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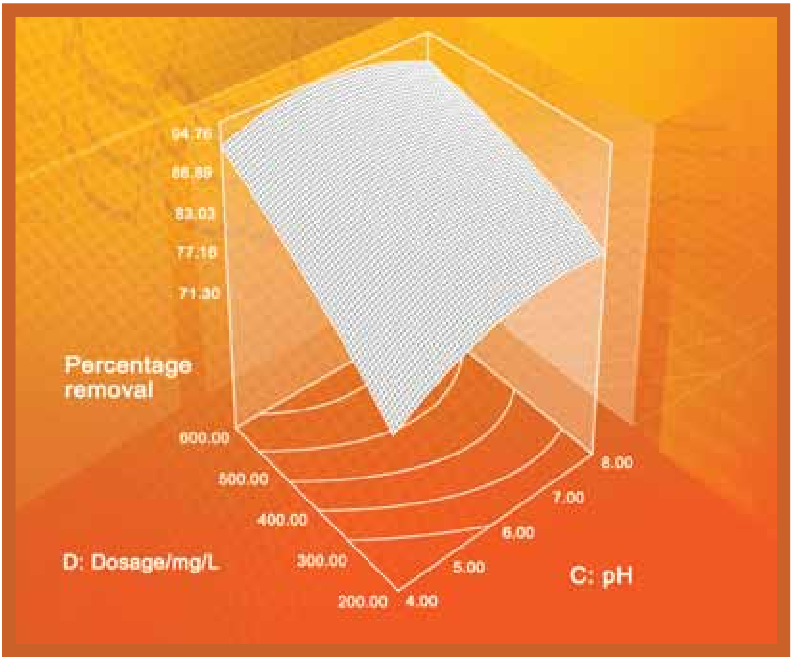

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1.	**Effects of Particle Sizes, Resin Content and Board Densities on the Properties of Phenol Formaldehyde Particleboard from Oil Palm Trunk Particles** *Jamaludin Kasim* *Siti Zalifah Mahmud* *Nurrohana Ahmad* *Shaikh Abdul Karim Yamani* *Siti Nor Ain Tamiran* *Nor Suziana Shahriman* *Nor Ashikin Razak*	1
2.	**Seam Quality: Experimental and Modelling Works Using the Structural Equation Methodology** *Suzaini Abdul Ghani* *Hugh Gong*	13
3.	**A Modified Integer Programming Model for Cleaning Services Scheduling** *Zuraida Alwadood* *Hamidah Ayub* *Muhamad Ariff Izzudin Razali*	37
4.	**Response Surface Methodology as a Tool to Study the Removal of Amido Black Dye from Aqueous Solution Using Anionic Clay Hydrotalcite** *Yamin Yasin* *Nur Syahirah Abdul Latif* *Abdul Hafiz Abdul Malik*	51

5. **Lipase Catalyzed Betulinic Acid Derivatives and its Cytotoxic Activity** 65
Yamin Yasin
Faujan Ahmad

Scientific Research Journal *Vol. 7 No. 1, 51-64, 2010*

Response Surface Methodology as a Tool to Study the Removal of Amido Black Dye from Aqueous Solution using Anionic Clay Hydrotalcite

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ABSTRACT

Anionic clay hydrotalcite was used as an adsorbent to remove amido black dye from aqueous solutions. Response surface methodology (RSM) based on a five-level, four-variable Central Composite Rotatable Design (CCRD) was employed to evaluate the interactive effects of various optimization parameters. The parameters were contact time (6-10 hrs), solution pH (4-8), adsorbent dosage (200-600 mg) and dye concentration (50-100 mg/l). Simultaneously increasing contact time, initial concentration and amount of adsorbent dosage increased the quantity of amido black dye removed. The optimum conditions derived via RSM for the reaction were a reaction time of 8.48 hrs, a concentration of 58.09 mg/l, an adsorbent dosage of 431.24 mg/L and a solution pH of 6.27. The experimental percentage removal was 85.55 % under optimum conditions, which compares well with the maximum predicted value of 87.95 %.

***Keywords**: Response surface methodology (RSM), optimization hydrotalcite, adsorption, amido black dye*

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Introduction

Hydrotalcite is a class of anionic clays with high anion exchange capacities, which have been used as effective adsorbents for the removal of a variety of anionic pollutants. The chemical composition of hydrotalcite is described by the formula $[M^{2+}_{1-x} M^{3+}_{x} (OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$ (1), where M^{2+} and M^{3+} are metal cations, for example Mg^{2+} and Al^{3+}, that occupy octahedral sites in the hydroxide layers, A^{n-} is an exchangeable anion, and x is the ratio $M^{3+}/(M^{2+} + M^{3+})$. Carbonates act as the interlayer anions in naturally occurring mineral hydroxides, which are members of this class of material. The hydrotalcite's anion exchange ability, large surface area and regeneration ability means that it is an effective adsorbent, which can be used in wastewater purification.

The presence of dyes in aqueous solution may pose several environmental problems. For instance, water coloration by dyes may interfere with light penetration thus affecting the aquatic ecosystem [1]. Hence, color removal of dyes from aqueous solution is a major environmental concern. There are various conventional methods for removing dyes including coagulation and flocculation, oxidation or ozonation, and membrane separation [2]. However, these methods are not widely used due to their high cost and economic disadvantage. Chemical and electrochemical oxidation and coagulation are generally not feasible in large scale industries. In contrast, adsorption techniques are by far the most versatile and widely used, and have been proven to be successful in removing dyes from aqueous solution.

Conventional and classical methods to study a process by maintaining other factors involved at an unspecified constant level does not depict the combined effect of all the factors involved. The results of adopting a conventional analytical method to elucidate the impact of factors on the removal of amido black from aqueous solutions using hydrotalcite are presented in a previous paper [3]. That study required a large number of experiments in order to determine the optimum adsorption levels for all parameters considered, but it was almost impossible to evaluate the interactions between the parameters. The limitations posed by using a conventional analytical method can be eliminated by optimizing all the affecting parameters collectively using a statistical experiment design such as Response Surface Methodology (RSM). RSM is an effective statistical technique, which provides an investigative approach towards parameter optimization. RSM is a collection of mathematical and statistical techniques used to evaluate the relative significance of several affecting factors in an optimum manner, even in the presence of complex interactions [4]. The main reason for implementing RSM is to determine the optimum operational conditions for the process or to determine a region that satisfies the operating specifications [5]. RSM comprises of a four level-four-factor Central Composite Rotatable Design (CCRD), which has been used in this study to evaluate the interactive effects and to obtain the optimum conditions for amido black dye (Figure 1) removal from aqueous solutions using an anion clay hydrotalcite adsorbent.

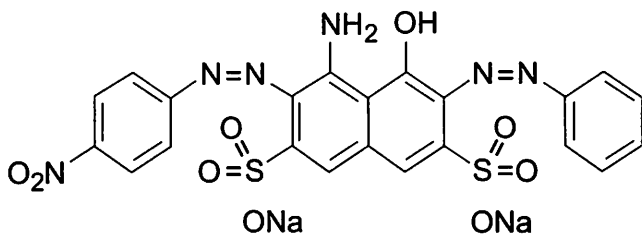

Figure 1: Amido Black Molecular Structure

Materials and Methods

Preparation and Characterization of Hydrotalcite

Hydrotalcite was prepared from magnesium sulphate hydrate [$Al_2(SO_4)_3.16H_2O$], aluminium sulphate hydrate [$Mg(SO_4).7H_2O$] and sodium carbonate at moderate conditions following Reichle's procedure [6]. X-ray diffraction (XRD) patterns of the sample powders were recorded on a Siemens diffractometer D500 with Ni filtered CuKα radiation at 40Kv and 20 mA, whereby the sample was mounted on a glass slide and scanned from 2 ° to 65 ° 2θ/min at 0.003 ° steps. The basal spacing was determined via powder technique.

Experimental Design

A four-level-four-factor CCRD was employed in this study, requiring 21 experiments. The fractional factorial design consisted of 8 factorial points, 8 axial points and 5 center points. The variables and the levels selected to evaluate the removal of amido black dye were: time (6-10 hrs); pH (4-8); adsorbent dosage (200-600 mg/L) and initial amido black dye solution concentration (50-100 mg/l), Table 1. A second order polynomial equation of the form in equation (1) was used to describe the experimental data.

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} x_{ij} \qquad (1)$$

where, Y is the percentage of amido black removed; b_0, b_i, b_{ii}, b_{ij} are constant coefficients and x_i are the uncoded independent variables.

Table 1: The Level and Range of Independent Variables Considered with Respect to Amido Black Removal from Aqueous Solution

Factor	Variable	Unit	Range and level of actual and coded values	
			Low actual (−1)	High actual (+1)
A	Time	h	6	10
B	Concentration	mg/l	50	100
C	pH	-	4	8
D	Dosage	mg	200	600

Batch Adsorption and Analysis

Amido Black purchased from Merck was used for the adsorption experiments. Stock solutions of amido black were prepared using distilled water and diluted to a predetermined set of working concentrations. Amido black concentrations were measured using a Lambda 20 UV-visible spectrophotometer. 0.25 g of synthesized compound was placed in 25 ml of 50-100 mg/l amido black solution. Twenty five milliliters of amido black solution placed in a 250 ml conical flask was contacted with 0.25 g of hydrotalcite and agitated using a water batch shaker operating at 120 rpm. Experiments were performed according to the Central Composite Rotatable Design (CCRD) presented in Table 2. The response was expressed as a percentage of amido black removal, calculated as $[(C_0 - C_t) / (C_0] \times 100$.

Data Analysis

The data from the experiments performed have been analyzed using Stat-Ease design expert version 6.06. Analysis of the statistical results

Table 2: The Central Composite Rotatable Quadratic Polynomial Model, Experimental Data, Actual and Predicted Values for the Five-level-four-factor Response Surface Analysis

Run	A	B	C	D	Actual relative (% Removal)	Predicted relative (% Removal)
1	8.00	75.00	6.00	400.00	90	89.11
2	8.00	117.04	6.00	400.00	95	77.53
3	8.00	75.00	6.00	400.00	88	79.11
4	8.00	75.00	6.00	400.00	91	82.53
5	4.64	75.00	6.00	400.00	85	89.53
6	10.00	50.00	8.00	600.00	80	72.11
7	10.00	100.00	8.00	200.00	90	91.11
8	10.00	100.00	4.00	200.00	78	67.53
9	8.00	32.96	6.00	400.00	70	85.96
10	8.00	75.00	9.36	400.00	80	85.96
11	8.00	75.00	6.00	400.00	88	70.96
12	8.00	75.00	6.00	736.36	97	95.96
13	10.00	50.00	4.00	600.00	90	75.45
14	8.00	75.00	6.00	63.64	70	81.47
15	6.00	100.00	8.00	600.00	92	70.96
16	8.00	75.00	2.64	400.00	75	97.96
17	11.36	75.00	6.00	400.00	85	87.95
18	6.00	100.00	4.00	600.00	83	87.95
19	6.00	50.00	4.00	200.00	68	87.95
20	8.00	75.00	6.00	400.00	85	87.95
21	6.00	50.00	8.00	200.00	73	87.95

A = time (h); B = concentration (mg/l); C = pH; D = dosage (mg)

was composed of three steps; namely, analysis of variance (ANOVA), regression analysis and plotting the response surface in order to establish the optimum conditions for the removal of amido black dye.

Results and Discussion

Characterization of Hydrotalcite

The XRD patterns of the synthesized hydrotalcite are presented in Figure 2. It is evident that the hydrotalcite exhibits fairly good crystallinity with a d-spacing of 7.9 Å, which is a characteristic feature of hydrotalcite. The d-spacing value is characteristic of trigonal structures with symmetrical peaks assigned to the (003) and (006) planes, respectively. The interlayer spacing of the sample corresponds to the 006 plane and was found to be 4.5 Å. The result is similar to previously reported works [7], in which the XRD patterns contain sharp peaks signifying high crystallinity. Hydrotalcite at a ratio of 4 (Mg/Al), which yields the sharpest peaks, was subsequently chosen as the adsorbent for amido black removal in this study.

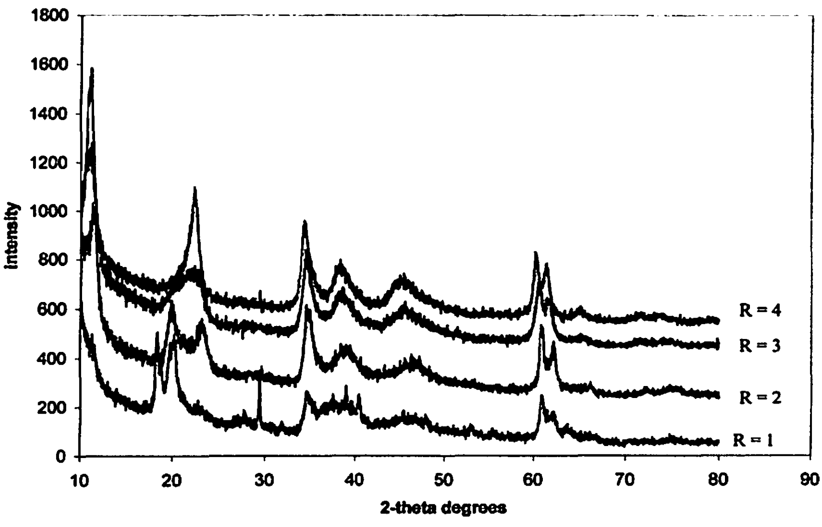

Figure 2: Synthesized Hydrotalcite XRD Patterns with Different Precursor Mg/Al Ratios (1 to 4)

Model Fitting and ANOVA

Experimental data for amido black removal using anion clay hydrotalcite are presented in Table 2. The predicted values presented were obtained from a model derived using software design expert version 6.06 based

Table 3: ANOVA for Amido Black Removal from Aqueous Solutions using Hydrotalcite

Source	Degree of Freedom	Sum of squares	Mean square	*F*-value	*P*
Model	14	1425.08	101.79	17.88	< 0.0010
Residual	6	34.16	5.69		
Lack of fit	2	12.96	6.48	1.22	not Significant
Pure error	42	1.20	5.30		
Total	20	1459.24			
Time (A)	1	0.000	0.000	0.000	1.000
Concentration (B)	1	312.50	312.50	54.89	0.0003
pH (C)	1	43.63	43.63	7.66	0.0325
Dosage (D)	1	364.50	364.50	64.02	0.0002

R-squared (R^2) = 0.9766; adjusted R-squared = 0.9220

upon the experimental data and correlate well with experimentally observed values. Various models (linear, two factorial, quadratic and cubic) were fitted to the experimental data; the corresponding ANOVA indicate that amido black removal from aqueous solution using hydrotalcite is best described by a quadratic polynomial model. The design expert the quadratic polynomial model is as follows:

$$\text{removal (\%)} = 87.95 + 0.00\,A + 7.43\,B + 1.79\,C + 8.03\,D - 0.70\,A^2 - 1.59\,B^2 - 3.35\,C^2 - 1.23\,D^2 + 3.53\,AB - 1.50\,AC + 3.43\,AD + 3.25\,BC - 2.75\,BD - 2.25\,CD \quad (2)$$

where A is the time; B the concentration; C the pH and D is the adsorbent dosage.

The computed model *F-value* of 17.88 is higher than the tabular *F*-value implying that the model is significant at a 1 % confidence level. The model has a very low pure error value of 5.30, which indicates good data reproducibility.

The high coefficient of determination ($R^2 = 0.9766$) and very small *P*-value (0.0001) from ANOVA indicates that a quadratic polynomial sufficient to represent the actual relationships that exist between the response (% removal) and the significant variables. The *P* values less than 0.0500 indicate that the model terms are significant. With respect to the results presented in Table 3, the concentration, pH and hydrotalcite dosage are the most significant in optimizing amido black adsorption using hydrotalcite from aqueous solutions. The low lack of fit-*F-Value* of 1.22 implies that the lack of fit is insignificant relative to the pure error and that the model describes the data well.

Response Surface Plots

The quadratic polynomial equation was used to plot response surfaces, whereby two parameters were plotted at a time on the x_1 and x_2 axes, respectively, whilst maintaining the two remaining parameters at their centre points values (coded level:0).

The response surface in Figure 3 shows the effect of time and initial amido black solution concentration on the percentage removal of amido black using anionic clay hydrotalcite. As expected, increasing the contact time between the dye and the adsorbent and the initial amido black solution concentration increases the percentage of amido black removed. A similar adsorption trend was reported for dyes removed using a novel adsorbent by Ravikumar *et al.* [8] in which the highest removal efficiency recorded at the highest contact time between the dye and adsorbent. As shown in Figure 3, the adsorption is fast at early stages and will approach equilibrium after 6 hours. The same trend of adsorption was reported in the removal of humic acid using fly ash [9] in which the percentage removal increases

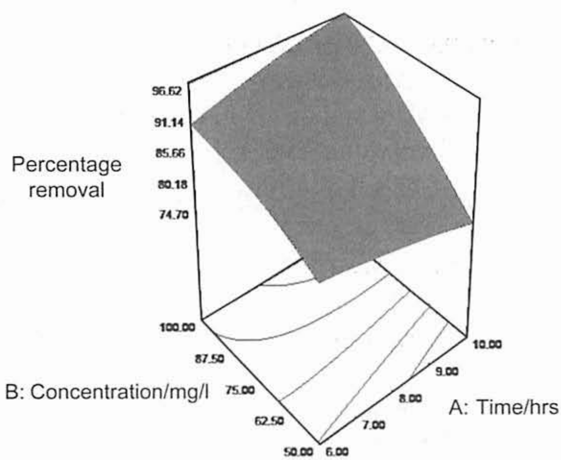

Figure 3: Response Surface Plot Showing the Effect of Contact Time and Concentration and their Mutual Effect on the Removal of Amido Black using Anionic Clay Hydrotalcite

with increase in concentration of humic acid. Adsorption was maximized with a high initial concentration of amido black and a longer contact time.

The response surface presented in Figure 4 shows the effect of contact time and pH on the percentage removal of amido black using anionic clay hydrotalcite. Adsorption at a moderate pH and with the highest contact time favors maximum percentage adsorption. The percentage removal of amido black decreases with increasing pH solutions. This explains a common observation that acidic dyes are absorbed much better than their ionized counterparts. Aamido black is acidic in nature and its percentage removal is better at lower pHs, which is in good agreement with other studies reported by other authors also performing optimization studies using RSM [8, 10].

The response surface plot presented in Figure 5 shows the effect of contact time and adsorbent dosage on the removal of amido black using hydrotalcite. It is evident that increased percentage removal is achieved with increasing adsorbent dosage and increased contact time.. This can be attributed to increasing adsorbent dosage increases the effective available adsorption area. Figures 6 and 7 present the response surface plots as functions of initial amido black solution concentration versus pH and initial amido black solution concentration versus adsorbent dosage, respectively. As expected, the percentage removal of amido black is

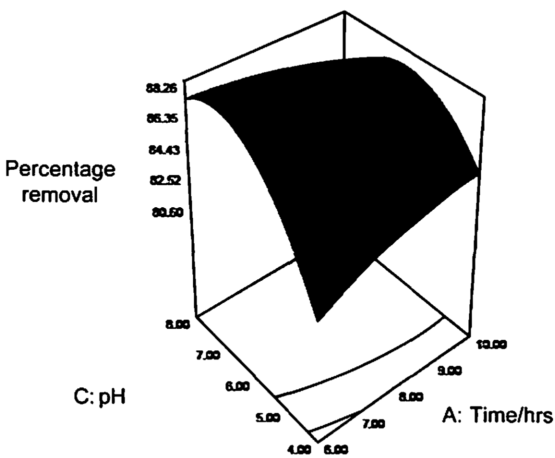

Figure 4: Response Surface Plot Showing the Effect of Time and pH and their Mutual Effect on the Removal of Amido Black using Anionic Clay Hydrotalcite

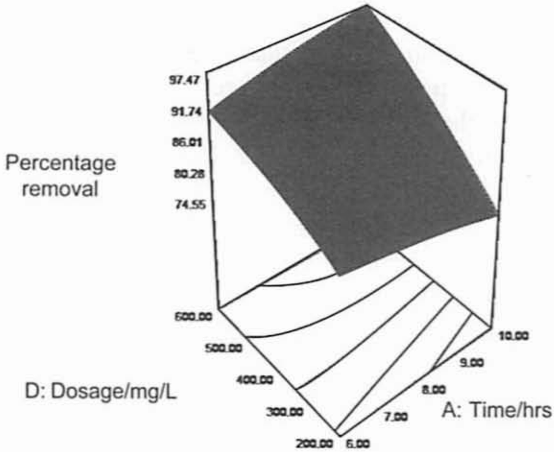

Figure 5: Response Surface Plot Showing the Effect of Time and Dosage and their Mutual Effect on the Removal of Amido Black using Anionic Clay Hydrotalcite

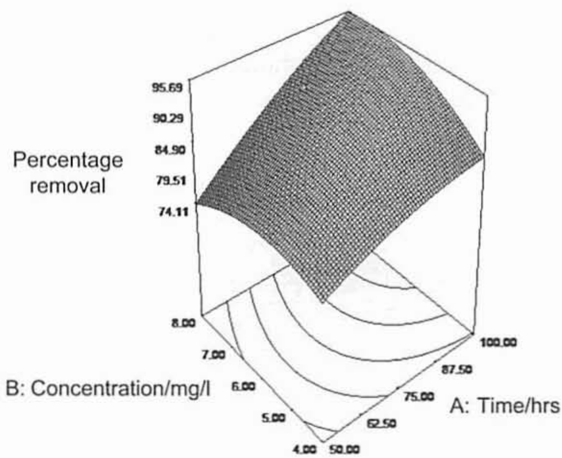

Figure 6: Response Surface Plot Showing the Effect of Concentration and pH and their Mutual Effect on the Removal of Amido Black using Anionic Clay Hydrotalcite

maximized with the highest initial amido black concentration and highest pH.

Figure 7 presents the effect of varying the initial amido black concentration and the hydrotalcite dosage. At low dosages and low

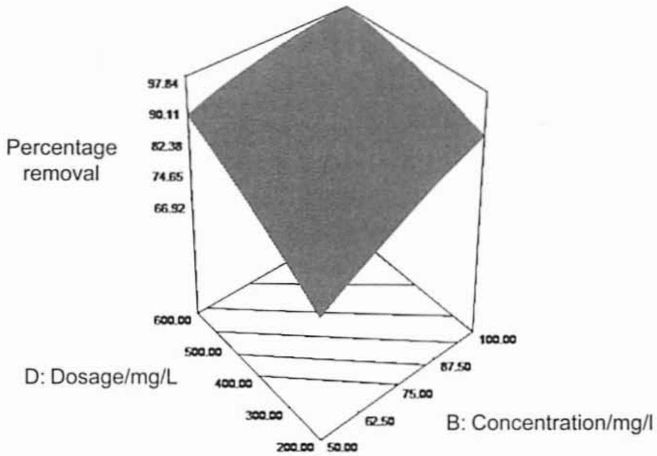

Figure 7: Response Surface Plot Showing the Effect of Concentration and Dosage and their Mutual Effect on the Removal of Amido Black using Anionic Clay Hydrotalcite

concentrations the percentage removal of amido black was lower and this can be attributed to a more limited effective adsorption area and the decreased probability of a dye molecule to find an adsorbent site. Higher percentage removal is achieved with high amounts of hydrotalcite and high initial concentrations of amido black solution, because larger initial quantities of amido black increases the adsorbate to adsorbent ratio thus promoting uptake. This relationship holds when there are no limiting factors, such as the presence of activators, inhibitors or mass transfer effects. Figure 8 presents the effect of varying the pH and the dosage of hydrotalcite; low dosages and low pH inhibit amido black percentage removal. Higher percentage removal is achieved with higher quantities of hydrotalcite and higher amido black solution pH.

Optimization of Adsorption

Within the experimental range studied, the optimum conditions for amido black removal using anionic clay hydrotalcite has been predicted using Design Expert's optimization function. The optimum conditions are presented in Table 4 along with their predicted and actual values. The analysis indicates that a maximum percentage removal of amido black requires an adsorption contact time of 8.48 hrs, an initial concentration of 58.09 mg/l, an adsorbent dose of 431.24 mg/L and a pH of 6.27. The

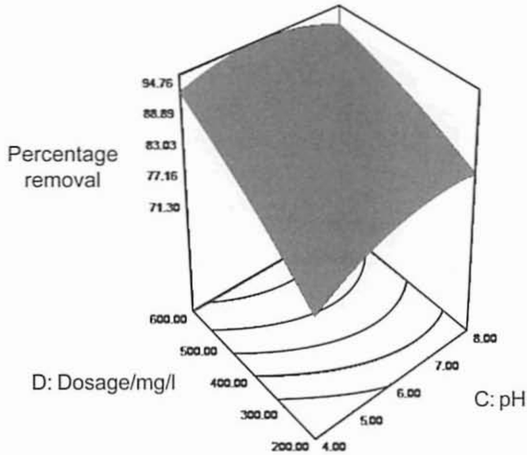

Figure 8: Response Surface Plot Showing the Effect of pH and Dosage and their Mutual Effect on Removal of Amido Black using Anionic Clay Hydrotalcite

Table 4: Optimum Conditions Derived by RSM

Optimal conditions				Actual removal (%)	Predicted removal (%)
A	B	C	D		
8.48	58.09	6.27	431.24	92.43	87.95

A = time (h); B = concentration (mg/l); C = pH; D = dosage (mg)

predicted and experimental percentage removal values under these conditions are in good agreement, implying that the empirical model derived from RSM could be used to adequately describe the relationship between the factors and response with respect to the removal of amido black using anionic clay hydrotalcite.

Conclusion

The adequacy of the predicted model was evaluated by performing additional independent experiments using the suggested optimal removal conditions. From the data obtained, the observed values were statistically near the predicted values and hence it can be concluded that the generated model adequately predicted the percentage removal. The removal of amido black using anionic clay Hydrotalcite has been successfully described through the development of a model using RSM fractional factorial design.

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