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Statistical Optimization of Dye Adsorption by Bottom Ash Using Response Surface Methodology

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Abstract Coal-based power generation units typically produce more than 20% bottom ash as a by-product. Bottom ash is made up of heterogeneous, multi-layered surfaces, which are available for adsorption, and also it is being used as structural fill, construction, and road base materials. Recently, there has been growing interest in utilizing bottom ash as a sorbent for various pollutants, especially water. The qualities like particle size, inherent large surface area, and high porosity of bottom ash make it a good choice for use as a low-cost adsorbent. The bottom ash sample from Ballari Thermal Power Station, Ballari, Karnataka, was collected to test the adsorption characteristics. This study is undertaken to optimize the percentage adsorption for both acid-washed and unwashed bottom ash samples. The process variables like contact time, dye concentration, and ash quantity were varied, and a regression model is developed for percentage adsorption using a statistical tool (MINITAB V 14). 3D response surface plots are generated for each pair of variables. The results indicate that the adsorption capacity of unwashed bottom ash is 1.4 times higher than the acid-washed bottom ash. The unwashed bottom ash has shown a maximum of 74% adsorption at 3g of ash quantity, 60 min of contact time for 10ppm dye concentration.

Keywords: *adsorption, bottom ash, dye, regression, statistics*

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1. Introduction

Electric power generation plays a vital role in the progress of any developing nation. India, being a developing country, needs a considerable amount of electricity for its overall development. India has vast reserves of coal and readily available at lower costs for the production of electricity. But Indian coals are known for their high ash content. Combustion of coal in thermal power plants and other industries generates millions of tons of ash and other by-products [1,2,3]. Thus obtained ash from coal-burning finds use in cement, ceramics, glass, etc. [3]. However, compared to the amount of ash produced, its utilization throughout the world is significantly less. Some of its users for landfilling [4] road-making and most of it are dumped without any use and impact the environment. Coal-burning produces two types of ashes, fly ash collected by electrostatic precipitation and bottom ash at the bottom of the furnace. In India, fly ash is mainly used to manufacture cement, road construction, and brick making. The amounts to only 25% of the ash generated annually. Each year utilization of coal is increasing by 2-3%, leading to more and more ash.

The literature survey shows that fly and bottom ash can be used as an adsorbent to remove pollutants in industrial and agricultural wastewaters. Reports indicate that using bottom ash pollutants like heavy metals and colouring matter from the industrial effluents can be removed significantly [5-13]. The morphological properties like particle size, surface area, and high porosity impart a perfect property to the bottom ash to use it as a low-cost adsorbent [14,15,16].

This research work aimed to know about the suitability of bottom ash generated from the nearby thermal power plant, Ballari Thermal Power Station (BTPS), to remove dyes present in the wastewaters released by the textile industries in and around Ballari. Chemical analysis and morphological studies of the bottom ash have been made. Adsorption experiments were carried out batch-wise by optimizing the parameters like adsorbent (Bottom ash) quantity, the concentration of the dye, and time of contact. And the Box–Behnken design has been employed to evaluate the effect of variable parameters on the % adsorption. The effect of each operating parameter on the % adsorption has been discussed using a 3D surface plot (Response Surface Methodology).

2. Materials and Methods

2.1. Chemical Composition and Morphological Studies

The bottom ash samples were obtained from the Ballari Thermal Power Station, Ballari, Karnataka, India. The ash sample was divided into two parts, and one of them was washed by using 1N HCl and dried and designated as acid-washed bottom ash (ABA). Another part is used as it is basis and designated as unwashed Unwashed Bottom Ash (UBA). The X-Ray diffraction and morphological characters have determined the chemical composition of both the adsorbents by scanning an Electron Microscope. Commercial dye samples were obtained from the local textile industry in powder form. A stock solution of a concentration of 1000 ppm was prepared by dissolving dyes in deionised water and further diluted to 5, 10, and 20 ppm.

2.2. Adsorption Experiments

A series of adsorption experiments were carried out by varying the parameters like Dye Concentration (5, 10, and 20 ppm), Contact Time (30, 60 and 90 minutes), and Bottom ash quantity (1, 2, and 3g). In each experiment, 50 ml of the dye solution was taken in a beaker containing the desired amount of the adsorbent and constantly stirred on a magnetic stirrer at room temperature. After the stipulated time, the contents were allowed to stand for an hour and centrifuged. The dye concentration after the adsorption was measured by taking the supernatant solution using HACH DR 3900 Spectrophotometer.

3. Results and Discussion

3.1. Characterization of the Adsorbents

The UBA and ABA are analyzed for specific surface areas, pore volumes, and pore diameters and are given in Table 1.

Table 1 depicts the BET surface areas of the prepared Bottom ashes, as shown on were very low compared to conventional adsorbents, which are in the order of 100-1000 m2/g. The average pore diameters were 9.5 nm. The chemical pre-treatments may alter only the chemical properties of the functional groups on the surfaces. The X-ray diffractograms of both UBA and ABA are shown in Figure 3. Figure 3 show that mullite, silicon oxide, Alumina, Biotite are the predominant crystalline form substances. Acid washed bottom ash showed that silica is present partly in the crystalline forms of quartz and combination with the alumina as mullite.

The scanning electron microscope (SEM) pictures of UBA and ABA adsorbents are shown in Figure 1 & Figure 2. The morphology of the bottom ash samples was affected by the combustion temperature and cooling rate during the incineration process. According to Chindaprasirt et al. [18], the bottom ash is more porous than the fly ash, and its particles are irregular and with pores in its cavities. In Figure 1, obtained by EDS, within the region delimited by the square in the Figure 1, it is possible to confirm the presence of the main elements present in bottom ash, among which are Si, Al, O, and Fe, and the sample contains a more sandy and grittier texture which is drastically reduced in the acid-washed bottom ash sample as shown in Figure 2. Figure 2 showed reduced net surface area because of acid washing.

Table 1. Physical characteristics of adsorbents

Adsorbent	Surface Area (m2/g)	Pore Volume (cm3/g)	Pore Diameter (Å)
Raw Bottom Ash (UBA)	6.5	10.2 x 10-3	69.4
Acid Washed Bottom Ash (ABA)	6.9	8.9 x 10-3	49.8

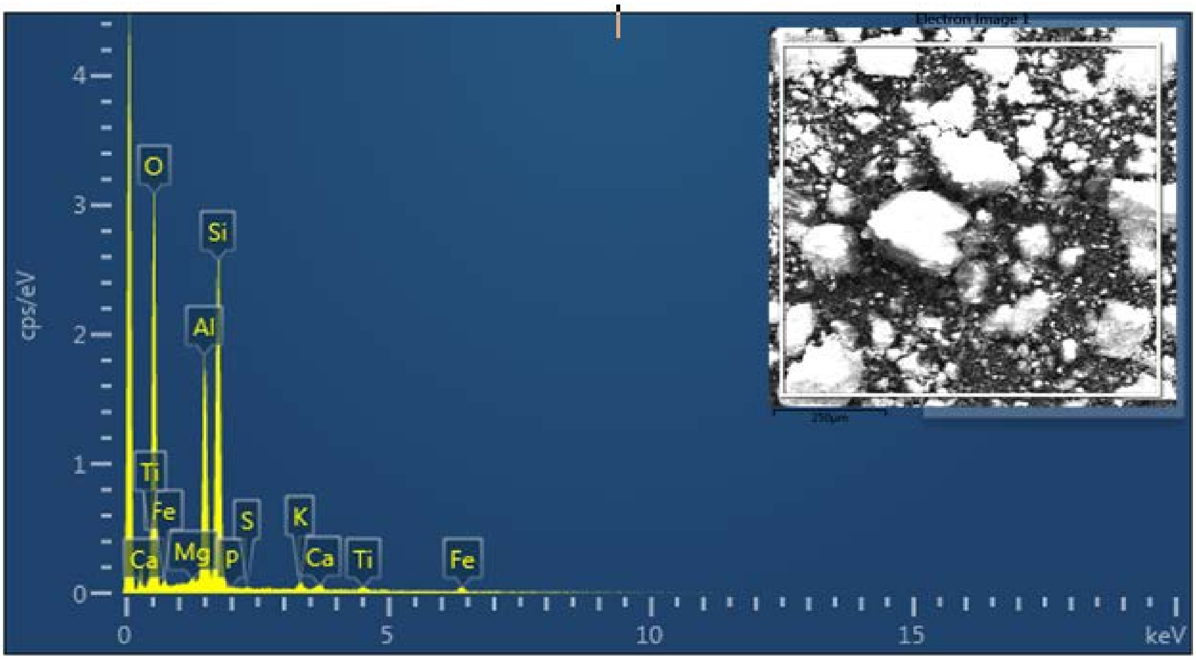

Figure 1. SEM of Un-Washed Bottom Ash sample

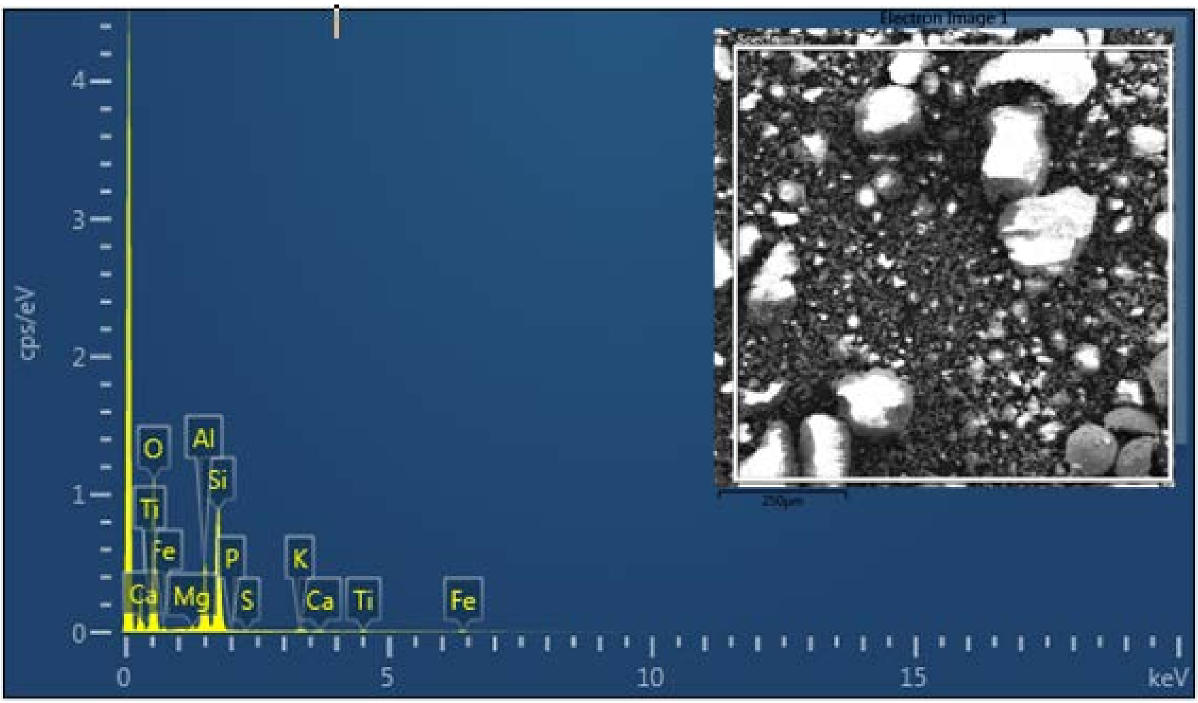

Figure 2. SEM of Acid Bottom Ash sample

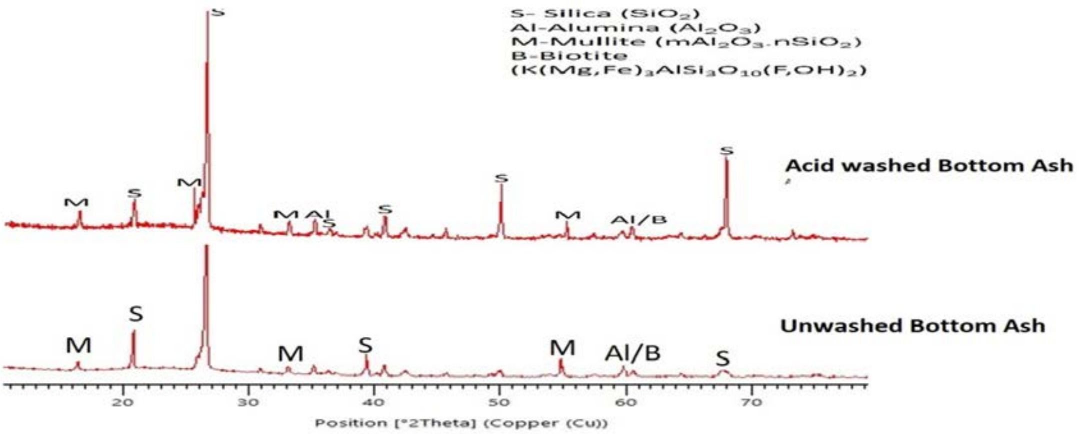

Figure 3. XRD pattern of Unwashed and Acid washed bottom Ash sample

3.2. Adsorption Studies

Adsorption experiments were carried on both un-washed bottom ash (UBA) and acid-washed bottom ash (ABA) by varying the Dye concentration, time, and ash quantity to remove dye from the aqueous solution. The levels of each variable are selected based on the preliminary test results. The details of the variables, the levels considered in the present test work, and the results of the adsorption experiments are depicted in Table 2.

Table 2. Experimental Design of Adsorption studies and results

Test Run	A: Dye concentration (ppm)	B: Time (Min)	C: Qty of Adsorbent (gms)	Acid washed Bottom Ash.	Unwashed bottom ash
				% Adsorption	% Adsorption
1	5.0	15.0	2.0	8.0	14.0
2	15.0	15.0	2.0	37.0	49.0
3	5.0	60.0	2.0	24.0	24.0
4	15.0	60.0	2.0	55.0	62.0
5	5.0	30.0	1.0	14.0	12.0
6	15.0	30.0	1.0	38.0	55.0
7	5.0	30.0	3.0	32.0	20.0
8	15.0	30.0	3.0	51.0	63.0
9	10.0	15.0	1.0	26.0	51.0
10	10.0	60.0	1.0	45.0	60.0
11	10.0	15.0	3.0	36.0	51.0
12	10.0	60.0	3.0	54.0	74.0
13	10.0	30.0	2.0	37.0	57.0
14	10.0	30.0	2.0	37.0	57.0
15	10.0	30.0	2.0	37.0	57.0

It is observed from Table 2 that the maximum adsorption of 74% to the unwashed bottom ash is reported at an intermediate level of dye concentration (10 ppm) and a higher level of time (60 min) with a higher level of adsorbent quantity (3 gms). Similarly, the maximum adsorption of 55% is reported to the acid-washed bottom ash at higher levels of dye concentration (15ppm) and time (60 min) with an intermediate value of an adsorbent quantity (2 gms). The results indicate that the percentage of adsorption varies from 8 to 55 in ABA, whereas it is 14 to 74 in UBA. Furthermore, the higher adsorption found in UBA is attributed to finer particles which increase the gross surface area for adsorption. Whereas, in the case of ABA, HCl removes the finer particles and a considerable amount of coarser-sized particles, thereby decrease the surface area available for adsorption. The influence of variables on the adsorption is also evaluated using 3D surface plots, explained in subsequent sections.

3.3. Statistical Analysis

The adsorption results obtained from the laboratory investigations were analyzed statistically using Minitab 17.0.0 software. A set of 15 runs were carried out by varying the Dye Concentration (A), Contact Time (B), and Ash quantity (C) following the complete factorial design of experiments. Statistical analysis tools such as the analysis of variance (ANOVA) and regression equations have been proposed for the response (% Adsorption) studied as a function of response variables. The analysis of variance (ANOVA) method was adopted to evaluate the main and interaction effects of variables on the responses. Table 3 depicts the details of ANOVA on adsorption of dye in aqueous solution by both UBA and ABA. The influence of selected variables and their interaction between the time and adsorbent quantity (B.C.) on the adsorption is significant at the 95% confidence level since the calculated F-ratio values of these sources are higher the F-table (P) values. Order of significance of the primary variables on the adsorption as follows A > B > C for both UBA and ABA. Similarly, the order of significance among the interactions of variables is in the order A.C.> A.B.> B.C. A second-order polynomial equation is developed to fit the experimental results. This model represents process variables (A, B, C) and their interactions on the response variables (% Absorption). The general form of the model chosen is represented as follows.

$$Y = \beta 0 + \beta 1A + \beta 2B + \beta 3C + \beta 12AB + \beta 13AC + \beta 23BC + \beta 11AA + \beta 22BB + \beta 33CC \quad (1)$$

Where,

Y is the predicted response, β0is model constant; β1, β2, and β3are linear coefficients; β12, β13, β23 are cross-product coefficients, and β11, β22, β33 are the quadratic coefficients.

Equation (1) can be rewritten by considering significant variables at the 95% confidence level, and the equations (in coded values) for different responses are given (in coded values) below:

$$\% \ \mathbf{Adsorption}\ (\mathbf{ABA}) = -32.5 + 7.91A + 0.335 - B2.83C - 0.2500A*A + 0.00049B*B + 3C*C + 0.0044A*B - 0.250A*C - 0.0111B*C \quad (2)$$

$$\% \ \mathbf{Adsorption}(\mathbf{UBA}) = -87.8 + 24.72A - 0.070B - 4.37C - 1.05\ A*A + 0.00494\ B*B + 2.75\ C*C + 0.0067\ A*B - 0.0333\ B*C \quad (3)$$

Equations (2, 3) could be used to predict the adsorption values for both UBA and ABA adsorbents to any unknown variables that fall within the Study range of the present investigation. The response values of the adsorption process were predicted using the model equations (Equations (2, 3)) and compared with the experimental data. The significance of the models is described in different ways, and the results are given in Table 3 From Table 3, it is clear that all the statistical terms for these models are within the limits of reliable statistics, and the model prediction values for the adsorption responses closely match the experimental data. Furthermore, the influence of operating variables on ABA and UBA is analyzed following three-dimensional (3D) response surface plots. These plots help show the functional relationship between the response and three independent variables. The experimental results and the predicted values obtained using model Eqs. (3) are shown in Table 4 and Figure 4. The relationship of predicted and the observed data point are indicating that the % Absorbent model has made a good agreement (R2 of 0.978) of the response equation.

Table 3. ANOVA table on Adsorption studies

Source	Un-washed Bottom Ash					Acid Washed Bottom Ash			
	DF	Sum of Square	Mean Square	F-Value	P-Value	Sum of Square	Mean Square	F-Value	P-Value
Dye Concentration A	1	3160.13	3160.13	357.08	0.001	1326.13	1326.13	120.01	0.001
Time B	1	364.5	364.5	41.19	0.001	630.13	630.13	57.02	0.001
Adsorbent Qty C	1	231.13	231.13	26.12	0.004	312.5	312.5	28.28	0.003
A*A	1	2544.23	2544.23	287.48	0	144.23	144.23	13.05	0.015
B*B	1	23.08	23.08	2.61	0.167	0.23	0.23	0.02	0.891
C*C	1	27.92	27.92	3.16	0.136	33.23	33.23	3.01	0.143
A*B	1	2.25	2.25	0.25	0.636	1	1	0.09	0.776
A*C	1	0	0	0	1	6.25	6.25	0.57	0.486
B*C	1	2.25	2.25	0.25	0.636	0.25	0.25	0.02	0.886
Lack-of-Fit	3	44.25	14.75	*	*	**55.25**	**18.42**	*	*

Table 4. Adsorption Model Parameters

Parameters	Adsorbents	
	UBA	ABA
Model F-value	81.3	357.08
Model P-value	0.001	0.001
Correlation coefficient (predicted R2)	0.9932	0.9781
Adjusted R2	0.9809	0.9387

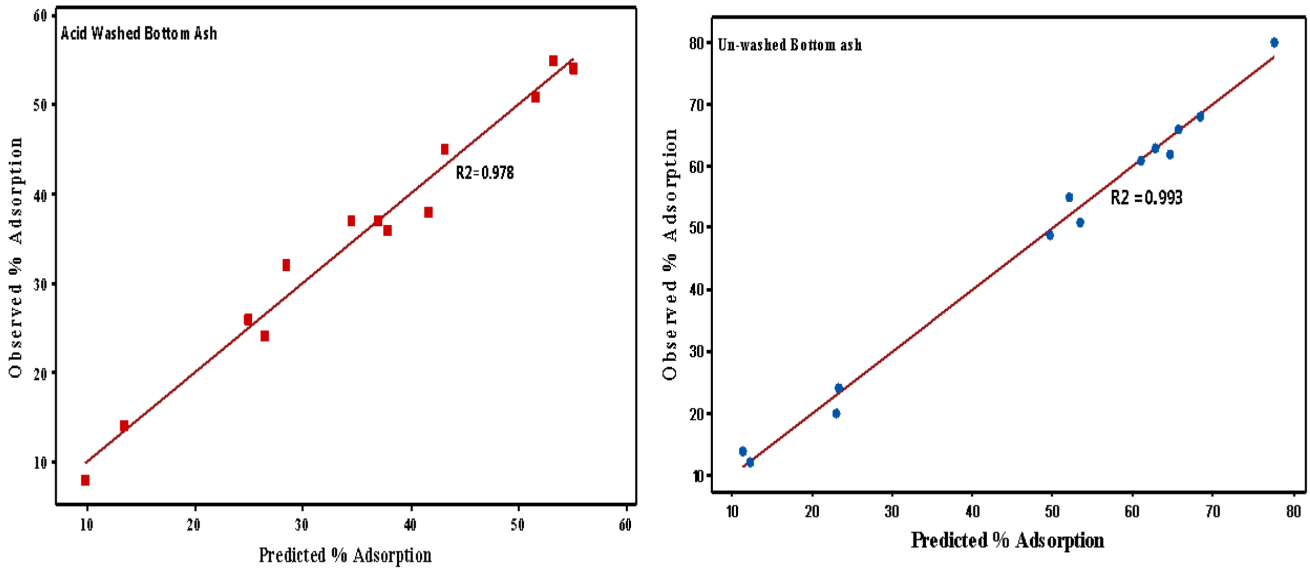

Figure 4. Observed and predicted % Adsorption values of UBA and ABA

Table 5. Actual and Predicted values of adsorption results

Test Run			UBA		ABA	
			% Adsorption			
Dye concentration (ppm)	Time (Min)	Qty of Adsorbent (gms)	Actual	Predicted	Actual	Predicted
5.0	15.0	2.0	14.0	11.4	8.0	9.8
15.0	15.0	2.0	49.0	49.6	37.0	34.5
5.0	60.0	2.0	24.0	23.4	24.0	26.5
15.0	60.0	2.0	62.0	64.6	55.0	53.3
5.0	30.0	1.0	12.0	12.3	14.0	13.4
15.0	30.0	1.0	55.0	52.0	38.0	41.6
5.0	30.0	3.0	20.0	23.0	32.0	28.4
15.0	30.0	3.0	63.0	62.8	51.0	51.6
10.0	15.0	1.0	51.0	53.4	26.0	24.9
10.0	60.0	1.0	60.0	68.4	45.0	43.1
10.0	15.0	3.0	51.0	65.6	36.0	37.9
10.0	60.0	3.0	74.0	77.6	54.0	55.1
10.0	30.0	2.0	57.0	61.0	37.0	37.0
10.0	30.0	2.0	57.0	61.0	37.0	37.0
10.0	30.0	2.0	57.0	61.0	37.0	37.0

3.4. Effect of Process Variables on % Adsorption

Dye absorption is determined as a function of time to determine an optimum contact time and the ash quantity for dye adsorption on bottom ash. The dye adsorbed onto adsorbent was calculated by the difference between the dye concentration and percentage of dsorption expressed. The results are plotted in a 3D surface plot to identify the effect of each process variable like contact time, ash quantity, and dye concentration. Figure 5(a) & Figure 6(a) show that % adsorption of both UBA and ABA was rapid up to 10 ppm dye concentration, and after that, it proceeded at a slower rate and reached saturation. The % adsorption was 74% and 54% at 60 minutes for 3g of UBA and ABA, respectively. Figure 5(b) & Figure 6(b) observed that the adsorption is increased by 1.4 times with 3 g UBA than ABA and shows that the acid washing may have reduced the adsorption % due to the acid-soluble washing, thereby decreasing the surface area of the bottom ash. Figure 5(c) & Figure 6(c) depict higher % adsorption at 3g of UBA at 60 min of contact time than ABA.

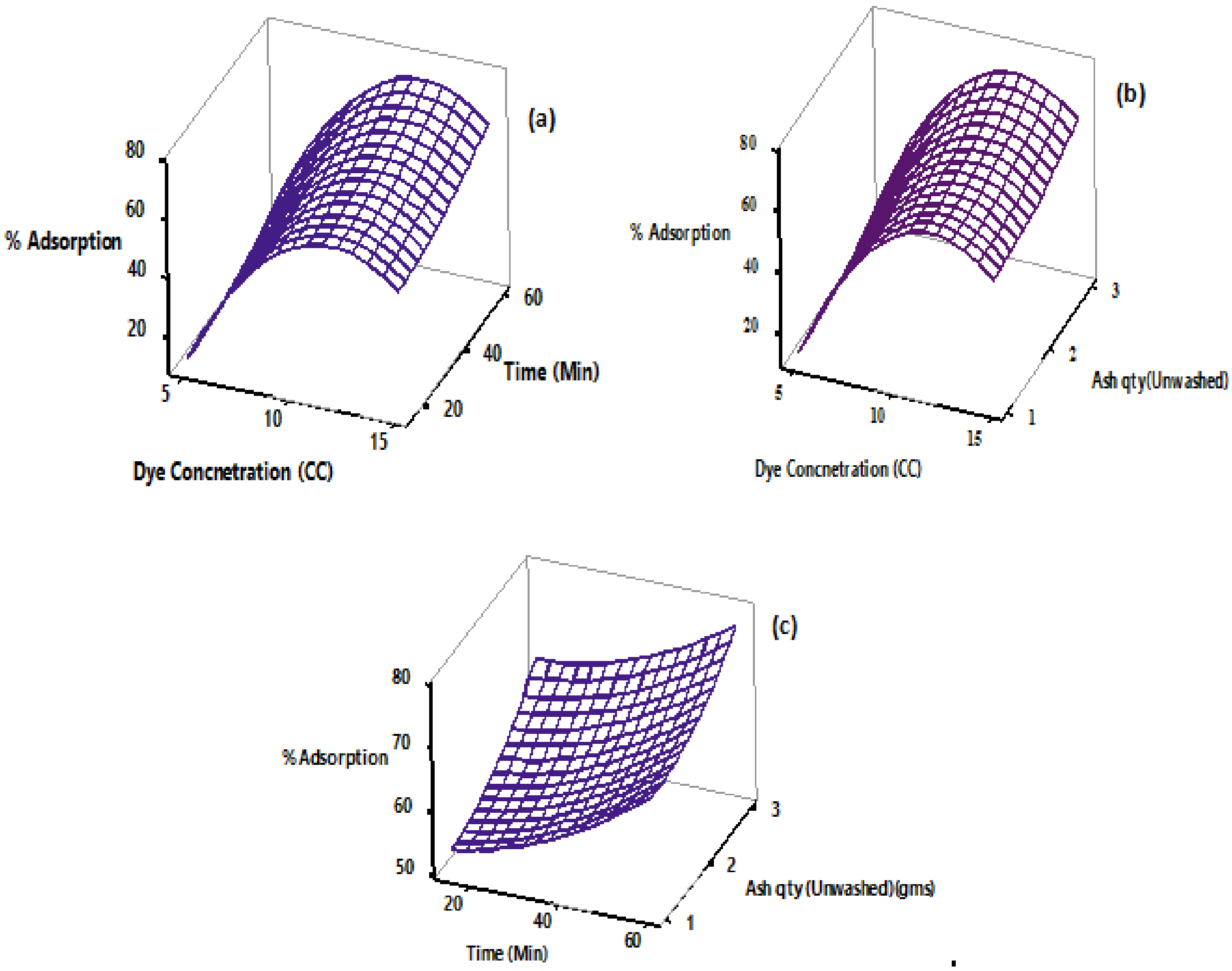

Figure 5. Effect of (a) Dye Concentration and Time on % Adsorption; (b) Un-washed Bottom Ash Qty and Dye Concentration on % Adsorption; (c) Un-washed Bottom Ash Qty and contact time on % Adsorption

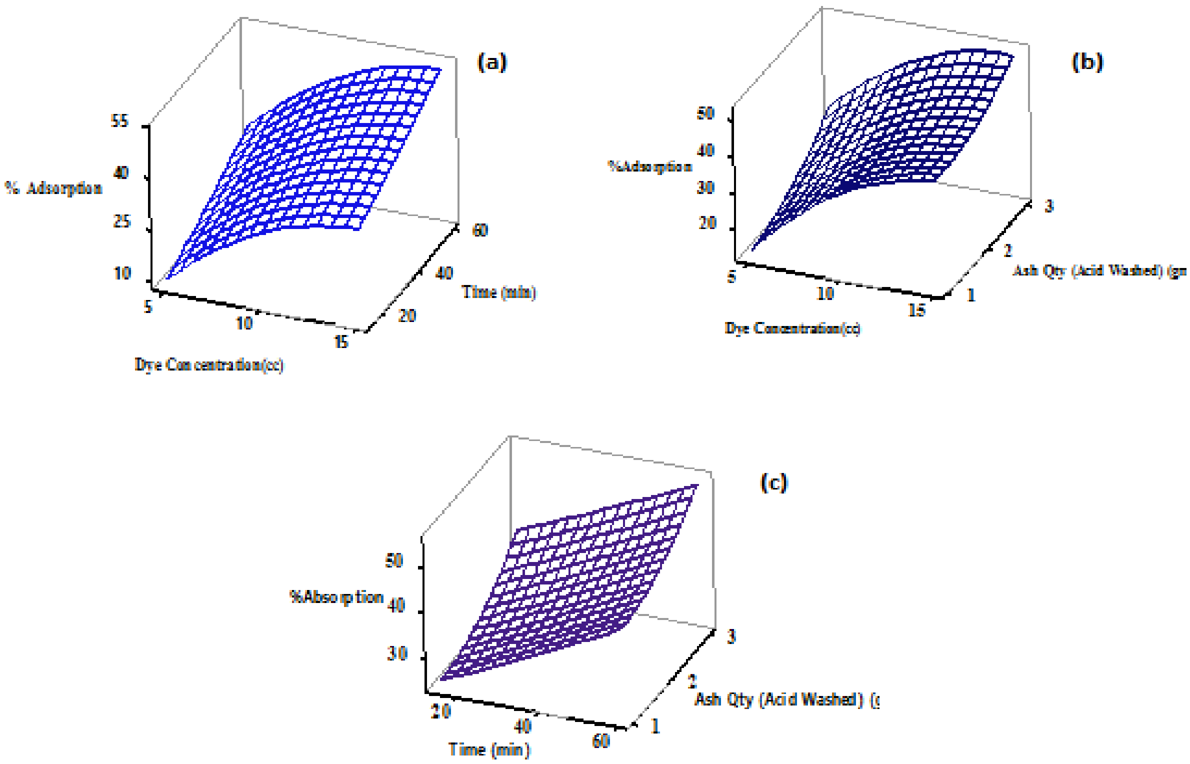

Figure 6. Effect of (a) Dye Concentration and Time on % Adsorption; (b) Acid washed Bottom Ash Qty and Dye Concentration on % Adsorption; (c) Acid-washed Bottom Ash Qty and contact time on % Adsorption

4. Conclusions

Bottom ash is made up of heterogeneous, multi-layered surfaces, which are available for adsorption. This study aims to assess the effectiveness of unwashed bottom ash and acid-washed bottom ash as adsorbents for dye adsorption in wastewater. Detailed characterizations of both unwashed and acid-washed bottom ash were performed using SEM and XRF. The results showed that the significant amounts of silica and alumina detected on the surface of the bottom ash help to adsorb dye in wastewater.

The tests were also carried out to understand the effect of pre-treatment of bottom ash to assess dye adsorption using statistical software (MINITAB V17). The adsorption processes were strongly affected by parameters such as the surface area, porosity, and contact time. Hence, the adsorption capacity of unwashed bottom ash is 1.4 times higher than that of acid-washed bottom ash. The unwashed bottom ash has shown a maximum of 74% adsorption at 3g of ash quantity, 60 min of contact time, and 10 ppm dye concentration.

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