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Auramine ‘O’ dye adsorption onto de-oiled cotton seed cake biochar: process optimization using Response Surface Methodology for maximizing adsorbate removal

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Abstract : Biochar, produced from de-oiled cottonseed cake was used as an adsorbent for Auramine ‘O’ dye removal from the aqueous solution. The effects of adsorbent dose, pH, temperature, initial dye concentration and contact time were investigated and were optimized using Response surface methodology based on Box-Behnken design to identify the conditions that maximize the adsorbate removal. Results indicate that basic pH favours the adsorption. The dye removal increased with increase in process parameters. Freundlich isotherm best fits the experimental data and the adsorption follows pseudo second order kinetics. The optimum conditions identified are pH of 10, initial dye concentration of 20 mg/L and adsorbent dose of 6 mg/L and temperature of 50^0C for 98.98% removal.

Keywords : Pyrolysis, Auramine ‘O’, Adsorption, Isotherm, RSM, De-oiled cotton seed cake.

1. Introduction

Dyes are extensively used in different types of industries[1], such as textiles, pulp and paper, dyeing, tannery, paint industries and also, in the chemical and radiochemical laboratories for the analytical purposes[2, 3]. Waste waters emanating from these industries as well as from biological laboratories are polluted with dyes. In general, dyes are not easily biodegradable and they can deleteriously affect the photosynthetic aquatic life due to reduction in light penetration. Also, many dyes and their reaction products, such as aromatic amines[4] are very harmful due to the presence of toxic or even carcinogenic groups. Therefore, dyes should be removed from effluent water before its discharge to the environment.

Auramine-O ($C_{17}H_{22}ClN_3$), bis[4-(dimethylamino)phenyl] methaniminium chloride, is a dye used traditionally for dyeing silk, leather, cotton, bamboo, linen and paper. The dyes bearing wastewaters have high COD to BOD ratio and they offer considerable resistance to biodegradation due to thermo- and photo-stability of the dyes[5]. Hence, the conventional methods like oxidation or biodegradation used in waste water treatment are insufficient in removing these contaminants. Other procedures, for instance nano-filtration, electro-dialysis, reverse osmosis, coagulation and flocculation and adsorption can be used for the treatment of dye-containing wastewaters [6, 7]. But most of these techniques are limited in their application due to higher cost, sludge production, formation of by-products, long retention time and reduced efficiencies for all the dyes. Adsorption has an edge over other methods when compared in terms of initial cost, simplicity of design, ease of operation, applicability to all dyes and insensitivity to toxic substances [8]. The sludge generated from the treatment can be used as a substrate for solid state fermentation (SSF) by white-rot fungi. Fermented substrate is rich in protein and can be used as a soil conditioner[9].

Various kinds of natural and synthetic adsorbents have been proposed, but adsorption onto activated char has gained wide acceptance due to its relatively high capacity[10] and efficiency. It is cheap and can be produced easily. Carbonaceous sources such as peat, wood, lignite, coal etc. are generally used to produce activated carbon but agricultural wastes having high carbon can be used as a low cost source which will reduce the cost of adsorption process. Numerous low-cost agricultural wastes such as sugar bagasse[11], ginger waste[12], coconut husk[13], bamboo waste[14], coir pith[15], rice husk[16] and apricot[17], Palm kernel shell[18] have been used for the production of activated carbon for the removal of the textile dye effluents. Adsorption onto activated de-oiled soya along with bottom ash of power plant[19, 20] and char produced from de-oiled mahua seed cake[21], mustard de-oiled seed cake[22] have also been observed. In the present study activated bio char produced through the pyrolysis of de-oiled cotton seed cake (DCSC) followed by chemical activation was used for the removal of Auramine 'O' dye. De oiled cotton seeds cakes are residual product after oil extracted from cotton seeds or cotton seeds cakes and usually it is consumed as cattle feed in India.

Pyrolysis is most widely used technique for production of carbon/char. The char obtained by this process usually has high porous structure which correspondingly gives high surface area for adsorption. Surface morphology of the char produced can be changed by activating with chemical reagents like KOH, NaOH, Na_2CO_3, K_2CO_3, H_3PO_4, and $ZnCl_2$. These activating agents affect the porosity, surface area and pore structure of the char. Activation with $ZnCl_2$ and H_3PO_4 results in large surface area in the temperature range of 500^0C to 600^0C while for activation with KOH, NaOH, Na_2CO_3 and K_2CO_3, the temperature requirement is above 800^0C[23].

Present work attempts to conduct the optimization of adsorption process parameters for the removal of Auramine 'O' dye by activated de-oiled cotton seed cake biochar (ABC), using the response surface methodology (RSM)[24, 25] with the process variables being the pH, concentration of adsorbate, adsorbent dose and the temperature. RSM is a collection of the mathematical and statistical techniques based on the fit of polynomial equation to the experimental data, and also, one of the multivariate techniques which can deal with multivariate experimental design, statistical modeling and process optimization[26, 27, 28].

2. Materials and methods

2.1 Preparation of adsorbent

The solvent extracted DCSC, purchased from Indore, India, was dried in hot air oven for 24hrs at the temperature of 50 ± 5^0c and pyrolysed to obtain biochar. The pyrolysis was performed in a pit type furnace with reactor wherein the temperature was raised upto 550^0C at the rate of 20^0C/min and maintained for 1 hr. The produced char was activated by mixing with 85% H_3PO_4 in the ratio of 1:1.5 and heating in a hot air oven at the temperature of 100 ± 5^0C for 6 hours followed by washing with Millipore water till the attainment of neutral pH. It was then dried in the air oven at 80 ± 5^0C temperature for 12 hrs to obtain ABC.

2.2 Preparation of dye stock solution

Auramine-O was purchased from local market at Raipur, India. A dye stock solution of 1000 ppm was prepared and diluted to get the solutions of required concentrations. A calibration curve was also plotted by analysing the different concentrated solutions of Auramine-O dye using UV-visible spectrophotometer at 431 nm.

2.3 Characterisation of ABC

For Fourier transform infrared spectrum (FTIR) analysis, pellets were prepared from the mixture of KBr and biochar. The pellets thus obtained were analysed between frequency ranges of 500 to 4000 cm^{-1} by averaging 16 scans for each spectrum. X-ray powder diffraction (XRD) data were collected on a PANalytical 3 kW X'pert Powder diffractometer using Cu $K\alpha l$ radiation.

2.4 Batch adsorption experiment

The adsorption experiments were conducted in 100 ml conical flasks. 50 ml dye solution of different initial concentrations (1-10 mg/L) was taken for each experiment. Accurately weighed biochar was added to dye solutions and kept in an orbital shaker (D.K. Scientific Technologies, India) at temperature of 30±1^{0}C for 2 h to reach equilibrium of the solid-solution mixture. pH of the solution was measured using pH meter (Chemi Line Technologies, India) and adjusted using 0.1N HCL and 0.1 N NaOH. Similar procedure was followed in another set of flasks, containing the same dye concentration without biochar, to be used as a blank. The standard curve was developed at maximum wavelength (431nm) for Auramine 'O' dye at different concentrations, through the measurement of the dye solution absorbance by UV-visible spectrophotometer (UV-1800, Shidmadzu, Japan).The same spectrophotometer was used to analyse the filtrate obtained from filtration of the samples.

The concentration retained in the adsorbent phase (q_e, mg/g) and dye removal percentage was calculated by using Eq. (1) and (2) respectively:

$$\text{Adsorption Capacity, } q_e = \frac{(C_i - C_f)V}{m} \qquad (1)$$

$$\text{Percentage removal} = \frac{C_i - C_f}{C_i} \times 100 \qquad (2)$$

Where C_i and C_f are the initial and final concentrations (mg/L) of dye, respectively, m is the mass (g) of adsorbent, and V is the volume(L) of the dye solution.

The parameters under study were contact time, pH, initial dye concentration, adsorbent dose and temperature.

2.5. Design of experiments

RSM using Box-Behnken experimental design is utilized for the optimization of process parameters. The four parameters considered for optimization are pH (A), concentration of adsorbate (B), adsorbent dose (C) and temperature (D) while the response variable is percentage removal (Y) of the adsorbate. The Box-Behnken design recommends 27 experiments for a four factor design. The upper , centre and lower level values of the parameters respectively are pH -(3,6.5,10), concentration- (10,15,20 mg/L), adsorbent dose – (6,8,10 g/L) and temperature – (30,40,50 ^{0}C). The experimental conditions with their results are shown in Table 1.

Table-1 Experimental Data

Run	Factor				Y(% R)
	A	B	C	D	
1	3	15	8	50	68.50
2	6.5	15	10	30	84.80
3	3	20	8	40	58.10
4	6.5	15	6	50	79.90
5	10	20	8	40	96.20
6	10	10	8	40	94.20
7	10	15	8	30	94.89
8	3	15	6	40	61.60
9	3	15	10	40	74.20
10	10	15	8	50	95.85
11	6.5	15	10	50	85.94
12	6.5	10	8	30	82.10
13	6.5	15	6	30	76.56
14	6.5	20	6	40	77.02
15	6.5	20	8	50	80.10
16	6.5	15	8	40	81.28

17	6.5	10	10	40	88.37
18	3	15	8	30	65.71
19	6.5	20	8	30	78.06
20	10	15	6	40	94.97
21	6.5	10	8	50	85.80
22	6.5	20	10	40	81.15
23	6.5	15	8	40	81.28
24	10	15	10	40	95.33
25	6.5	15	8	40	81.28
26	3	10	8	40	73.88
27	6.5	10	6	40	79.51

An empirical second degree polynomial equation, which correlates the response to the process variables as represented below, was utilized.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i\ 1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j + \sum_{=i=1}^{n} \beta_{ii} X_i^2 \qquad (3)$$

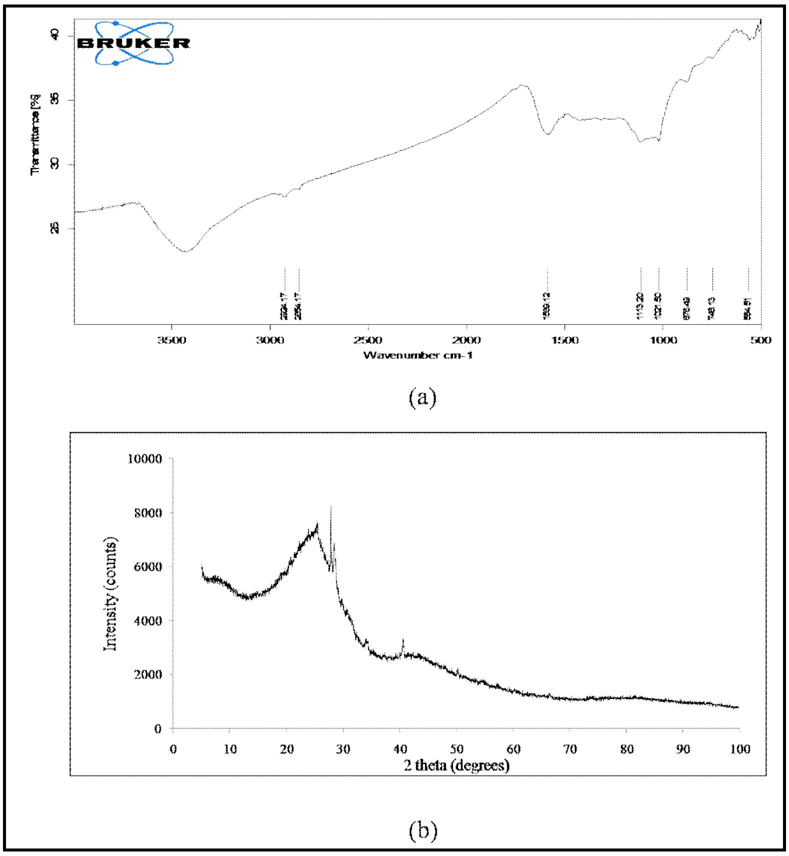
where Y is the predicted response, β_0 is a constant, β_i is the linear coefficient, β_{ij} is the interaction coefficients, β_{ii} is the quadratic coefficients, and X_i and X_j are the coded values of the process variables. The results of experiments were analyzed using statistical computing software Minitab 16.1 utilizing the model equation and the analysis of variance (ANOVA).

3. Results and discussion

3.1 Characterisation of ABC

3.1.1 FTIR and X-ray diffraction analysis

Fig. 1 (a) displays the FTIR spectra obtained for ABC. Each peak in the spectrum corresponds to different bond of different functional groups. Peak between 3500 and 3200 cm^{-1} indicates the presence of O-H stretch bonds of alcohols and phenols. Presence of H-C stretch bond of alkenes is represented by peaks at 2924.17 cm^{-1}. Peaks between 1690 and 1630 cm^{-1} indicate the C=O stretch bond of esters. Peaks between 1320 and 1000 cm^{-1} indicates C-O stretch bonds of alcohols, carboxylic acids, ethers and esters. X-ray diffraction pattern of ABC is shown in Fig. 1 (b). It has crystalline structure as represented by the peaks.



(a)

(b)

Fig 1 (a): FTIR spectrum of ABC, (b) X-ray diffraction pattern of ABC

3.2 Batch adsorption studies

3.2.1 Effect of adsorbent dose

The adsorbent dose was varied from 1g/L to 10 g/L of adsorbent. The adsorption was observed to be increasing upto an optimum adsorbent dose of 6 g/L after that it became constant. The variation is shown in Fig. 2 (a). The increase in percentage removal may be because of increase in surface area and thus due to increase in availability of active sites with increment in adsorbent dose. After the optimal dose, adsorption remains steady. This may be because the initial dye concentration is kept constant while increasing the adsorbent dose i.e. the amount of dye to be removed remains identical.

3.2.2 Effect of pH

pH plays a vital role in the adsorption of dye molecules. The variation in percentage removal with pH is shown in Fig. 2 (b). It is clear that at acidic pH, percentage removal is low and found to increase when the pH was increased upto basic pH. The percentage removal increased from 62.3% to 89.5 % as the pH increases from 3 to 11. A similar trend was seen in Auramine 'O' dye removal by treated ginger waste [6]. At low pH, concentration of H^+ ions is high which will compete with the cations of Auramine 'O' dye[29]. Also the surface of adsorbent get protonated at low pH which develops an electrostatic repulsive force between positively charged adsorbent surface and Auramine 'O' cations. At basic pH, more OH^- ions on the surface of biochar increase the attractive force between dye molecule and surface which tends to increase the amount of adsorption[30, 12].

3.2.3 Effect of contact time

Variation in percentage removal of the dye with contact time is shown in Fig.2 (c). Percentage removal of dye was found to increase with increasing contact time. Adsorption was very rapid in the first 40 min and then it was increased slowly with time until equilibrium was attained. This was due to the reason that initially there is maximum concentration difference (driving force) but with passage of time it decreases. After 90 min, the percentage removal reaches a constant value of 76%, 85.1% and 88.2% corresponding to the temperatures of 293K, 303K and 313K respectively. So, the optimum time needed was 120 min and this time was taken in further experiments.

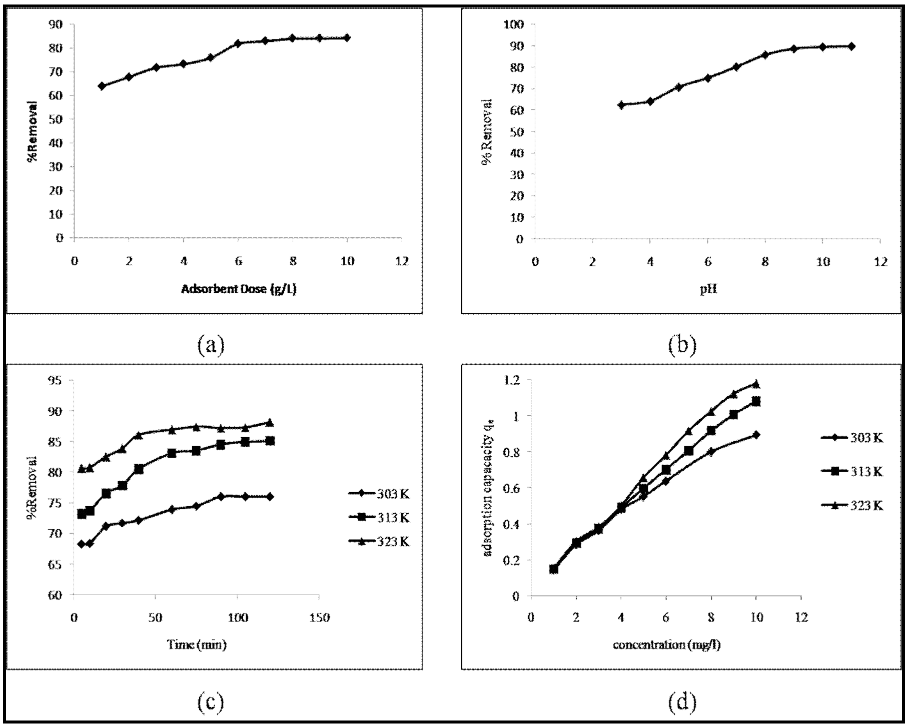


Fig 2 (a). Effect of adsorbent dose, (b) Effect of pH, (c) Effect of contact time, (d) Effect of initial dye concentration

3.2.4. Effect of initial dye concentration

The effect of initial dye concentration was studied by varying the concentration from 1 to 10 mg/L for 0.3 g/50 ml of adsorbent dose. Adsorption capacity was found to increase with initial dye concentration (Fig. 2 (d)), because the resulting higher concentration difference reduces the mass transfer resistances between adsorbent and adsorption media. Initially the number of molecules of adsorbate competing for the available sites on the surface of ABC was high, resulting in higher Auramine 'O' dye adsorption capacities. At lower initial concentrations higher adsorption yields were obtained due to low ratio of dye to the available sorption sites. The percentage of adsorption was observed to decrease with increase in dye concentration. This may be due to saturation of the surface and available active sites of the adsorbent[31].

3.2.5 Effect of temperature

Temperature is an important parameter which determines whether the process is endothermic or exothermic. It is clear that the adsorption capacity and percentage removal are increasing with temperature. At 303K, adsorption capacity was 0.8 mg/g of adsorbent which increased to 1.2 mg/g of adsorbent when the temperature was increased by 30 K. Increase in temperature decreases the solubility of dye molecule thereby increasing the adsorption[32]. Furthermore, at higher temperature, external boundary layer thickness is small[33] and kinetic energy of the molecule is high[34]. These two effects together increase the mobility of dye molecule through the boundary layer hence molecule will get sufficient energy for adsorption. So it can be concluded that the adsorption process of Auramine 'O' dye onto ABC was endothermic in nature.

3.3. Adsorption Isotherm and Kinetics

3.3.1 Adsorption isotherms

The purpose of the isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface. The results were analyzed using the Freundlich, Langmuir, and Temkin isotherms [35]. The basis for Langmuir adsorption model is the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of dyes from aqueous solutions. The expression of the Langmuir model is given by Eq. (4)

$$\frac{C_e}{q_e}=\frac{1}{Q_0 b}+\frac{C_e}{Q_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where C_e (mg/L) and q_e (mg/g) are the unadsorbed dye concentration in the solution and the amount of adsorbed dye per unit mass of the sorbent at equilibrium, respectively.Q_0 is the maximum amount of the dye per unit mass of the sorbent to form a complete monolayer on the surface bound at high C_e, and b (L/mg) is a constant related to the affinity of the binding sites[36] .

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where K_F and n are Freundlich constants with K_F $\{(mg/g)(L/mg)^{1/n}\}$, the adsorption capacity of the sorbent and 1/n, the magnitude of the exponent, gives an indication of the favourability of adsorption. The constants K_F and n, can be determined from the graph of $\ln(q_e)$ vs $\ln(C_e)$.

The Temkin isotherm equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is decreased. This model suggests that the heat of adsorption of all the molecules in the sorbent layer would decrease linearly with increasing adsorption. The Temkin isotherm has generally been applied in the following form:

$$q_T = B_T \ln K_T + B_T \ln C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (6)$$

Where $B_T = (RT)/b$ is the Temkin constant (J/mol) and $K_T = RT/bT$ is related to the heat of adsorption (mg/L). These values can be determined from the graph between $\ln C_e$ vs q_T. Dubinin and Raduskevich (D-R) isotherm is generally used to describe the sorption isotherms of single solute systems. The D-R isotherm apart from being analogue of Langmuir isotherm, is more general than Langmuir isotherm as it rejects the homogeneous or constant adsorption potential. It is expressed as:

$$\ln q_e = \ln q_m - B\varepsilon^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where ε can be correlated as

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(8)$$

where q_m is the maximum amount of adsorbate that can be adsorbed on the adsorbent, B is the constant related to energy and C_e is the equilibrium concentration (mg/L). R is the universal gas constant, 8.314 J/molK, T is the temperature (K). The mean free energy E of the adsorption per molecule of adsorbate can be calculated using the following equation:

$$E=\frac{1}{(2B)^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

The values of coefficients of all the isotherms are given in table 2.

Table 2: Isotherm coefficients for the adsorption of Auramine 'O' dye.

Isotherms	Parameters	303 K	313 K	323 K
Langmuir	Q_0(mg/g) b R^2	1.335 0.472 0.977	2.347 0.250 0.960	3.345 0.185 0.974
Freundlich	K_F(L/g) n R^2	0.178 1.422 0.995	0.484 1.480 0.997	0.656 2.045 0.979
Temkin	B_t(J/mol) K_T(L/mg) R^2	0.372 18.68 0.882	1.398 1.960 0.932	1.273 3.050 0.924
D-R	Q_m(mg/g) K_{ad} R^2	0.560 $6.71*10^{-4}$ 0.931	0.632 $6.71*10^{-4}$ 0.880	0.690 $3.35*10^{-4}$ 0.859

A parameter of the Langmuir isotherm can be expressed in terms of the dimensionless constant called separation factor R_L, to detect the favorability of adsorption process

$$R_L = 1/(1+bC_0) \quad ....(10)$$

where C_0 is the initial concentration of dye and b is the Langmuir constant. The values of R_L indicate the type of the isotherm, irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), and unfavourable ($R_L > 1$). The values of R_L at temperatures 303,313 and 323 K are 0.472, 0.250 and 0.185 respectively, which indicates that the process is favourable in the given temperature range.

3.3.2 Adsorption Kinetics

Kinetic studies are important since it gives the solute uptake rate, which determines the residence time required for completion of adsorption reaction [37]. Also, kinetic information gives a scale of adsorption apparatus and base to determine the performance of adsorption systems. The adsorption kinetic data of dyes are analyzed using the Lagergren first order rate equation given by

$$\log(q_e - q_t) \quad \log q_e - \frac{K_1 t}{2.303} \quad ....(11)$$

where q_e and q are the amounts of dyes adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the Lagergren rate constant of first order adsorption (1/min). Values of q_e and k_1 were calculated from the slope of the plots of log ($q_e - q_t$) versus t.

The second order kinetic model can be represented as [38]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad ....(12)$$

where k_2 is the equilibrium rate constant of second order adsorption (g/ mg min). Values of k_2 and q_e were calculated from the plots of t/q versus t. Values are given in Table 3.

Table 3 : Kinetic constants for Auramine 'O' adsorption on ABC

Temp. (K)	$Q_{e,exp}$ (mg/g)	Pseudo first order			Pseudo second order		
		$Q_{e,calc}$ (mg/g)	K_1 (1/min)	R^2	$Q_{e,calc}$ (mg/g)	K_2 (g /mg min)	R^2
303	0.89	0.00069	0.007	0.977	1.270	0.723	0.999
313	1.13	0.05800	0.023	0.920	1.472	0.205	0.999
323	1.18	0.01000	0.013	0.979	1.483	0.415	0.999

3.4 RSM Modelling

The polynomial regression equation constructed by Box-Behnken method was used to analyze the correlation between the process variables and the response variable. The percentage removal was found to vary from 58.10 to 96.20% in response to variations in the experiments. The final empirical model in terms of coded factors is

$$\begin{aligned}Y&=81.28+14.12A-2.77B+3.35C+1.164D-0.325A^2-0.2B^2+0.414C^2 0.27D^2+4.41A*B\\&-3.06A*C-0.46A*D-1.18B*C-0.415B*D-0.55C*D\end{aligned} \qquad \ldots\ldots.(13)$$

The appropriateness of a model equation to fit the experimental responses can be assessed based on the coefficient of determination (R^2) which is the ratio of explained to total variation[39]. The R^2 value for percentage removal (Y) is 0.999 which is close to unity, indicating appropriateness of the model equation in fitting the data. The coefficients of the model equation along with the significance of each of the model parameters are listed in Table 4. The lower the value of P or higher the value of F or T, the more significant are the model parameters[40].

Table 4: Estimated coefficients using response surface quadratic model for adsorbate removal

Term	Coefficient	T	P
Constant	81.2800	201.281	0.000
A	14.1208	69.938	0.000
B	-2.7629	-13.715	0.000
C	3.3525	16.604	0.000
D	1.1642	5.766	0.000
A*A	-0.3254	-1.074	0.304
B*B	-0.1929	-0.637	0.536
C*C	0.4146	1.369	0.196
D*D	0.2721	0.898	0.387
A*B	4.4450	12.710	0.000
A*C	-3.0600	-8.750	0.000
A*D	-0.4575	-1.308	0.215
B*C	-1.1825	-3.381	0.005
B*D	-0.4150	-1.187	0.258
C*D	-0.5500	-1.573	0.142

$R^2 = 99.79\%$, $R^2(\text{adj}) = 99.54\%$

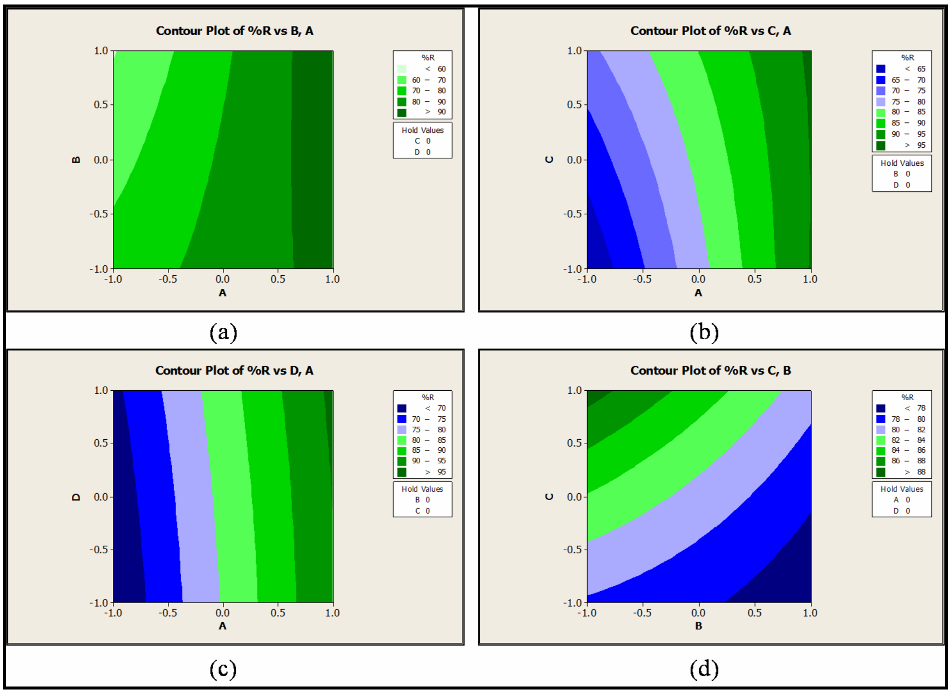
Table 5: Analysis of Variance (ANOVA) for RSM model for adsorbate removal

Source	df	Sum of squares (SS)	Mean squares (MS)	F	P
Model	14	2763.82	197.42	403.55	0.000
Linear	4	2635.93	658.98	1347.08	0.000
Square	4	3.07	0.77	1.57	0.245
Interaction	6	124.822	20.8	42.52	0.000
Residual error	12	5.87	0.49	-	-
Lack of fit	10	5.87	0.59	-	-
Pure Error	2	0.00	0.00	-	-
Total	26	2769.69			

Table 5 shows the results of ANOVA for adsorbate removal. 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[24]. In ANOVA, the sum of squares is used to estimate the square of deviation from the grand mean and mean squares are estimated by dividing the sum of squares by degrees of freedom. F-ratio is defined as the ratio of mean square for the term to the mean square for the residual[39]. The ANOVA of these models demonstrates that the models are highly significant, as it is evident from the F value (403.55) and probability value ($P < 0.05$) for Y.

3.4.1 Adsorbate removal

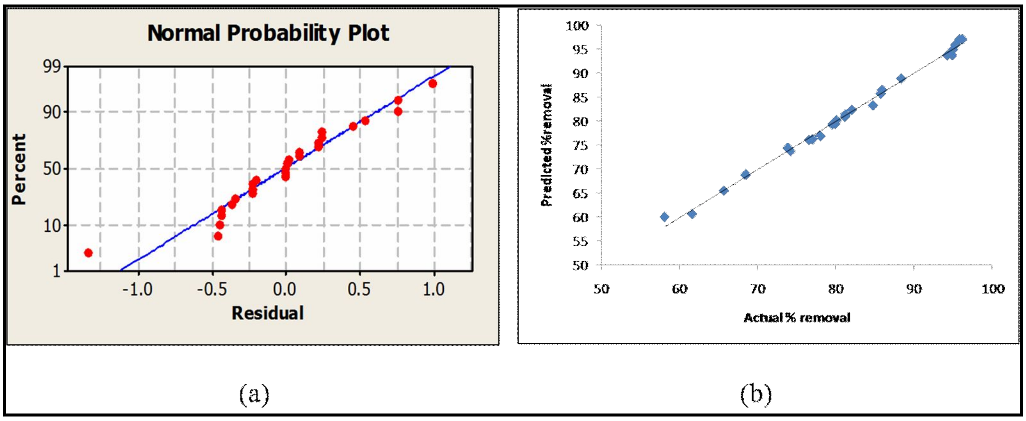
The effects of pH, adsorbate concentration, adsorbent dose and temperature on adsorbate removal were studied. Fig. 3(a) shows the contour plot of adsorbate removal with respect to the pH and adsorbate concentration, while Fig. 3(b) shows the contour plot of adsorbate removal with respect to the pH and adsorbent dose, 3(c) shows the contour plot of adsorbate removal with respect to the pH and temperature, 3(d) shows the contour plot of adsorbate removal with respect to the adsorbate concentration and adsorbent dose with the other process parameters fixed in the mid-range. The removal was found to increase with increase in pH and decreases with increase in adsorbate concentration. From Fig. 3(b) and 3(c), the removal increases with increase in dose and temperature.



(a) (b)

(c) (d)

Fig. 3(a) Contour plot of pH and adsorbate concentration on adsorbent removal, (b) Contour plot of pH and adsorbate dose on adsorbent removal, (c) Contour plot of pH and temperature on adsorbent removal, (d) Contour plot of adsorbate concentration and adsorbate dose on adsorbent removal



(a) (b)

Fig:4(a) Normal probability vs residuals for adsorbate removal, (b) Predicted versus Experimental % removal

The normal probability plot is shown in Fig. 4 (a). It indicates that errors are normally distributed, as all the points lie close to diagonal line. Fig. 4 (b) shows the comparison of predicted removal with experimental removal of adsorbate.

3.4.2. Process optimization

he optimum process conditions were estimated using the optimizer tool in Minitab 16.1. The values are provided in the form of graph (Fig. 5). The optimum process conditions estimated are pH value of 10, adsorbate concentration of 20 mg/L, adsorbent dose of 6 g/L and temperature of 50^{0}C to obtain maximum removal of 98.97%.

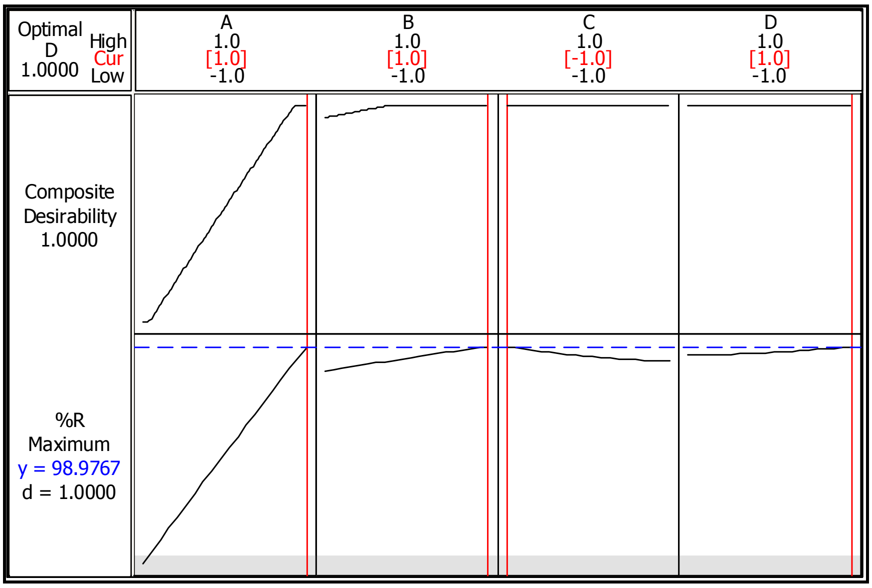


Fig. 5: Graphical representation of numerical optimisation of all factors and responses

4. Conclusion

ABC was prepared through pyrolysis followed by chemical activation with H_3PO_4 and used as an adsorbent for dye removal. It was found suitable for adsorption of Auramine ‘O’ dye from the aqueous solution. The functional groups on the adsorbent are given by FTIR spectrum. Analysis of X-ray diffraction pattern shows its crystalline structure. Percentage removal increased with pH up to pH 10 and then it becomes constant. The process is endothermic in nature. Effects of pH, adsorbent dose, contact time and temperature were studied and found that percentage removal increases with these parameters. Freundlich isotherm best fits the process. R_L values between zero and one show that the adsorption was favourable in the temperature range of 303K to 323K. Adsorption follows pseudo second order kinetic model. Process optimization was performed to obtain conditions that maximize the adsorbate removal. The regression equations follows the experimental data with good accuracy (R^2 = 0.994). The optimum conditions obtained from Box-Behnken design are pH value of 10, adsorbate concentration of 20 mg/L, adsorbent dose of 6g/L and temperature 50^{0}C for 98.98% removal.

Nomenclature

C_i :	Initial concentration of Auramine ‘O’ dye
C_f:	Final concentration of Auramine ‘O’ dye
m:	Mass of adsorbent
V:	Volume of the Auramine ‘O’ solution
qe:	Amount of Auramine ‘O’ adsorbed per unit mass of the adsorbent
q:	The amount of Auramine ‘O’ is adsorbed at time t
% R:	Percentage removal of Auramine ‘O’
Q_0:	Maximum adsorption capacity (Langmuir parameter)
K_1:	Rate constant of pseudo-first-order kinetics
K_2:	Rate constant of pseudo-second-order kinetics

R_L:	Free energy of adsorption (Langmuir parameter)
b:	Langmuir isotherm constant
K_T:	Equilibrium binding constant
K_F:	Freundlich adsorption coefficient
B_1:	Constant related to the heat of sorption.
B:	Constant of the D-R isotherm
FTIR:	Fourier transform infrared spectroscopy
PPM:	Parts per million
ANOVA	Analysis of Variance
DCSC	De-oiled cotton seed cake
ABC	Activated de-oiled cotton seed cake biochar

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