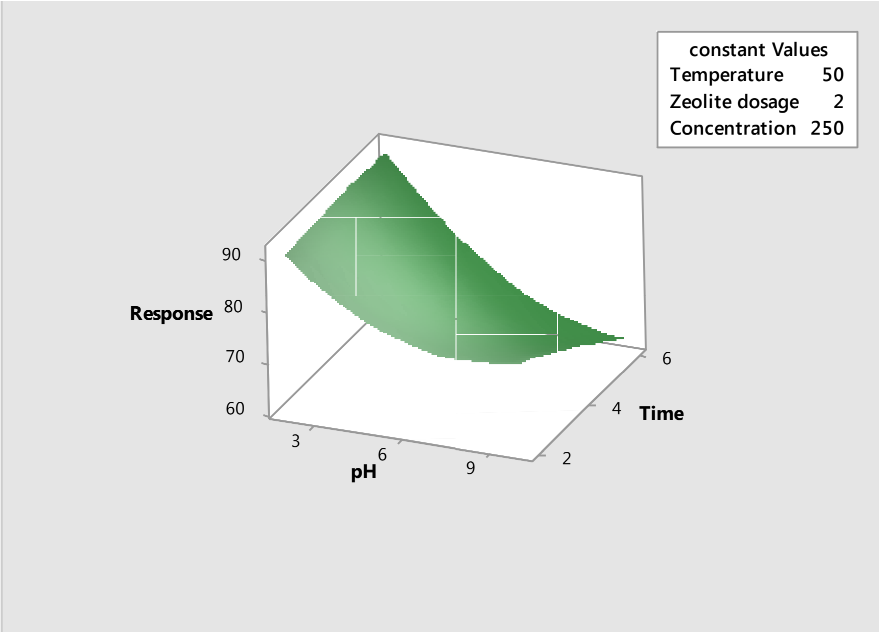

Fig. 10: Effect of pH and time

Optimization of Operating Parameters

The optimum conditions were one of the objectives of the experimental design so that the high dye removal can be achieved. The optimum conditions of AFD removal by zeolite 5A was achieved at pH, temperature, weight of zeolite, initial dye concentration and time of 2, 50 °C , 2g, 250 ppm and 6 hr, respectively. At these conditions, AFD removal was 94.944 %. Table 8 shows the model validation were the predicted and experimental values of the responses for AFD are presented. Model desirability approaching unity and with low error value displays the applicability of the model towards the responses. Relatively small errors less than 0.5 and 6 2.77 % were obtained for the predicted and the actual values, respectively, indicate that the models are suitable in predicting the responses efficiently.

Table 8: Model validation for AFD removal by zeolite5A

Model desirability	pH	Temperature	Weight f adsorbent	Concentration	Time	%Removal Predicted	% Removal Experimental	Error (%)
0.90388	2	50	2	250	6	90.9317	94.944	2.77

Conclusion

Acid fuchsin dye was successfully removed from aqueous solutions onto zeolite 5A. The obtained data for the adsorption is best fitted with the Langmuir isotherm. The thermodynamic parameters (ΔG, ΔH and ΔS) indicate the spontaneous, endothermic, and randomness increase of the adsorption respectively.

The adsorption complies with pseudo second order reaction. The statistical approach, 2^5 response surface CCD was successfully employed for experimental design and analysis of results, to study the linear, quadratic and interaction effects between the variables and also to optimize those variables for maximum removal of AFD.

Appropriate regression model was developed for predicting the removal for AFD and satisfactorily predicted the experimental values. Graphical surface response plots were used to obtain the optimum points. The best conditions for maximum AFD removal (94.944%) were obtained at pH: 2; dye concentration: 250 mg/L; contact time: 6 hr temperature: 50 °C and zeolite dosage: 2g. Optimum values were confirmed by validation experiments.

Nomenclature

Ce: Equilibrium concentrations of AF dye solution (mg/L)
Co: Initial concentrations of AF dye solution (mg/L)
Ct: Concentration of AF dye at time t (mg/L)
K1: First order kinetic model constant (1/min)
K2: Second order kinetic model constant (g/mg.min)
K3: Intraparticle diffusion rate constant (mg/g.min1/2)
Kd: Adsorption distribution Coefficient
KF: Freundlich isotherm equation constant ((mg/g).(L/mg)1/n)
KL: Langmuir isotherm equation constant (L/mg)
KS: Sips isotherm equation constant (L/mg)1/m
m: Sips isotherm equation parameter
M: Mass of adsorbent used (g).
n: Freundlich isotherm equation constant
N: Normality of sodium thiosulfate solution (mole/l)
AF: Acid Fuchsin
qe: Uptake of AF dye at equilibrium (mg/g)
q_L: Langmuir maximum uptake of AF dye per unit mass of zeolite5A (mg/g)
q_S: Sips maximum uptake of AF dye per unit mass of zeolite5A (mg/g)
qt: Uptake of AF dye at time t (mg/g)
R: Universal gas constant (8.314 J/mole.K)
R^2: Correlation coefficient
T: Temperature (K)
V: Volume of solution (L)
ΔH: Change in enthalpy (J/mole)
ΔG: Change in free energy (J/mole)
ΔS: Change in entropy (J/mole.K)
MS: Square error
DF: Degree of Freedom
S: Standard error of the regression

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