Original Research Article

Development of Composite Adsorptive Biosorbent from H_3PO_4-NaOH-$BaCl_2$ Activated Almond Shell: Experimental and Statistical Approach

ABSTRACT

This study aimed to use an experimental and statistical approach to develop a cost-effective composite adsorptive biosorbent from acid, base and salt-activated biomass. Almond Shell samples were washed, milled to uniform particle sizes (425 µm) and then activated with H_3PO_4, NaOH, and $BaCl_2$ separately. The three active samples were combined to form a tricomposite biosorbent based on the Simple Lattice Design (SLD) under the Mixture Methodology of the Design Expert Software (11.0.1), within the ranges of 20-60%. The adsorptive capacity of each within tricomposite consisting of different percentage compositions of the activated Almond shell samples was investigated based on the Methylene Blue Number (MBN) Test. The results obtained were subjected to statistical analysis. The maximum adsorption capacity (MBN) of 896.12 mg/g was obtained from the tricomposite almond shell comprising mixture ratio of 20% (H_3PO_4), 20% (NaOH) and 60% $BaCl_2$. The combination is well fitted to Linear Model ($MBN = +885.00A + 847.07B + 826.36C$) with Std. Dev. of 13.25, R^2 of 0.6452, Adjusted R^2 of 0.5565, Predicted R^2 of 0.4566 and Adeq Precision of 8.472 (>4). The numerical optimization of the experimental data was obtained at 0.980 desirability. The experimental values obtained were in good agreement with the predicted values from the models, with relatively small errors (0.13%) between the predicted and the actual values. This shows that the Optimisation process via the SLD was very fit and reliable to optimize the process.

Keywords: *Almond Shell, Dye, Methylene Blue Number, Optimisation, Wastewater*

1. INTRODUCTION

The rapid increase in harmful and pathogenic dye-laden wastewater released from various industries constitutes a critical public health issue and a top environmental protection concern. The use of dyes as colouring materials for nearly all commodities is as old as the existence of man. In contrast to most organic compounds, dyes have colour because of the ability to absorb light in the visible spectrum; possession of a colour-bearing group called chromophore; the presence of a structure with alternating double and single bonds and lastly, the ability to exhibit resonance of electrons. The absence of any of the above-mentioned attributes in the molecular structure constitutes a loss of colour in any substance, material, or compound. Dyes chemically bond to the substrate to which they are applied; this distinguishes dyes from pigments that do not chemically bond to the material they colour. Some of these dyes are found to be very toxic to living organisms, being carcinogenic and mutagenic, while some are known to have suppressed the activities of enzymes in living organisms [1].

Methylene Blue (MB) belongs to the group of an organic compound containing a ring of four carbon, one nitrogen and one sulfur atom with a molecular formula of $C_{16}H_{18}ClN_3S$ and a molecular weight of 319.85 g/mol. It has a characteristic deep blue color and possesses water-soluble properties. The molecules of MB have a positively charged cationic group, that makes them susceptible to attraction by negatively charged surfaces. This attribute is also responsible for the above-mentioned ability of MB to be easily adsorbed onto various materials. MB dye has been the subject of numerous scholarly investigations because of its huge usefulness in the textile industry, its ability to stain biological samples in laboratories, and as an effective photosensitizer in photodynamic therapy for cancer treatment due to its ability to generate reactive oxygen species under light irradiation [2]. The extensive use of MB in industries such as textiles, tanneries, and paper among others leads to its significant presence in industrial wastewater. The concentration of MB in different industrial effluents is determined by the typical processes involved. For instance, wastewater from textile and printing industries may contain as high as between 10 to 1000 mg/L [3]. In addition, pharmaceutical industry wastewater where MB plays a staining role, may contain significant amounts of the dye. The release of tanneries and MB-laden wastewater into natural water bodies is detrimental to both life on land and in water. Due to its adverse interference with the respiratory and metabolic processes of aquatic animals, MB has proven to be toxic to life. Moreover, the persistence of MB in the environment and its potential to bio-accumulate pose long-term health and environmental risks [2]. Consequently, there is a need to drastically reduce the release of dye, especially as it constitutes a critical health risk. The remediation of dye-infested water before being released into the environment is necessary in other to avoid the attendant health risks. There are different techniques employed for treating wastewater containing dyes depending on the class of dye, the severity of contamination, legislation, budget, efficiency, and safety. The benefits and challenges of different treatment technologies were discussed. The three well-established categories through which the dye remediation process can be achieved have been identified as physical, chemical, and biological, though they have their respective merits and demerits. The physicochemical technique of adsorptive removal of dyes from wastewater using activated carbon or graphene is widespread and the benefits of this technology have been documented [4]. However, the adsorbents are expensive, possess poor selectivity properties, and require costly regeneration before they can be reused.

Commented [H1]: It should be order not other

Biological treatment is the most economical option for treating dye in commercial wastewater relative to the other methods. Biodegradation, bioaccumulation, bioremediation and biosorption techniques are often used in the management of industrial effluents since certain microorganisms, such as microbes, yeasts, algae, and fungi, may absorb and destroy numerous contaminants [5].

Biosorption, a mechanism that uses bio-based materials as sorbent to remediate the toxic pollutants from wastewater is a method that belongs to the sorption process in which the sorbent, substance is biological. This particular process has proven to be cost-effective, affordable, and easy to operate as has been demonstrated by many researchers [6, 7]. As the biosorbent possesses a wide range of the desired properties, biosorption has thus attracted increasing attention over time. Significant advances have brought forward in-depth competence of biosorption technique through the evolvement of the twin sorption isotherm and kinetics phenomena that have assisted in determining various parameters such as removal efficiency and other factors that influence adsorption rate.

Almonds (*Prunus amygdalus*) belong to the Rosaceae family and are one of the most popular tree nuts on a worldwide basis and rank number one in tree nut production. They are typically used as snack foods and as ingredients in a variety of processed foods, especially in bakery and confectionery products. Almond shell is the ligneous material forming the thick endocarp or husk of the almond tree (*P. amygdalus L.*) fruit. When the fruit is processed to obtain the edible seeds, big ligneous fragments are separated. These materials remain available as waste products for which no important industrial use has been developed, so they are normally incinerated or dumped without control [8].

The present work aimed at using experimental and statistical approaches to develop a cost-effective composite adsorptive biosorbent from H_3PO_4-NaOH-$BaCl_2$ activated Almond Shell. The Methylene Blue Number Test (the milligrams of methylene blue dye adsorbed by 1g of dried activated carbon; which is a measure of the mesopore content of the activated carbon) was used to determine the efficiency of the developed biosorbent Methylene blue was considered for this study because of its known strong adsorption onto solids and its recognized usefulness in characterizing adsorptive material [9]. The structure of this dye is shown in Fig. 1

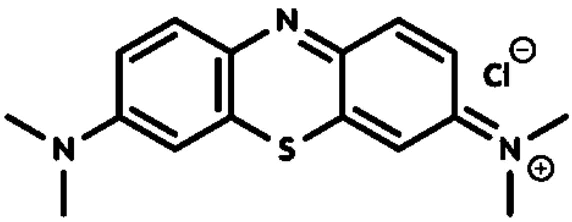


Fig. 1. Structure of Methylene Blue

2. MATERIALS AND METHODS

2.1 Materials

The major material used in this study was Almond shell. The reagents used include distilled water, H_3PO_4, NaOH, $BaCl_2$ and Methylene blue dye. All the reagents were analytical grades obtained from reliable chemical suppliers and were used without further purification.

2.2 Experimental Method

2.2.1 Materials preparation

The almond shell was collected at Ladoke Akintola University of Technology Ogbomoso, opposite MKO Lecture Theatre, Oyo State. The almond shells were washed severally with tap water and thoroughly rinsed with distilled water to remove any soluble materials attached to the almond shells [10]. They were cut into pieces of about 3 to 4 cm size then dried to constant weight before being ground to smaller sizes in a Miller and sieved to 425 µm. The powder was separated, stored in Bama bottles, and used as Biosorbent.

2.2.2 Multiple activation

A preliminary test with water was carried out to establish the impregnation ratio, thus, 25g of each sample in 100 mL of water was selected as the best activation ratio after leaving it for 24 h [11]. Phosphoric acid solution (0.1 M) was prepared by dissolving 14.16 mL of H_3PO_4 in 1L of distilled water. Sodium hydroxide (0.1 M) was prepared by dissolving 4 g of NaOH in distilled water. Barium Chloride (0.1 M) was prepared by dissolving 24.426 g of $BaCl_2$ in distilled water to obtain 0.1 M Barium chloride solution. The solutions were stirred in a magnetic stirrer and kept in an Amber bottle, separately, for further use as the acid, base and salt activants. The dried Almond Shell (25g) was mixed with 100 mL

Commented [H2]: Title to be placed at the center

Commented [H3]: It should be several times

Commented [H4]: Using what type of sieves? Why specifically 425 micrometer? Why not other sizes? Any particular significance of choice of this size?

Commented [H5]: What is the significance of using acid, base and salt combo?

Commented [H6]: Spell check

of 0.1 M phosphoric acid solution. The mixture was kept at room temperature for 24 h and later boiled off in a fume cupboard to pasta. The mixture was allowed to cool and then washed with distilled water to remove excess reagent until the pH was between 6.9 and 7.1. It was filtered and the residue, which is the activated almond shell obtained was oven-dried at 105 °C to constant weight and kept for further use [12]. The procedure was repeated for the 0.1 M Sodium hydroxide solution (100 mL) and 0.1 M Barium chloride solution. The resultant materials were classed as H_3PO_4-Activated Almond Shell, NaOH-Activated Almond Shell and $BaCl_2$ Activated Almond Shell.

2.3 Methylene Blue Number (MBN) test for Best Adsorptive Composite

The Simple Lattice Design in the Design Expects software (11.0.4.0) was used to generate the number of experimental runs at random for the formation of a composite mixture of the three activated Almond Shell samples. The range selected for each sample mix ratio was 20-60% which were fed into the software (Table 1).

Commented [H7]: It should be was, not were

Table 1. Experimental design showing the factors level of biocomposite used

Component	unit	Composition Level (%)	
		Low	High
H_3PO_4-Activated Almond Shell	%	20	60
NaOH-Activated Almond Shell	%	20	60
$BaCl_2$ Activated Almond Shell	%	20	60

The three activated Almond Shell samples were mixed in the ratios suggested by the software at each experimental run. Each mixture composition makes 100% in the summation of the three factional compositions. The three were thoroughly mixed to homogenous and their adsorption capacities were estimated using a standard Methylene Blue Number (MBN) test. The amount of methylene blue adsorbed was determined by measuring 1 mg of the homogeneous composite 100 mL of 100 mg/L of methylene blue solution for 24 h at room temperature [13]. The remaining concentration of unabsorbed methylene blue was analysed using UV/Vis spectrophotometer and the adsorption capacity and the removal efficiency of the process were determined according to Equation 1.

$$\text{Methylene Blue Number}\left(\frac{\text{mg}}{\text{g}}\right) = \frac{(C_0 - C_e)\times V}{M} \quad (1)$$

where C_0 *(mg/L)* is the initial concentration at the initial time (*t=0*), C_e (*mg/L*), the concentration of the methylene blue at equilibrium time, $V(L)$ is the volume of the solution treated and M *(g)* is the amount of the adsorbent and q_e (mg/g) is the adsorption of the methylene blue.

2.4 Statistical Analysis

A second-order polynomial regression was used to develop the model for predicting the response variables of the process.

$$Y = \propto_0 + \propto_1 x_1 + \propto_2 x_2 + \propto_3 x_3 + \propto_{12} x_1x_2 + \propto_{13} x_1x_3 + \propto_{23} x_2x_3 + \propto_{11} x_1^2 + \propto_{22} x_2^2 + \propto_{33} x_3^2 \quad (2)$$

Where *Y* represents the predicted response (Methylene blue number and Removal Efficiency); α_o is the intercept term; α_1, α_2, α_3 are the linear coefficients; α_{12}, α_{13}, α_{13} are the interaction coefficients; α_{11}, α_{22}, α_{33} are the quadratic coefficients; and x_1, x_2, x_3 are the coded independent variables.

The fitted polynomial equation was plotted as contour and surface plots to visualize the relationship between the response and observed levels of each variable and deduce the maximum conditions. Analysis of variance (ANOVA) was used to calculate the lack-of-fit to know the breakdown of the total variability in the response variable and to identify the impact of the model terms on the MBN obtained. The coefficient of determination (R^2), adjusted R^2 and predicted R^2, represented in Equations 3-5, were used to appraise the quality of fit of the polynomial model [14, 15]. The *p*-value and F-value were used to evaluate the statistical significance based on adequate precision ratio, coefficient of variation (*CV*) and standard deviation (*SD*) (Equations 6-8) [15]. The significance of the model was based on the principle of Fisher's statistical test (F-test) and it generates the F-value, which represents the ratio of the mean square of regression to the mean error. The significance of the model terms was further tested based on lower probability (*p*-value) which may lie between 90% confidence levels [16]. Lack of fit, which is usually preferred to be insignificant, [17] was also used as a diagnostic test to determine the adequacy of any model developed

$$Coeficient\ of\ determination\ R^2 = 1 - \frac{SS_{residual}}{SS_{model}+SS_{residual}} \quad (3)$$

$$Adjusted\ R^2 = 1 - \frac{SS_{residual}/DF_{resiaual}}{(SS_{model}+SS_{residual})/(DF_{model}+DF_{resudal})} \quad (4)$$

$$Predicted\ R^2 = 1 - \frac{Press}{SS_{total}+SS_{block}} \quad (5)$$

$$\text{Adequate precision} = \frac{\max(\hat{Y}) - \min(\hat{Y})}{\sqrt{\frac{\rho\sigma^2}{n}}} \quad (6)$$

$$Coeficient\ of\ variation\ (CV) = \frac{\sqrt{MS_e}}{\frac{1}{N}\sum_1^N Y} \times 100 \quad (7)$$

$$Standard\ deviation\ (SD) = \sqrt{MS_e} \quad (8)$$

Where σ^2 is the residual mean square from ANOVA, *CV* is the coefficient of variation, *DF* is the degree of freedom, MS_e is the residual mean square, *n* is the number of experimental runs, *p* is the number of model variables, *PRESS* is the predicted residual error sum of squares, *SD* is the standard deviation, *SS* is the sum of squares, *Y* is the observed response, and Ŷ is the predicted response.

3. RESULTS AND DISCUSSION

3.1 Model Summary Statistics for the adsorption capacity of almond shell tricomposite biosorbent

The model summary statistics presented in Table 2 indicate that a linear model was best suggested for the MBN (mg/g) response. The highest R^2 values of 0.7196 were obtained for Cubic and Special Quartic models, but because they were 'Aliased', they were not suitable. The next highest R^2 of 0.7176 was obtained of Special Cubic and was equally not suitable because it was characterized by negative Predicted R^2 (-0.1585), similar reason could be advanced for the Quadratic Model (Predicted R^2 = -1.6858). Eventually, the Linear Model was the most suitable model for the MBN test values obtained (Std. Dev. = 13.25, R^2 = 0.6452, Adjusted R^2 =0.5565 and Predicted R^2 = 0.4566) [18].

Table 2. Model Summary Statistics

Source	Std. Dev.	R²	Adjusted R²	Predicted R²	PRESS
Linear	13.25	0.6452	0.5565	0.4566	2152.28*
Quadratic	15.84	0.6834	0.3668	-1.6858	10637.50

Special Cubic	16.72	0.7176	0.2940	-0.1585	4588.39
Cubic	23.56	0.7196	-0.4018		**
Special Quartic	23.56	0.7196	-0.4018		**

*Suggested, and ** Aliased

3.2 Adsorption Capacities of Various Almond Shell Tricomposite biosorbent Mixing Ratios

The adsorption capacities are presented in Table 3. The maximum and minimum adsorption capacities are 896.12 mg/g and 816.21 mg/g respectively, this means that the composite which gave the best adsorption capacity is a mixture of 20%, 20% and 60% of Almond Shell samples activated with H_3PO_4, NaOH, and $BaCl_2$, respectively.

Commented [H8]: Of course, only these % compositions were worked out, not other permutations and combinations

Table 3. Methylene Blue Number (MBN) of the Tricomposite

Run	Components Composition (%)			Response
	A: M1	B: M2	C: M3	MBN (mg/L)
1	20.000	60.000	20.000	840.18
2	26.667	46.667	26.667	845.32
3	60.000	20.000	20.000	886.21
4	20.000	40.000	40.000	816.21
5	26.667	26.667	46.667	836.76
6	33.333	33.333	33.333	842.47
7	46.667	26.667	26.667	827.63
8	40.000	40.000	20.000	876.14
9	20.000	20.000	60.000	832.19
10	20.000	20.000	60.000	896.12

11	20.000	40.000	40.000	861.30
12	20.000	60.000	20.000	853.88
13	60.000	20.000	20.000	839.61
14	40.000	20.000	40.000	852.17

M_1 (material activated with Acid (H_3PO_4)), M_2 [materials activated with Base (NaOH)], and M_3 [materials activated with Salt ($BaCl_2$)] respectively

3.3 ANOVA of Adsorption Capacity and Removal Efficiency

The analysis of variance (ANOVA) procedure was used to determine the significance of the variable and to substantiate the adequacy of the quadratic regression model obtained in this study. The results of the ANOVA are represented in Table 4. The Model F-value of 7.27 implies the model is significant and there is only a 1.59% chance that an F-value this large could occur due to noise. Similarly, the linear model is significant at $p<0.0159$ and all the model terms A, B, and C are significant (at $p<0.0159$), based on the 95% Confidence interval that indicated that P-values less than 0.0500 indicate model terms are significant. The Lack of Fit F-value of 0.09 implies the Lack of Fit is not significant relative to the pure error and there is a 99.08% chance that a Lack of Fit F-value of this magnitude to occur due to noise. Generally, a non-significant lack of fit is good is desired for any statistical analysis. The Predicted R^2 of 0.4566 is in reasonable agreement with the Adjusted R^2 of 0.5565; i.e. the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio and a ratio greater than 4 is desirable [19], thus a ratio of 8.472 obtained indicates an adequate signal, thus this model can be used to navigate the design space.

Table 4. ANOVA for response surface model analysis for the MBN

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**
Model	2555.23	2	1277.61	7.27	0.0159*
(1)Linear Mixture	2555.23	2	1277.61	7.27	0.0159*
Residual	1405.35	8	175.67		

Lack of Fit	294.95	6	49.16	0.0885	0.9908^
Pure Error	1110.40	2	555.20		
Cor Total	3960.58	10			
Std. Dev.	13.25	C.V. %	1.56	Adjusted R^2	0.5565
Mean	849.37	R^2	0.6452	Predicted R^2	0.4566
				Adeq Precision	8.4718

* Significant and ^ not significant

3.4 Regression Model Equation for the Responses

The final model equation (Equation 9) was developed in terms of coded factors, for the MBN. The equations also indicate the presence of only linear variables without square and crossed terms for the three variables investigated. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Generally, positive and negative coefficients indicate positive and negative influences, respectively, of the independent variables on the selected responses [18]. The linear model obtained is characterized by a positive coefficient and shows that the components selected played important roles in influencing the adsorptive capacity of the tricomposite almond shell-based biosorbent produced.

$$MBN = +885.00A + 847.07B + 826.36C \tag{9}$$

3.6 Diagnostic Case Study for Adsorptive Capacity (MBN) and the Tricomposite Biosorbent

The actual value, predicted value, and residual values for the MBN are shown in Table 5. The difference between the experimental (actual) values and the predicted (software-generated) values generated is indicated as the residual values. The residual with positive values implies that the actual value is less than the predicted value, while the residual with Negative values indicates that the actual value was greater than the predicted value [20]. A situation where there is no difference (positive or negative) between the actual and predicted values is regarded as Zero residual values means that the actual was equivalent to the predicted value on which its comparison was based. Experimental Run 1. 2,4, 5, 6, and 14 have a negative residual value of -6.89, -4.62, -20.51, -2.83, -10.34 and -3.51 respectively, while experimental Run 3. 8, 9, 11, and 12 have a positive residual value of 1.40, 10.10, 5.83, 24.58, and 6.81, respectively (Table 5). The trend is further illustrated in the Predicted versus Run diagram generated by the Design Expert Software (Figure 2), where all the points above the midpoints are the positive residuals and those below are the negative residuals. The correlation between the predicted values from the experiment and the actual values were plotted against each other for the MBN (Figure 3). The correlation observed from the plots was relatively high with values of 0.6452, though less than the minimum 0.7 required, and this is obvious from the degree of scattering of the data point from the normal line. The closer the data points to the normal line the higher the R^2 [21].

Table 5. Diagnostic case study for MBN

Run Order	Actual Value	Predicted Value	Residual
1	840.18	847.07	-6.89
2	845.32	849.94	-4.62
3	886.40	885.00	1.40
4	816.21	836.72	-20.51
5	836.76	839.59	-2.83
6	842.47	852.81	-10.34
8	876.14	866.04	10.10
9	832.19	826.36	5.83
11	861.30	836.72	24.58
12	853.88	847.07	6.81
14	852.17	855.68	-3.51

A.V. = Actual Value, P.V. = Predicted Value

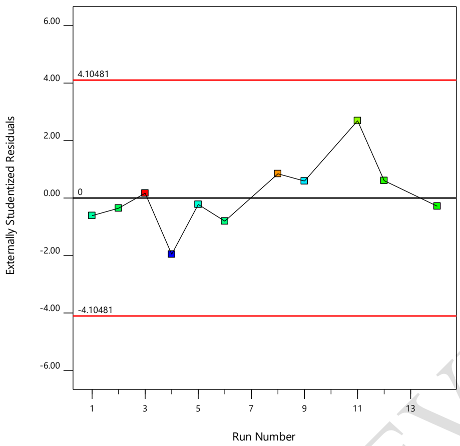


Fig. 2. Trend of Predicted Values versus Experimental Runs

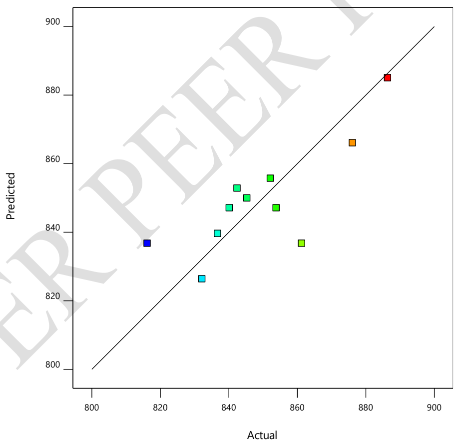


Figure 3. Plot of predicted vs. actual values for MBN

4.7 Effects of Interaction of Composition of the H_3PO_4-Activated, NaOH-Activated and $BaCl_2$-Activated Almond Shells on the MBN of the Composite

The interactions of the selected Composition ranges of the H_3PO_4-Activated, NaOH-Activated and $BaCl_2$ Activated Almond Shells on the MBN of the tricomposite developed are shown in Figures 4a-c, as contour plots. Generally, the contour plots rotated for the three components indicated that the interactions of compositional variations of the three components affected the adsorption capacity of the Tricomposite biosorbent developed from the Almond shell [4]. The 'red zones' on the contour plots indicated the section with the highest impact on the MBN, the 'blue zone' indicated where the least impact on the MBN is effective, while the "green zone' and 'yellow zone' indicated the section with feasible positive impact on the MBN of the tricomposite developed. The corresponding three-dimensional (3D) representations of these trends are illustrated in Figure 5a-c for the MBN. The curves observed in these figures are 'flat' or 'plain' thus indicating that the model equation is linear [20].

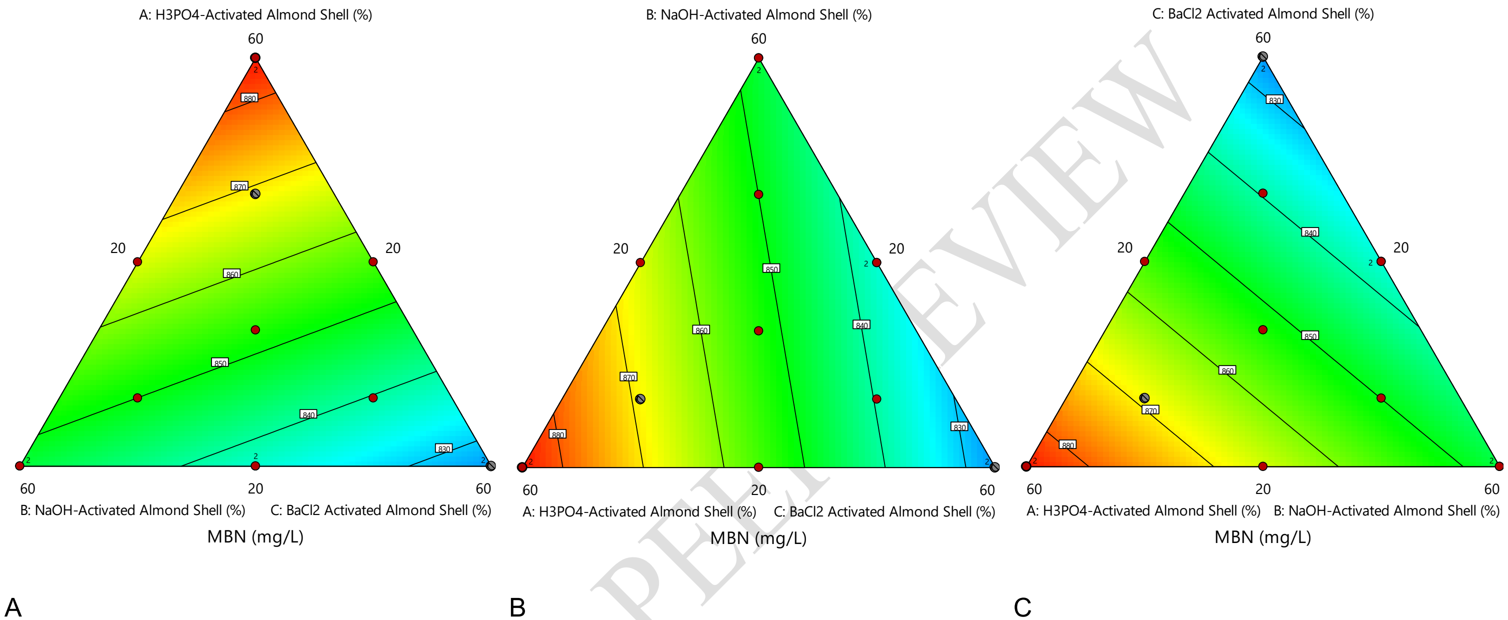
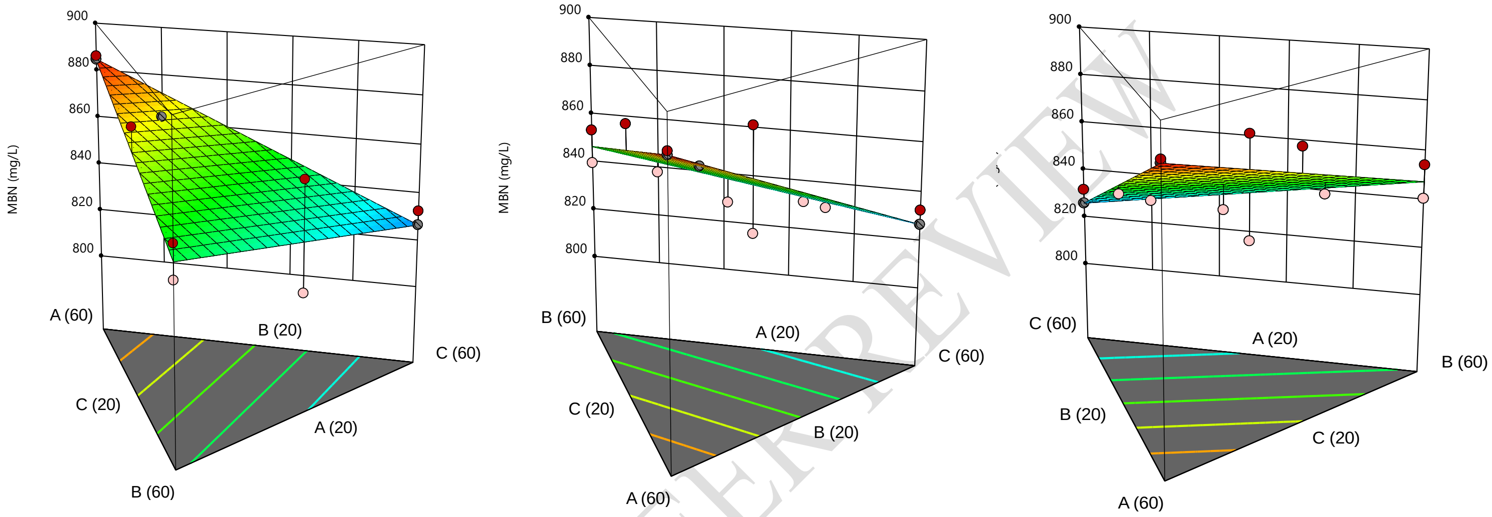


Fig. 4. Contour plot of Composition ranges of the H_3PO_4-Activated, NaOH-Activated and $BaCl_2$ Activated Almond Shells on the MBN



A B C

Fig. 5. 3D plot of Composition ranges of the H_3PO_4-Activated, NaOH-Activated and $BaCl_2$ Activated Almond Shells on the MBN

4.8 Process Optimization for MBN

The component composition (20-60%) for the MBN was optimized numerically using Simple Lattice Design (SLD) under the Mixture Methodology of the Design Expert software (11.1.0). The percentage compositions of the H_3PO_4-Activated, NaOH-Activated and $BaCl_2$ Activated Almond Shells were set 'in ranges' while the responses; on the MBN were set to 'maximize' (Table 6). The numerical value obtained from the software at **0.980** desirability (Figure 6) was compared with the experimental values in order to evaluate the errors between the experimental and the numerical Optimisation. Validations of these factors were confirmed by comparing the predicted values with the measured ones [22, 23]. It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors (0.13%) between the predicted and the actual values. This shows that the Optimisation process via the SLD was very fit and reliable to optimize the process because the percentage error fell within the 10% error permissible and further justified the reproducibility of the process [20, 24].

Table 6. Process Optimisation for MBN

Name	**Goal**	**Lower Limit**	**Upper Limit**	**Numerical Value**	**Experimental Value**	**Percentage Error (%)**
A:H3PO4-Activated Almond Shell	is in range	20	60	60	NA	NA
B: NaOH-Activated Almond Shell	is in range	20	60	20	NA	NA
C: BaCl2 Activated Almond Shell	is in range	20	60	20	NA	NA
MBN	maximize	816.21	886.4	885.004	886.21	0.13%

NA – Not Applicable

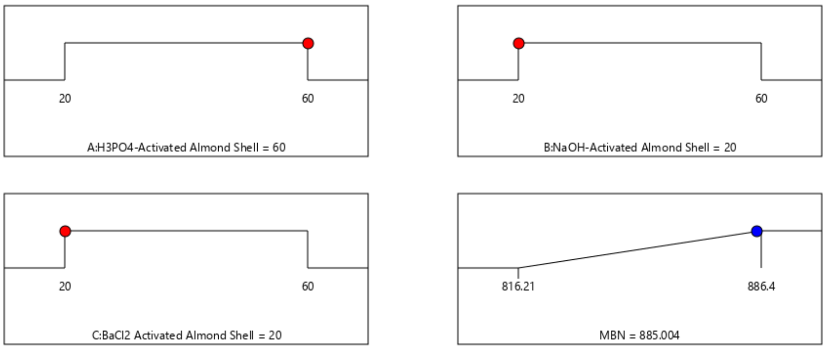


Fig. 6 Numerical Optimum value for the tricomposite composition

4. CONCLUSION

This study has established the feasibility of developing a composite biosorbent from almond shells activated with acid, base and salt-based activants. The synergetic tendency of the three materials to function as synergetic effective adsorbents was verified based on the Methylene Blue Number test. The maximum adsorptive strength of 89.61% was obtained from the tricomposite almond shell based on a 20% (H_3PO_4), 20% (NaOH) and 60% $BaCl_2$ combination. The statistical approach further indicated that the Simple Lattice experimental design could be effectively engaged to combine the activated materials to generate tricomposite biosorbent from waste almond shells with potency for the removal of dye from wastewater.

CONSENT

Not applicable to this study

ETHICAL APPROVAL

Not applicable

REFERENCES

1. Roy U, Manna S, Sengupta S, Das P, Datta S Mukhopadhyay A, Bhowal A. Dye Removal Using Microbial Biosorbents. In: Crini, G., Lichtfouse, E. (eds) Green Adsorbents for Pollutant Removal. Environmental Chemistry for a Sustainable World, vol 19. Springer: Cham; 2018 https://doi.org/10.1007/978-3-319-92162-4_8

2. Dimbo D, Abewaa M, Adino E, Mengistu A, Takele T, Oro A, Rangaraju M. Methylene blue adsorption from aqueous solution using activated carbon of *Spathodea campanulata*, Results in Engineering. 2024; 21: 101910. https://doi.org/10.1016/j.rineng.2024.101910

3. Ravikumar M, King P. Equilibrium, kinetic and thermodynamic studies of Congo red biosorption from textile wastewater using *spathodea campanulata* leaves. Rasayan J. Chem. 2019; 12 (4): 2318-27

4. Dada EO, Ojo IA, Alade AO, Afolabi TJ, Amuda OS, Jameel AT. Biosorption of Bromophenol Blue from Aqueous Solution Using Flamboyant (*Delonix regia*) Pod. Chemical Science International Journal. *2020; 29(5): 32-50*. http://www.journalcsij.com/index.php/CSIJ

5. Saravanan P, Josephraj J, Thillainayagam BP. A comprehensive analysis of biosorptive removal of basic dyes by different biosorbents. Environmental Nanotechnology, Monitoring & Management, 2021; 16:100560. https://doi.org/10.1016/j.enmm.2021.100560

6. Abdulwasiu SO. Biosorption of Heavy Metals from Aqueous Solutions: An Insight and Review. Archives of Industrial Engineering. 2020;3(1): 1-31. 10.31829/2637-9252/aie2020-3(1)-113.

7. Jegan J, Praveen S, Pushpa TB, Gokulan R. Sorption kinetics and isotherm studies of cationic dyes by *Arachis hypogaea* shell derived biochar as low-cost adsorbent. Applied Ecology and Environmental Research 2020; 18(1): 1925–39

8. Esfahlan AJ, Jamei R, Esfahlan RJ. The importance of almond (*Prunus amygdalus L.*) and its by-products. Food Chemistry, 2020;120(2); 349-60, https://doi.org/10.1016/j.foodchem.2009.09.063

9. Khan I, Saeed K, Zekker I, Zhang B, Hendi AH, Ahmad A, Ahmad S, Zada N, Ahmad H, Shah LA, et al. Review on Methylene Blue: Its Properties, Uses, Toxicity and Photodegradation. Water. 2022; 14(2):242. https://doi.org/10.3390/w14020242

10. Alade AO, Amuda OS, Ogunleye OO, Okoya AA. Evaluation of Interaction of Carbonization Temperatures and Concentrations on the Adsorption Capacities and Removal Efficiencies of Activated Carbons Using Response Surface Methodology (RSM). J Bioremed Biodegrad 2012;3:134. doi:10.4172/2155-6199.1000134

11. Aremu MO, Alade AO, Araromi DO, Bello A. Optimization of Process Parameters for the Carbonization of Flamboyant Pod Bark (*Delonix regia*). European Scientific Journal 2017; 13(24): 165. Accessed September 12, 2024. https://eujournal.org/index.php/esj/article/view/9834

12. Alade AO, Amuda OS, Afolabi TJ, Okoya AA. Adsorption of naphthalene onto activated carbons derived from milk bush kernel shell and flamboyant pod. Journal of Environmental Chemistry and Ecotoxicology. 2012; 4(7): 124132.

13. Hesas RH, Wan-Daud WA, Sahu JN, Arami Niya A. Preparation and Characterization of Activated Carbon from Apple Waste by Microwave-Assisted Phosphoric Acid Activation. BioResources, 2013;8(2), 2950-66

14. Freund RJ, Wilson WJ, Mohr DL. Multiple Regression. In: Freund RJ, Wilson WJ, Mohr DL (eds) Statistical Methods (3rd Ed) Academic Press, 2010, pp. 375-471. https://doi.org/10.1016/B978-0-12-374970-3.00008-1

15. Lori M, de Lima VL, Martello S, Miyazawa FK, Monaci M. Exact solution techniques for two-dimensional cutting and packing. European Journal of Operational Research. 2021; 289(2): 399-415. https://doi.org/10.1016/j.ejor.2020.06.050

16. Hijazi A, Mcheik A, Rammal H, Annan WR. Biosorption of Methylene Blue from Waste Water using Lebanese *Cymbopogon citratus*. European Scientific Journal, 2015;11(21): 27-51.

17. Patilea V, Sánchez-Sellero C. Testing for lack-of-fit in functional regression models against general alternatives. Journal of Statistical Planning and Inference. 2020; 209: 229-51. https://doi.org/10.1016/j.jspi.2020.04.002

18. Montgomery DC. Design and Analysis of Experiments. 6th Edition, New York, John Wiley & Sons; 2005. New York.

19. Draper NR, Smith H. (1998) On Worthwhile Regressions, Big F's, and R2. In: Applied Regression Analysis [Internet]. John Wiley & Sons, Ltd; 243-250. Accessed on 03 sept 2024. https://onlinelibrary.wiley.com/doi/abs/10.1002/9781118625590.ch11.

20. Chatterjee S, Hadi AS. Regression analysis by example. John Wiley & Sons; 2015.

21. Kiernan D. Natural Resources Biometrics. Suny Open Textbooks 2012. Accessed 12 September 2024. Available: https://textbooks.opensuny.org/natural-resources-biometrics/.

22. Mandlik SK, Adhikari S, Deshpande A. Application of Simplex Lattice Design in Formulation and Development of Buoyant Matrices of Dipyridamole. Journal of Applied Pharmaceutical Science 2012; 2(12):107-111. DOI: 10.7324/JAPS.2012.21221

23. Nouioura G, Tourabi M, El Ghouizi A, Kara M, Assouguem A, Saleh A, et al., Optimization of a New Antioxidant Formulation Using a Simplex Lattice Mixture Design of *Apium graveolens L.*, *Coriandrum sativum L.*, and *Petroselinum crispum M.* Grown in Northern Morocco. Plants (Basel). 2023;12(5):1175. doi: 10.3390/plants12051175. PMID: 36904035; PMCID: PMC10005385.

24. Chitturi SR, Ratner D, Walroth RC, Thampy V, Reed EJ, Dunne M, Tassone CJ, Stone KH. Automated prediction of lattice parameters from X-ray powder diffraction patterns. J Appl Crystallogr. 2021;54:1799-1810. doi: 10.1107/S1600576721010840. PMID: 34963768; PMCID: PMC8662964.