Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: Optimization by response surface methodology

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A B S T R A C T

Activated carbon, prepared from an agricultural waste, cashew nut shell (CNS) was utilized as an adsorbent for the removal of methylene blue (MB) dye from aqueous solution. Batch adsorption study was carried out with variables like pH, adsorbent dose, initial dye concentration and time. The response surface methodology (RSM) was applied to design the experiments, model the process and optimize the variable. A 2^4 full factorial central composite design was successfully employed for experimental design and analysis of the results. The parameters pH, adsorbent dose, initial dye concentration, and time considered for this investigation play an important role in the adsorption studies of methylene blue dye removal. The experimental values were in good agreement with the model predicted values. The optimum values of pH, adsorbent dose, initial dye concentration and time are found to be 10, 2.1846 g/L, 50 mg/L and 63 min for complete removal of MB dye respectively.

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1. Introduction

Synthetic dyes are being extensively used in various industrial dyeing and printing processes. The textile industry is the largest consumer of synthetic dyes utilizing about 56% of the total world dye production per annum (7 x 10^8 t) [1,2]. The dye effluents are considered to be highly toxic to the aquatic species and affect the symbiotic process by disturbing the natural equilibrium by reducing photosynthetic activity and primary production due to the colorization of the water [3]. Effluents contain significant level of organic contaminants, which are toxic as they create odor, bad taste, unsightly color, foaming, etc. These substances are often resistant to degradation by biological methods and are not removed effectively by conventional physico-chemical treatment methods. Removal of these dyes from effluents in an economic fashion remains a major problem for textile industries [4,5]. The most commonly used methods for color removal are biological and chemical precipitation. However, these processes are effective and economic only in cases where solute concentrations are relatively high [6]. There are advantages and disadvantages of various methods of dye removal from the wastewaters [7]. Many physicochemical methods have been tested, but only that of adsorption was considered to be superior to other techniques. This is attributed to its low cost, easy availability, simplicity of design, high efficiency, easy operation, biodegradability and ability to treat dyes in more concentrated forms [8,9]. The adsorption technique has been proven to be an excellent way to treat effluents, offering advantages over conventional process, especially from the environmental point of view [4]. Weber and Morris [4] had identified many advantages of adsorption over several other conventional treatment methods. The adsorption of dyes onto various types of materials has been studied in detail. These include activated carbon [10], peat [11], chitin [12], silica [13], hardwood [14], hardwood sawdust [15], bagasse pith [16], fly ash [17,18], mixture of fly ash and coal [19], chitosan fiber [20], paddy straw [21], rice husk [22], slag [23], chitosan [24], acid treated spent bleaching earth [25], palm fruit bunch [26], bone char [27], copper-doped zinc sulfide nanoparticles loaded on activated carbon [28], gold nanoparticles loaded on activated carbon [29], copper nanowires loaded on activated carbon [30] and tin sulfide nanoparticle loaded on activated carbon [31]. Activated carbon adsorption is one such method which has a great potential for the removal of dyes from wastewater [32–37]. Carbon is being used as a potential adsorbent because of its high efficiency [38]. Commercially available activated carbons are usually derived from natural materials such as wood or coal which is considered expensive [39]. Enhancement of the price of activated carbon results in economic difficulties for developing countries like India. Hence, alternate adsorbents with an equivalent potential of activated carbon are the current thrust area of research. Consequently, low-cost activated carbons based on agricultural solid wastes are being investigated for a long time.

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http://dx.doi.org/10.1016/j.wri.2015.07.002
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Agricultural byproducts and waste materials used for the production of activated carbons include plum kernels [40], cassava peel [41], bagasse [42], jute fiber [43], palm-tree cobs [44], rice husks [45], olive stones [46], date pits [47], fruit stones and nutshell [48], rattan sawdust [49], peach stones [50], oil palm shell [51], orange peel carbon [52] and Egyptian rice hull [53].

Methylene blue, a basic dye, used for dyeing of silk, leather, plastics, paper, and cotton mordant with tannin, as well as for the production of ink and copying paper in the office supplies industry [54–61]. The discharge of this dye to the environment is disturbing for both toxicological and aesthetic reasons as dyes impede light penetration, damage the quality of the receiving streams and are toxic to food chain organisms [62]. The chemical structure of methylene blue dye is given in Fig. 1. Since this dye has a synthetic origin and complex aromatic molecular structures, it is an inert and difficult to biodegrade when discharged into waste streams. This aspect has always been overlooked in their discharge [63]. The removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic and, consequently, their treatment cannot depend on biodegradation alone [64,65].

The present investigation deals with removal of methylene blue dye from the aqueous solution by adsorption onto activated carbon prepared from the new, low-cost agricultural waste, cashew nut shell and optimization of process variables such as solution pH, adsorbent dose, initial dye concentration, and time using Response Surface Methodology. The conventional and classical methods of studying a process by changing one variable at a time and maintaining other factors of the process at a constant level does not depict the combined effect of all the factors involved. This method is also time consuming and requires large number of experiments to determine optimum levels, which are unreliable. These limitations of the classical method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as Response Surface Methodology (RSM) [66]. Response surface methodology, first described by Box and Wilson [67], is an experimental approach to identify the optimum conditions for a multivariable system. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications [68]. The application of statistical experimental design techniques in adsorption process development can result in improved product yields; reduce process variability, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs [69].

2. Experimental

2.1. Preparation and characterization of CNSAC

The CNS was collected from Pudukkottai District, Tamilnadu, India. It was washed with hot distilled water to remove the dust like impurities. After that it was dried and then the material was finally sieved to discrete sizes. The raw material was then carbonized at 700 °C under nitrogen atmosphere for 1 h. The produced char was then soaked with potassium hydroxide (KOH) at impregnation ratio of 1:1. The mixture was dehydrated overnight in an oven at 105 ± 1 °C, then pyrolysed in a stainless steel vertical tubular reactor and placed in a tube furnace under high-purity nitrogen (99.99%) at flow rate of 150 cm³/min to a final temperature of 850 °C for 2 h soaking. Once the final temperature was reached, the nitrogen gas flow was switched to carbon dioxide and activation was continued for 2 h. The activated product was then cooled to room temperature and washed with deionized water to remove remaining chemical. Subsequently the sample was transferred to a beaker containing 250 mL solution of HCl (about 0.1 mol/L) stirred for 1 h, and then washed with hot deionized water. The textual characterization of the CNSAC was carried out by N₂ adsorption at 77 K using Autosorb I, supplied by Quantachrome Corporation, USA. The Brunauer Emmette Teller (BET) [70] (N₂, 77 K), the most usual standard procedure was used to find the BET surface area, average pore diameter and pore volume of the CNSAC are 984 m²/g, 2.52 nm and 0.552 cm³/g, respectively.

2.2. Adsorbate

Methylene blue dye supplied by Merck India was used as an adsorbate for the present adsorption studies. A stock solution of MB dye solution was prepared (500 mg/L) by dissolving the 0.5 g of dye powder in double distilled water then diluted with double distilled water to obtain desired dye concentration. MB dye has a molecular weight of 373.9 g/mol, which corresponds to methylene blue hydrochloride with three groups of water.

2.3. Analysis

The concentration of MB dye in the supernatant solution before and after adsorption was determined by using a double beam UV–vis Spectrophotometer (Shimadzu, Kyoto, Japan) at 668 nm. It was found that the supernatant from the CNSAC did not exhibit any absorbance at this wavelength and also that the calibration curve is very much reproducible and linear over the concentration range used in this work.

2.4. Adsorption experiment

Adsorption experiments were carried out as per the design developed with the response surface central composite design methodology. The experiments were conducted in 250 mL Erlenmeyer flasks with the working volume of 100 mL of aqueous solution. The initial pH of the solution was adjusted to the desired value by adding 0.1 M NaOH or HCl. The required amount of adsorbent dose was also taken in the flasks. The flasks were shaken for the specified time period in a temperature controlled incubation shaker at 120 rpm. The flasks were withdrawn from the shaker after the desired time of operation. The supernatant and the spent adsorbent were separated by using the centrifugation operation (5000 rpm, R-24 REMI Centrifuge, Mumbai, India). The residual dye concentration in the supernatant was analyzed by using the UV–vis spectrophotometer. Dye concentration in the supernatant was calculated from the calibration curve. The maximum wavelength (λ max) values of the wastewater samples varied by ± 10 nm from the λ max values of pure sample. Each determination is repeated three times and the results given were their average value. The percentage of CR removal was taken as a response (Y) of the experimental design and calculated as.
The adsorption experiments were performed at the specified design are at the operational limits. The center point replicates were chosen to verify any change in the estimation procedure, as a measure of precision property. The experimental plan showing the coded value of the variables together with the dye removal efficiency for MB dye are given in Table 2. For statistical calculations, the variables $X_i$ are coded as $x_i$ according to the following relationship:

$$X_i = \frac{X_i - X_0}{\delta x}$$  \hspace{1cm} (2)

where $x_i$ dimensionless coded value of the variable $X_i$, $X_0$ is the value of the $X_i$ at the center point and $\delta x$ is the step change.

The behavior of the system is explained by the following quadratic equation:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ij} x_i x_j$$ \hspace{1cm} (3)

where $\beta_0$ is the offset term, $\beta_i$ is the linear effect, $\beta_{ij}$ is the squared effect, $x_i$ is the interaction effect, $x_i$-dimensionless coded value of the variable $X_i$.

The results of the experimental design are studied and interpreted by MINITAB 14 (PA, USA) statistical software to estimate the response of the dependent variable.

### Table 2

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<tr>
<th>Sl.no.</th>
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<tr>
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</table>

% MB dye removal = \( \left( \frac{C_f - C_i}{C_i} \right) \times 100 \)  \hspace{1cm} (1)
combinations of the physical parameters using statistically designed experiments in order to study the combined effects of these factors. The main effects of all the variables are presented in Fig. 2. From the figure it was clear that the variables taken into consideration for this investigation plays an important role in the adsorption studies of MB dye removal since each variable has significant contribution on the percentage dye removal. A main effect occurs when the mean response changes across the levels of a factor. The main effect plots were used to plot data means when multiple factors are involved in the system/process and also to compare magnitudes of marginal means. The points in the plot were the means of the response variables at the various levels of each factor, with a reference line drawn at the grand mean of the response data. Grand mean is the mean of all observation, as opposed to the mean of individual variables. The line drawn across the plot (center line) represents the grand mean. From Fig. 2, it is clear that the grand mean of the response falls at around 35% dye removal. Out of the variable considered, adsorbent dose and time are the dominant factors for the percentage of dye removal when compared to other variables.

The effect of pH on the adsorption is significantly changed over the pH value of 2–10. The lowest % removal is recorded at pH 2. This is due to the fact that dyes adsorb poorly when they are ionized [71]. Lower adsorption of MB at acidic pH is probably due to the presence of excess H⁺ ions competing with the cation groups on the dye for adsorption sites. At higher pH, the surface of CNSAC particles may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction [72,73]. The influence of solution pH on the dye removal can also be discussed with the help of zero point charge of the adsorbent (pHZpc). At solution pH is lower than the pHZpc, the adsorbent surface becomes positive. This indicates that the limited dyes removal was observed because of the high competition between the hydronium ions and dye molecules to the adsorbent surface. At solution pH is greater than the pHZpc, the removal of dyes was increased because of the less competition of dye molecules with the hydronium ions to the adsorbent surface [74].

The percentage of dye removal was varied with the varying adsorbent dose and it was increased with the increase in adsorbent dose. At higher adsorbent dose to solute concentration ratio, there is very fast superficial sorption onto the adsorbent surface that produces a lower solute concentration in solute than when adsorbent to solute concentration ratio is lower. The increase in the % of dye removal with increasing adsorbent dose was due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent.

The effect of initial dye concentration on % dye removal, it is evident that the amount of dye adsorbed gets increased with increase in the initial dye concentration, whereas the percent dye removal decreases for an increase in initial dye concentration. The initial dye concentration provides the necessary driving force to overcome the resistance to the mass transfer of MB between the aqueous phase and the solid phase. The increase in initial dye concentration also enhances the interaction between MB and CNSAC. Therefore, an increase in initial concentration of MB enhances the adsorption uptake of MB. The rate of adsorption also increases with the increase in initial dye concentration due to increase in the driving force.

The percentage dye removal increases rapidly with time up to 60 min and thereafter the adsorption rate gets decreased gradually. This indicates that higher the contact time between dye and adsorbent, higher is the removal efficiency till the equilibrium time is reached. The same trend is found by McKay et al. [12] for dye removal on chitin. Aggregation of dye molecules with the increase in contact time makes it almost impossible to diffuse deeper into the adsorbent structure at highest energy sites. This aggregation negates the influence of contact time as the micro pores get filled up and start offering resistance to diffusion of aggregated dye molecules in the adsorbents.

Response surface methodology has been successfully applied for optimizing conditions for MB dye removal. The experimental results are analyzed through RSM to obtain an empirical model for the best response. The regression model equations (second-order polynomial) relating the removal efficiency and process parameters are developed and given in Eq. (4). The mathematical expressions of relationship between the independent variables and dependent response are given in terms of uncoded factors. Apart from the linear effect of the parameter for the dye removal, the RSM also gives an insight into the quadratic and interaction effect of the parameters. These analyses are done by means of Fisher’s ‘F’ test and Student ‘t’ test. The student ‘t’ test is used to determine the significance of the regression coefficients of the parameters. The P values are used as a tool to check the significance of each of the interactions among the variables, which in turn may indicate the patterns of the interactions among the variables. In general, the larger the magnitude of ‘t’ and smaller the value of P, the more significant is the corresponding coefficient term [75]. The regression coefficient, ‘t’ and P values for all the linear, quadratic and interaction effects of the parameters are given in Table 3. From the high ‘t’ values and very smaller ‘P’ values it is observed that the

<table>
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<th>Term</th>
<th>Coefficient</th>
<th>Standard deviation</th>
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<td>R² = 99.7%, R²(adj) = 99.4%</td>
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coefficients for the linear effect, quadratic effect and interaction effects of all the factors are highly significant. The significance of these interaction effects between the variables would have been lost if the experiments are carried out by conventional methods. The experimental results and the results of theoretically predicted responses (using the model equation) are shown in Table 2.

\[ y = (1.230) + (3.340X_1) + (10.619X_2) − (0.252X_3) + (0.900X_4) \\
− (0.263X_1^2) − (4.135X_2^2) + (0.001X_1^2) − (0.006X_2^2) \\
+ (0.345X_1X_2) − (0.005X_1X_3) + (0.025X_2X_4) + (0.012X_3) \\
+ (0.111X_3X_4) − (0.001X_3X_4) \]

(4)

The model Eq. (4) is optimized using Multistage Monte-Carlo Optimization technique [76]. The optimal values of the process parameters are first obtained in coded units and then converted to uncoded units by using Eq. (2). The optimum value of the process variables for the maximum removal efficiency are 10, 2.1846 g/L, 50 mg/L and 62.8693 min for the variables pH, adsorbent dose, initial dye concentration and time respectively. The % dye removal at the optimum conditions simulated from the model is 100%. The experiments are done at the optimum conditions and the % dye removal obtained is 99.97% which has a very close agreement with the model. These results closely agree with those obtained from the response surface analysis, confirming that the RSM could be effectively used to optimize the process parameters in complex processes using the statistical design of experiments.

The statistical significance of the ratio of mean square variation due to regression and mean square residual error is tested using analysis of variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [77]. According to the ANOVA (Table 4), the ‘F’ Statistics values for all regressions are higher. The large value of F indicates that most of the variation in the response can be explained by the regression equation. The associated values of ‘F’ lower than 0.01 indicates that the model is statistically significant [28,29,31,78]. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct and has very good agreement with the experimental value.

The \( F_{\text{Statistics}} \) Values of 161.8 is greater than the tabulated \( F_{14,18} \) indicates that the fitted model exhibits lack of fit of 0.000 at the 99% confidence level. The analysis of variance (ANOVA) indicates that the second-order polynomial model Eq. (4) is highly significant and adequate to represent the actual relationship between the response (percent removal efficiency) and variables, with \( P \) values (0.0000) and a high value of coefficient of determination (99.7%). This implies that 99.7% of the sample variation is explained by the independent variables. The \( R^2 \) value (99.4%) of the models are very close to the values of \( R^2 \), the value of \( R^2 \) always increases by adding terms to the model whereas the value of \( R^2_{\text{adj}} \) will decrease if non-significant terms are added to the model. Hence the value of \( R^2 \) should be very close to the value of \( R^2_{\text{adj}} \). When the values of \( R^2 \) and \( R^2_{\text{adj}} \) differ dramatically, there is a good chance for non-significant terms to be included in the model [79] which means that all the model parameters in the model are very much significant.

The response surface plots to estimate the removal efficiency over independent variables adsorbent dose and time is shown in Fig. 3. The peak of the surface plot shows the optimum value of the % dye removal for the relative effects of variable adsorbent dose and time by keeping the other two variables at the optimum conditions. The response surfaces of mutual interactions between the variables are found to be elliptical. A similar type of trend is observed for heavy metal removal using biosorbent by Gopal et al. [80]. The stationary point or central point is the point at which the slope of the contour is zero in all the directions. The coordinates of the central point within the highest contour levels in each of these figures will correspond to the optimum values of the respective constituents. The maximum predicted yield is indicated by the surface confined in the smallest curve of the surface diagram [80]. The optimum values drawn from these figures are in close agreement with those obtained by optimizing the regression model Eq. (4).

<table>
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<th>Source</th>
<th>Degree of freedom (DF)</th>
<th>Sum of squares (SS)</th>
<th>Mean square (MS)</th>
<th>( F_{\text{Statistics}} )</th>
<th>( P )</th>
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</tr>
<tr>
<td>Interaction</td>
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<td>2393.00</td>
<td>398.83</td>
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</tr>
<tr>
<td>Residual Error</td>
<td>18</td>
<td>160.80</td>
<td>160.80</td>
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<tr>
<td>Lack-of-fit</td>
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<tr>
<td>Pure error</td>
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<td></td>
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<tr>
<td>Total</td>
<td>32</td>
<td>20398.90</td>
<td></td>
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</tbody>
</table>

Table 4

ANOVA results for the quadratic model.

Fig. 3. Response surface plots on the removal of MB dye molecules.

4. Conclusion

A novel, low cost adsorbent prepared from agricultural waste, cashew nut shell, is successfully applied for the removal of methylene blue dye from its aqueous solution. The specific surface area, pore volume and average pore diameter are calculated by BET equation which states the effectiveness of CNSAC adsorbent for the removal of MB from its aqueous solution. The effect of pH, adsorbent dose, initial dye concentration and time on the adsorption is studied with the 33 experiments designed by \( 2^4 \) full factorial central composite designs. This study clearly showed that the response surface methodology is one of the suitable methods to optimize the best operating conditions to maximize the dye removal. The statistical analysis results proved the significance of the model developed from experimental data to optimize the parameters. The experimental values were in good agreement with the model predicted values. The optimum values of pH, adsorbent dose, initial dye concentration and time are found to be 10, 2.1846 g/L, 50 mg/L and 63 minutes for complete removal of MB dye respectively.


