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Short communication

Optimization of process parameters for acrylonitrile removal by a low-cost adsorbent using Box–Behnken design

Arvind Kumar [1], B. Prasad *, I.M. Mishra

Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India

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Abstract

In the present work, acrylonitrile removal from wastewater was investigated using an agri-based adsorbent-sugarcane bagasse fly ash (BFA). The effect of such parameters as adsorbent dose (w), temperature (T) and time of contact (t) on the sorption of acrylonitrile by BFA was investigated using response surface methodology (RSM) based on Box–Behnken surface statistical design at an initial acrylonitrile concentration, $C_0 = 100$ mg/l as a fixed input parameter. The results of RSM indicate that the proposed models predict the responses adequately within the limits of input parameters being used. The isotherm shows a two-step adsorption, well represented by a two-step Langmuir isotherm equation. Thermodynamic parameters indicate the sorption process to be spontaneous and exothermic.

Keywords: Box–Behnken; Response surface methodology (RSM); Acrylonitrile; Adsorption; Bagasse fly ash (BFA); Langmuir isotherm; Thermodynamics

1. Introduction

Acrylonitrile (AN) is an important industrial raw material frequently used in the manufacture of AN-butadiene-styrene (ABS) and AN-styrene (AS) resins [1]. AN is emitted from the industrial plants in the form of vapours and aqueous effluents; and is toxic and hazardous to aquatic life as well as human beings [2–4]. AN is the third in the EPA list of 129 priority pollutants [5]. Cyanide bearing effluents cannot be discharged without detoxification into the environment. The US-Health Service cites 0.01 mg/l as the guideline and 0.2 mg/l as the permissible limit for cyanides in water. The German and Swiss regulations have set limits of 0.01 mg/l for cyanide for surface water and 0.5 mg/l for sewers [6]. The Central Pollution Control Board (CPCB), Delhi, India has set a minimal national standard (MINAS) for cyanide as 0.2 mg/l in the industrial discharges into surface waters [7]. The effluents generated from industries are required to be given a treatment to bring down the cyanide level $\leq$0.2 mg/l [6,7]. Thus, the concentration of AN in the wastewater to be discharged into surface waters should not exceed 0.2 mg/l. In a typical AN manufacturing unit, the low-volume wastewater obtained from the quench tower has high AN concentration in the range of 1000–2000 mg/l. However, the high volume wastewaters emanating from other sections of the unit contain AN in the range of 50–100 mg/l only. In such wastewaters, AN is present along with several other toxicants of AN family, namely, acrylic acid, acetonitrile, etc. Such wastewaters also have dissolved solids and heavy metals, high alkalinity and corresponding chemical oxygen demand (COD). The characteristics of a typical wastewater from the quench tower of an acrylonitrile plant in India are given in Table 1. This wastewater is concentrated and is almost always incinerated in the incinerator. However, the high volume wastewaters containing low concentrations of AN are generally sent to the biological treatment unit. The biological treatment unit, however, is not amenable to adapt to shock loads due to nitrile toxicity exerted on the microbial mass.

Several treatment methods, particularly biological or a blend of wet oxidation followed by biological treatment, have been used for the removal of AN from wastewaters [6,8]. Adsorption is also a very attractive treatment method for the removal of toxics from wastewaters. Apart from activated carbons, which suffer from high cost and loss during regeneration [9], several agri-based low-cost adsorbents have been used for the treatment of industrial wastewaters. Bagasse fly ash (BFA), which is

* Corresponding author. Tel.: +91 1332 285323; fax: +91 1332 2725736.
E-mail addresses: arvinpch@yahoo.co.in (A. Kumar), bashefch@iitr.ernet.in (B. Prasad), imishfch@iitr.ernet.in (I.M. Mishra).
[1] Present address: Department of Chemical Engineering, National Institute of Technology Rourkela, Rourkela 769008, Orissa, India.

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Table 1
Characteristics of a typical petrochemical industrial waste

Characteristics	Value
TDS (mg/l)	265,500
Conductivity (μS/m)	408,500
pH	8.2
Turbidity (NTU)	850
COD_{avg}(mg/l)	355,000
Alkalinity (mg/l)	30,000
Sodium (mg/l)	9600
Nitrate (mg/l)	8675
Sulphate (mg/l)	130,000
BOD_{avg} (3 days) at 27 °C (mg/l)	30,000
Acrylonitrile (mg/l)	1000–2000
Acrylic acid (g/l)	15,000
Acetonitrile (mg/l)	178
Adiponitrile (mg/l)	68
Benzonitrile (mg/l)	27
CN^- (mg/l)	50
Total CN (mg/l)	1500
Cd (mg/l)	14
Ni (mg/l)	56.4
Mn (mg/l)	9.7
Fe (mg/l)	89

obtained from the particulate removal equipment attached to the flue gas line of a bagasse fired boiler upstream of the stack, has been used by a number of investigators for the removal of COD, colour, dyes, heavy metals and volatile organics like pyridine and its derivatives [9–14]. It is available almost at a throwaway price and has a very high pollutant loading capacity, 20–30 mg/g for AN in the aqueous solution.

The objective of the present study is to investigate the feasibility of using BFA for the adsorptive removal of AN from aqueous solution having AN concentration of 100 mg/l. The study uses the Box–Behnken design in the optimization of experiments using RSM [15,16] to understand the effect of important parameters and their interactions on the adsorption process. The parameters used are the BFA dosage (w), temperature (T) and contact time (t) between BFA and AN bearing aqueous solution at the natural pH of the solution.

2. Experimental

2.1. Adsorbents and adsorbate

BFA used in the present work as an adsorbent was obtained from Deoband Sugar Mills, Deoband, U.P. (India). Detailed physico-chemical characteristics of the BFA have been presented in Table 2. Laboratory grade AN, inhibited with 200 mg/l hydroquinone mono methyl ether and supplied by S.D. Fine Chemicals Ltd., Mumbai, was used for the preparation of synthetic aqueous solution of AN of initial concentration, $C_0 = 100$ mg/l. The required quantity of the adsorbate was accurately weighed and dissolved in a small amount of double distilled water (DDW) and subsequently made up to 1 l in a measuring flask by adding DDW. Fresh stock solution as required was prepared everyday and was kept at ambient conditions in a glass stoppered glass container. The C_0 was ascertained before the start of each experimental run.

The specific surface area and the pore diameter of the adsorbent were measured via a nitrogen adsorption isotherm using an ASAP 2010 Micromeritics instrument and the data were analyzed by using the Micromeritics software. Scanning electron microscope (SEM) (Model Leo, 4 3SVP) was used to obtain micrographs of BFA particles.

FTIR spectra were obtained with a spectrometer (Nicolet Model Avtar 370 Csl, Thermo Electron Corporation, USA) using a pellet (pressure disk) technique. The pellets were prepared with KBr. The spectral range covered was 4000–400 cm^{-1}.

2.2. Batch experimental program

For each experiment, 50 ml of AN solution of known C_0 and a known amount of the BFA were taken in a 100 ml airtight conical flask with a glass stopper. This mixture was agitated in a temperature-controlled shaking water bath at a constant shaking speed of 250 rpm. The percentage removal (Y) of AN and the

Table 2
Physico-chemical characteristics of BFA

Characteristics	Value
Proximate analysis (sample as received) (%)	
Moisture	3.39
Ash	72.60
Volatile matter	4.81
Fixed carbon	19.20
Bulk density (kg/m^3)	185.51
Heating value (MJ/kg)	19.23
Average particle size (mm)	167.35
Ultimate analysis (dry basis) (%)	
C	16.36
H	9.77
N	2.55
S	–
Chemical analysis of ash (%)	
Insoluble Matter	78.35
Silica	2.46
Ferric and alumina	2.92
CaO	14.00
Mg	1.09
Surface area (m^2/g)	
BET	379.64
Langmuir	445.59
t-plot micropore	421.20
t-plot external	24.39
Single point surface area	376.22
BJH adsorption cumulative	29.83[a]
Pore volume (cm^3/g)	
Single point total pore volume	0.298
t-plot micropore volume	0.145
Meso-pore volume	0.153
BJH adsorption cumulative	0.032
Pore size (Å)	
BET Adsorption average pore width	31.45
BJH adsorption average pore diameter	49.30

[a] Pores between 17 and 3000 Å.

uptake of AN by BFA at any time, t was calculated as:

$$Y = 100\frac{C_0 - C_t}{C_0} \quad (1)$$

$$q_t = (C_0 - C_t)\frac{V}{w} \quad (2)$$

where C_0 is the initial adsorbate concentration (mg/l), V the volume of the wastewaters in the flask, C_t the adsorbate concentration (mg/l) after time t and w is the mass of the BFA (g) used in the experiment. At equilibrium conditions, q_t and C_t are replaced by q_e and C_e, respectively.

2.3. Analytical measurements

The concentration of AN in the aqueous solution was determined by using a high performance liquid chromatograph (HPLC) (Waters (India), Bangalore) at 196 nm wavelength [17]. Noval Pack, C18 column (size: 3.9 mm × 150 mm) was used in the HPLC for the measurement of AN. Degassed organics-free water was used as the solvent, keeping a flow rate of 1 ml/min as per specifications given in the user manual of the instrument. The calibration curve of the peak area versus AN concentration was used for the determination of the unknown concentration of AN from a sample. Wherever needed, the sample was appropriately diluted to have the AN concentration in the calibration range.

2.4. Box–Behnken design

The Box–Behnken design optimizes the number of experiments to be carried out to ascertain the possible interactions between the parameters studied and their effects on the removal of AN. Box–Behnken design is a spherical, revolving design; it consists of a central point and the middle points of the edges of the cube circumscribed on the sphere [18]. It is a three-level fractional factorial design consisting of a full 2^2 factorial seeded into a balanced incomplete block design. It consists of three interlocking 2^2 factorial designs having points, all lying on the surface of a sphere surrounding the center of the design. It has been applied for optimization of several chemical and physical processes; and the number of experiments are decided accordingly [19].

In the present study, the three-level three-factorial Box–Behnken experimental design is applied to investigate and validate adsorption process parameters affecting the removal of AN by BFA. Adsorbent dose (5–20 g/l), temperature (30–60 °C) and the contact time (5–295 min) are variable input parameters, while AN concentration of 100 mg/l was kept as a constant input parameter at its natural pH 6.46. The factor levels were coded as −1 (low), 0 (central point or middle) and 1 (high) [18].

Table 3 shows the experimental parameters and the experimental Box–Behnken design levels used. RSM was applied to the experimental data using statistical software, Design-expert V6 (trial version). Statistical terms and their definitions used in the Design-expert software are well defined elsewhere [20]. Linear and second order polynomials were fitted to the experimental data to obtain the regression equations. The sequential F-test, lack-of-fit test and other adequacy measures were used in selecting the best model [21]. To analyze a process or system including a response Y, where Y depends on the input factors x_1, x_2, …, x_k, the relationship between the response and the input process parameters are described as:

Table 3
Experimental design levels of chosen variables

Variables	Levels in Box–Behnken design		
Coded level	Low (−1)	Middle (0)	High (+1)
Dose, w (g/l)	5	12.5	20
Temperature, T (°C)	30	45	60
Time, t (min)	5	150	295

$$Y = f(x_1, x_2, \ldots, x_k) + \varepsilon \quad (3)$$

where, f is the real response function its format being unknown, and ε is the residual error which describes the differentiation that can be included by the function f. Because the relationship between the response and the input parameters can be described as a surface of the x_1, x_2, …, x_k coordinates in the graphical sense, so the study of these relationships is named as the response surface study. The same statistical software was used to generate the statistical and response plots. A manual regression method was used to fit the second order polynomial Eq. (4) to the experimental data and to identify the relevant model terms. Considering all the linear terms, square terms and linear by linear interaction items, the quadratic response model can be described as:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_{ii}^2 + \sum \beta_{ij} x_i x_j + \varepsilon \quad (4)$$

where β_o is the constant, β_i the slope or linear effect of the input factor x_i, β_{ij} the linear by linear interaction effect between the input factor x_i and x_j, β_{ij} is the quadratic effect of input factor x_i [22].

3. Results and discussion

3.1. Adsorbents characterization

The physicochemical characteristics of BFA are given in Table 2. BFA has very low-carbon content and low-surface area and porosity. The SEM micrographs presented in Fig. 1 show the surface texture and porosity of the blank, water loaded and AN loaded BFA particles. It is seen that the surface texture of the blank BFA changes drastically after AN loading.

BFA also has a wide pore size distribution giving a wide distribution of surface area, as can be seen from Fig. 2. The size analysis shows the dominance of micro pores ($d < 20$ Å) with pore surface area being 379.64 $m^2\ g^{-1}$. The BJH pore area ($17 < d < 2000$ Å) is found to be 29.83 $m^2\ g^{-1}$. The BET average pore size is 31.45 Å and the BJH average pore size is 43.31 Å. The pore size, area and volume distribution shows the heterogeneity of the BFA surface.

The FTIR spectra of the blank and AN loaded BFA are shown in Fig. 3. A broad band between 3100 and 3700 cm^{-1}

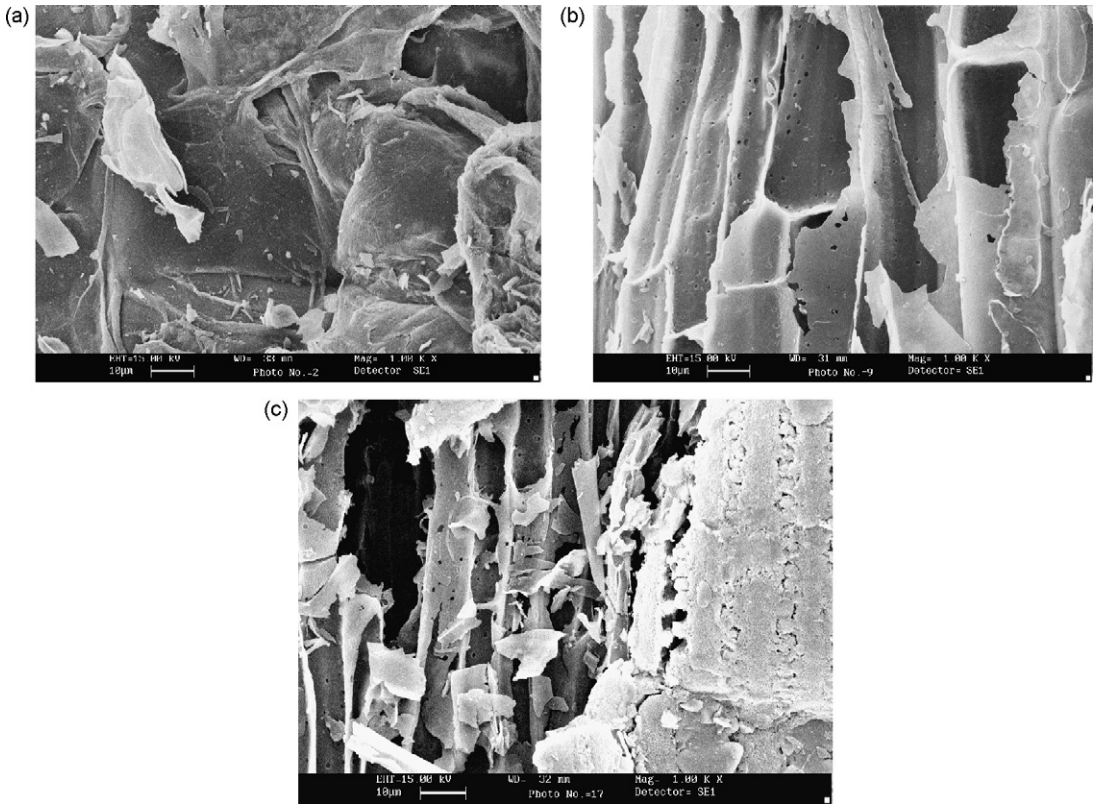

Fig. 1. SEM of (a) BFA virgin, (b) Water loaded BFA and (c) AN loaded BFA at 1.00 K×.

indicates the presence of both free and hydrogen bonded –OH groups on the adsorbent surface. This stretching is due to both the silanol group (Si–OH) and adsorbed water (peak at 3400 cm^{-1}) on the surface. The bands appearing in spectra of virgin BFA at 3452 cm^{-1} indicate hydrogen bonding; and at 2921 and 2847 cm^{-1} is assigned to O–H stretching vibration originating in the molecule. The bands appearing at 1626 cm^{-1} are assigned to symmetrical CO_2^- stretching. In loaded spectra of AN–BFA adsorption system, various new bands highlight the spectra. The peaks at 1604 and 1460 cm^{-1} correspond to C=C stretching. Bands appearing at 1247–1121 cm^{-1} are due to CH_2 deformation. The spectral analysis shows the heterogeneous nature of the BFA surface. Comparing the spectra for virgin BFA and AN-loaded BFA, it appears that a number of peaks corresponding to various functional groups –COO^-, –OH and Si–OH disappear after the AN loading onto BFA. This indicates that these functional groups are effective in the sorption process of AN onto BFA. It is also found that the spectra for a virgin BFA have less FTIR bands than the AN loaded BFA spectra. It appears that new functional groups get formed on the heterogeneous surface after the AN loading onto BFA.

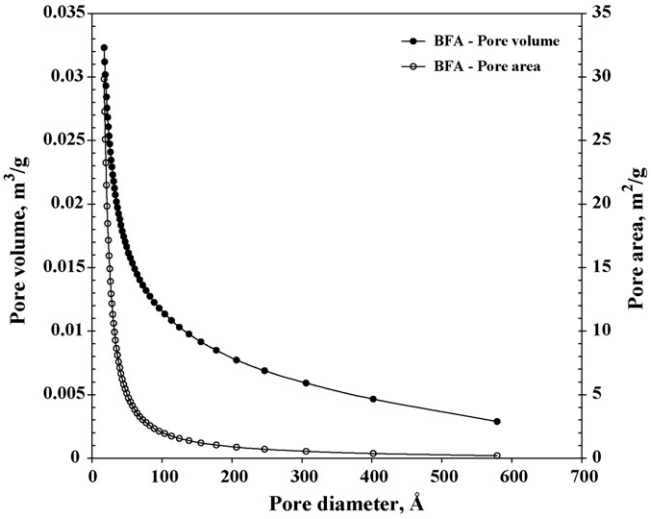

Fig. 2. Pore size distribution of BFA.

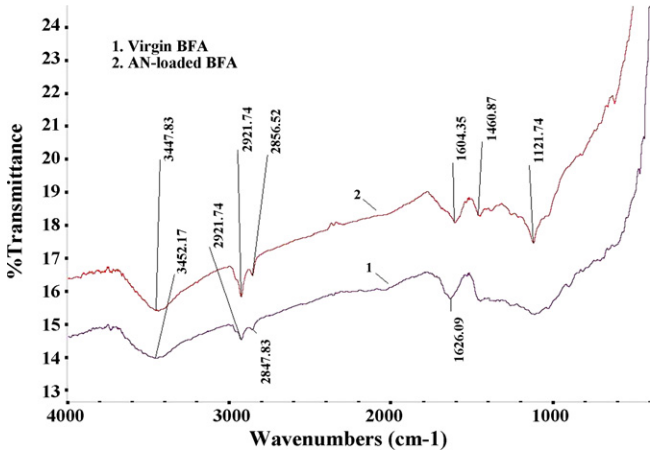

Fig. 3. FTIR spectroscopy of virgin and AN-loaded BFA.

Table 4
Experimental and predicted values of Y for AN onto BFA

Std. run order	w	T	t	Y[a]		ε
				Y_{exp}	Y_{pre}	
1	5	30	150	65.03	70.15	−5.12
2	20	30	150	93.72	93.05	0.67
3	5	60	150	60.31	60.98	−0.67
4	20	60	150	91.77	86.65	5.12
5	5	45	5	60.03	57.63	2.40
6	20	45	5	94.55	97.94	−3.39
7	5	45	295	76.56	73.17	3.39
8	20	45	295	79.02	81.42	−2.40
9	12.5	30	5	91.06	88.34	2.74
10	12.5	60	5	78.47	87.74	1.73
11	12.5	30	295	89.47	87.74	1.73
12	12.5	60	295	77.35	80.07	−2.72
13	12.5	45	150	82.77	82.62	0.15
14	12.5	45	150	83.42	82.62	0.80
15	12.5	45	150	82.42	82.62	−0.20
16	12.5	45	150	82.11	82.62	−0.51
17	12.5	45	150	82.39	82.62	−0.23

[a] Y_{exp} and Y_{pre} are experimental and predicted responses.

3.2. Box–Behnken statistical analysis

The most important parameters, which affect the efficiency of AN removal by BFA, are adsorbent dose (w), temperature (T) and time of contact (t) of adsorbate–adsorbent. In order to study the combined effect of these factors, experiments were performed for different combinations of the physical parameters using statistically designed experiments. The range of values for the input variables is given in Section 2.4.

The results of the Y (response) of AN onto BFA were measured according to design matrix [19] and the measured responses are listed in Table 4. Analyzing the measured responses by the Design expert software, the fit summary of the output indicates that the quadratic model is statistically highly significant for the present adsorbate-adsorbent system. Cubic model was not recommended for AN–BFA system as the Box–Behnken matrix has sufficient data to interpret the out come of the present system.

The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using the 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 [23]. According to ANOVA (Table 5), the F values for all regressions were higher. The large value of F indicates that most of the variation in the response can be explained by the regression equation. The associated p value is used to estimate whether F is large enough to indicate statistical significance. If $p > F$ value is lower than 0.05, then it indicates that the model is statistically significant [24].

To decide about the adequacy of model for AN removal by BFA, three different tests, viz., Sequential model Sum of Squares, Lack of Fit Tests and Model Summary Statistics were carried out in the present study. The p values for all the regressions were lower than 0.01 (Table 6). This means that at least one of the terms in the regression equation has a significant correlation with the response variable. As will be seen later, the interaction of two factors (2FI) was not significant using the RSM. 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 analysis shows that the form of the model chosen to explain the relationship between the factors and the response is correct [25].

The ANOVA result for the AN–BFA system shows the F-value to be 12.07, which implies that the terms in the model have a significant effect on the response. The model gives R^2 value of 0.94 and an adjusted R^2 value of 0.8617. Therefore, it can be assumed that the proposed model does not explain at least 6% of the experimental results. The probability p (∼0.0017) is less than 0.05. This indicates that the model terms are significant at 95% of probability level. Any factor or interaction of factors with $p < 0.05$ is significant. The ANOVA table obtained from the response surface quadratic model shows that w, T, w^2, wt, lack of fit and the constant, whose value is 56.47 (see Eq. (5)), are significant. The constant, which does not depend on any factors and interaction of factors, shows that the average removal of AN from aqueous effluents is 56.47%, and that this average removal is independent of the factors set in the experiment. The value of the predicted R^2 is the measure of the variation in data explained by the model. Predicted $R^2 = 1 - [\text{PRESS}/(\text{SS}_{\text{Total}} - \text{SS}_{\text{Block}})]$. The predicted $R^2 = 0.04$ implies that the present model has a large block effect. A value of (predicted R^2 − adjusted R^2) >±0.20, indicates a problem with either the data or the model [20]. The

Table 5
ANOVA for response surface quadratic model (Y)

Source	Sum of squares	d.f.	Mean square	F-Value	$p > F$	Remark[a]
Model	1701.54	9	189.06	12.07	0.0017	Significant
w	1179.28	1	1179.28	75.31	<0.0001	Significant
T	121.06	1	121.06	7.73	0.0273	Significant
w^2	139.86	1	139.86	8.93	0.0203	Significant
wt	256.96	1	256.96	16.41	0.0049	Significant
Residual	109.61	7	15.66	–	–	–
Lack of fit	108.59	3	36.20	142.58	0.0002	Significant
Pure error	1.02	4	0.25	–	–	–
Cor. total	1811.15	16	–	–	–	–

[a] $R^2 = 0.94$, predicted $R^2 = 0.04$; adjusted $R^2 = 0.86$, adequate precision = 13.28.

Table 6
Selection of adequate model for AN–BFA system

Source	Sum of squares	d.f.	Mean square	F	$p > F$	Remark
Sequential model sum of squares						
Mean	1.105E+005	1	1.105E + 005	–	–	–
Linear	1300.82	3	433.61	11.05	0.0007	Suggested
2FI	258.89	3	86.30	3.43	0.0602	–
Quadratic	141.83	3	47.28	3.02	0.1034	Suggested
Cubic	108.59	3	36.20	142.58	0.0002	Not recommended
Residual	1.02	4	0.25	–	–	–
Total	1.123E+005	17	6607.74	–	–	–

Source	Sum of squares	d.f.	Mean square	F	$p >$ F	Remark
Lack of fit tests						
Linear	509.31	9	56.59	222.91	<0.0001	Suggested
2FI	250.42	6	41.74	164.40	<0.0001	–
Quadratic	108.59	3	36.20	142.58	0.0002	Suggested
Cubic	0.000	0	–	–	–	Not recommended
Pure error	1.02	4	0.25	–	–	–

Source	S.D.	R^2	Adj. R^2	Pre. R^2	PRESS	Remark
Model summary statistics						
Linear	6.27	0.7182	0.6532	0.4213	1048.13	Suggested
2FI	5.01	0.8612	0.7779	0.3329	1208.22	–
Quadratic	3.96	0.9395	0.8617	0.0398	1739.06	Suggested
Cubic	0.50	0.9994	0.9978	–	–	Not recommended

value of the adequate precision, which is a measure of the S/N ratio is 13.29. A value greater than 4 is desirable in support of the fitness of the model [21].

The ANOVA analysis indicates a linear relationship between the main effects of the dose, temperature and time, and the quadratic relationship with dose and the product of dose and time. The final mathematical equation in terms of actual (natural) factors (confidence level above 95%) as determined by Design-expert software is given below:

$$Y = 56.47 + 5w - 0.67T - 0.102w^2 - 0.0074wt \quad (5)$$

Figs. 4 and 5 show response surface plots for the relationship between dose, temperature and time of contact on the removal of AN.

For the optimization of the process parameters, the point prediction option in the software is used. The optimized parameters obtained from statistical software are listed in Table 5. For their validation, duplicate confirmatory experiments were conducted using the optimized parameters. Table 7 summarizes the experimental conditions and the actual experimental values. It is found that the optimal BFA dose is 16 g/l at which the predicted AN removal is 97.84% as against the actual removal of 94%. Thus, the single stage adsorptive treatment of AN bearing wastewater will not meet the discharge standards for cyanide and may need a second stage treatment. However, the efficacy of the BFA in removing AN from wastewater is proved. The maximum AN loading onto BFA was found to be ~84.5 mg/g.

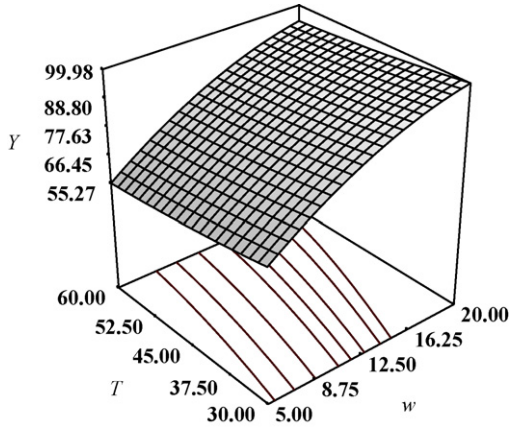

Fig. 4. 3D response surface graph for AN removal vs. adsorbent dose and temperature for AN–BFA adsorption system.

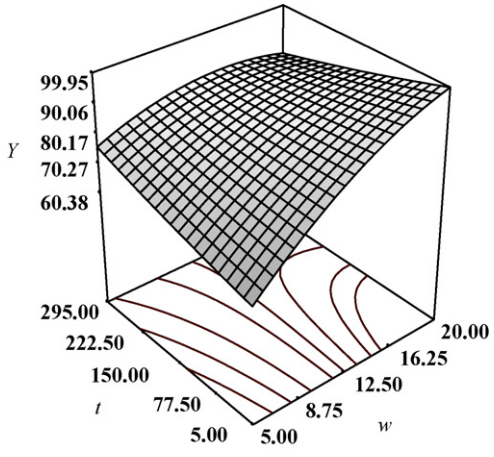

Fig. 5. 3D response surface graph for AN removal vs. adsorbent dose and time for AN–BFA adsorption system.

Table 7
Optimum and confirmative values of the process parameters for maximum removal efficiency

Processes parameters	Optimized values (predicted values)	Confirmation values (mean actual values)
% Removal, Y	97.84	94
Dose, w (g/l)	16	16
Temperature, T (°C)	30	30
Time, t (min)	25	25

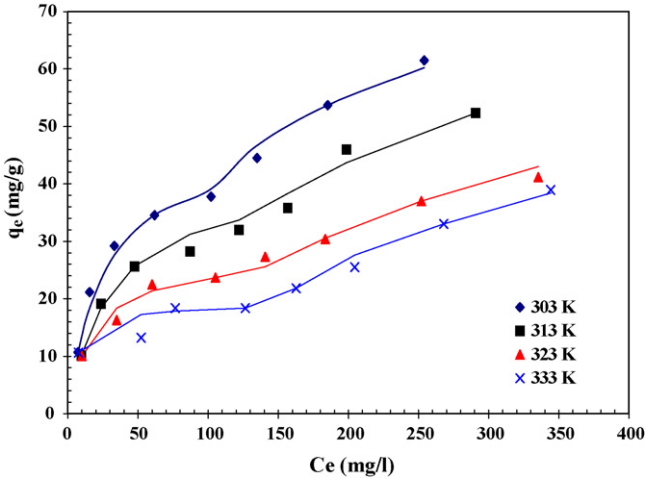

Fig. 6. Equilibrium isotherms for AN–BFA system at 303–333 K, $w = 4$ g/l and $t = 6$ h.

The results also show that the RSM is a very useful optimal design for experiments on the adsorption of toxics onto adsorbents.

3.3. Effect of temperature

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. Equilibrium isotherms for AN adsorption onto BFA at various temperatures are shown in Fig. 6. The effect of temperature on adsorption capacity of AN by BFA was studied by carrying out experiments at 30 to 60 °C using different initial AN concentrations at natural pH of the AN solution. The equilibrium uptake of AN by BFA was affected by temperature. The effect of temperature on the equilibrium adsorption capacity of BFA is presented in Fig. 6. It was indicated that the removal decreased with an increase in temperature. The decrease of adsorption capacity with the increased in temperature indicated that the adsorption of AN onto BFA is exothermic in nature. A similar trend was also observed by [26] with 4-chlorophenol adsorption by XAD-4 resin. The decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate species and also between the adjacent molecules of the adsorbed phase [27]. The optimum temperature for AN adsorption on BFA was found to be the 30 °C within the temperature range studied and the maximum adsorption capacity was found to be 84.47 mg/g onto BFA. The maximum adsorption capacity for AN onto PAC and GAC (Table 8) were found to be 51.72 and 46.62 mg/g, respectively at 30 °C [29]. The equilibrium uptake of the AN by BFA increases with C_0 for $50 < C_0 < 500$ mg/l. The initial concentration provides the necessary driving force to overcome the resistances to the mass transfer of AN between the aqueous solution and the solid phase. The increase in C_0 also enhances the interaction between the AN in the aqueous phase and the BFA. Therefore, an increase in the C_0 of the AN enhances the adsorption uptake of AN by BFA.

Table 8
Comparable maximum adsorption capacity of AN by BFA, PAC and GAC

Temperature (°C)	q_m (mg/g)		
	AN–BFA	AN–PAC	AN–GAC
30	84.4764	51.7210	46.6286
40	61.8295	46.6286	41.5545
50	46.3594	43.0980	39.1653
60	45.6206	42.5183	37.2139

3.4. Adsorption equilibrium study

Seeing the equilibrium adsorption data of AN–BFA system (Fig. 6) it appears to have two clearly identifiable portions, one for lower q_e and other for higher q_e. As the temperature increases the plateau gets enlarged. Comparing the isotherms with those given by Giles [30], L_4 types of isotherm appears to fit the adsorption data well. After the first degree of saturation of the surface, further adsorption takes place on new surface only. This kind of two-step isotherm is well explained by Giles [30] and other investigators [31–33]. Such two-step isotherms are well represented by Langmuir isotherm equation for each step separately. This equation is given as

Table 9
Two-step Langmuir isotherm parameters for AN adsorption onto BFA

Temperature (°C)	q_{m_1} (mg/g)	q_{m_2} (mg/g)	K_{L_1} (l/mg)	K_{L_2} (l/mg)	MPSD$_1$	MPSD$_2$	R_1^2	R_2^2
30	48	89	0.038	0.008	9.07	2.85	0.9918	0.9996
40	42.09	91.15	0.032	0.004	8.03	4.93	0.9931	0.9640
50	27.61	84.91	0.057	0.003	7.21	4.67	0.9779	0.9957
60	19.26	89.53	0.163	0.002	13.66	3.96	0.9417	0.9900

follows:

$$q_e = \frac{q_{m_1} K_{L_1} C_e}{1 + K_{L_1} C_e} + \frac{q_{m_2} K_{L_2} C_e}{1 + K_{L_2} C_e} \quad (6)$$

Non-linear regression fit of the data of the Langmuir isotherm is found to be adequate and satisfactory. The Langmuir parameters for the system at different temperatures are given in Table 9.

3.5. Estimation of thermodynamic parameters

The temperature dependence of AN uptake was studied by performing batch experiments at 30–60 °C. The standard enthalpy change was estimated by applying Van't Hoff equation:

$$\ln k_d = -\frac{\Delta H\circ}{R}\frac{1}{T} + \frac{\Delta S\circ}{R} \quad (7)$$

and

$$k_d = \left(\frac{C_0 - C_e}{C_e}\right)\left(\frac{V\rho}{w}\right) = \frac{q_e \rho}{C_e} \quad (8)$$

where ρ is the density of the solution (kg/m^3), ΔH° the standard enthalpy change (J/mol), ΔS° the standard entropy change (J/(mol K)), T the absolute temperature (K) and k_d is the distribution coefficient. The Van't Hoff plot for AN adsorption onto BFA is shown in Fig. 7. The ΔH° and ΔS° for AN can be calculated from the slope of the straight line. The value of ΔH° calculated from the slope of Van't Hoff plot for AN–BFA adsorption system was found to be −7.697 kJ/mol K. The value of ΔS° was found to be 34.624 kJ/mol. This indicates increased randomness at the solid–solution interface, and a decrease in the degree of freedom of the adsorbed species. The values of the thermodynamic parameters estimated are presented in Table 10. A negative value of ΔH° suggests that the adsorption is exothermic in nature. *A* negative value of ΔG° suggests the adsorption process is spontaneous and exothermic in nature [28,29].

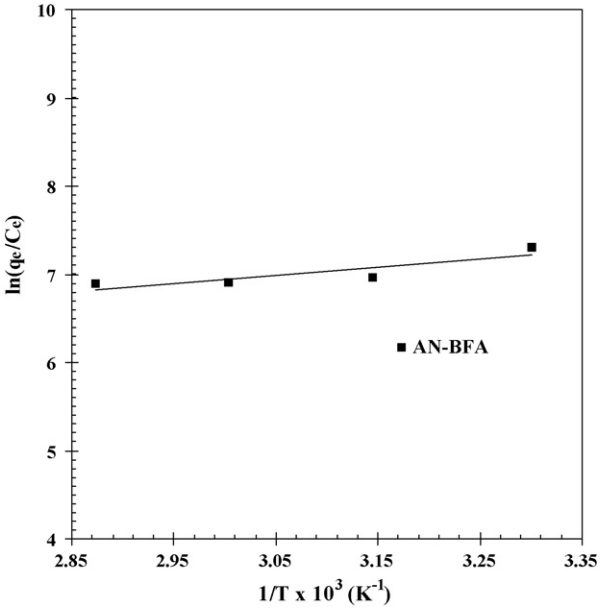

Fig. 7. The effect of temperature on the equilibrium distribution coefficient for AN onto BFA. $C_0 = 50$ mg/l, $t = 6$ h.

Table 10
Thermodynamic parameters for the sorption of AN–BFA system

Isotherm	AN–BFA
ΔG° (kJ/mol)	
30 °C	−18.4006
40 °C	−18.4011
50 °C	−19.1361
60 °C	−19.9369
ΔH° (kJ/mol)	−7.697
ΔS° (kJ/(mol K))	34.624

4. Conclusion

The following conclusions are drawn from this investigation:

- The Box–Behnken design can be employed to develop mathematical models for predicting AN removal geometry.
- The desired removal of AN can be achieved by choosing the predicted conditions using the developed models.
- Parameters interacting together can be identified in such a typical process like adsorption. The removal is sensitive to the adsorbent concentration in the present study.
- The value of $R^2 > 0.94$ for the present mathematical model indicates the high correlation between observed and predicted values.
- BFA is an effective adsorbent for the removal of AN from aqueous solutions. BFA is a low-cost adsorbent material and it may be an alternative to more costly adsorbent materials.
- The adsorption of AN by BFA exhibits Langmuir two-step model.
- The negative value of ΔG° signifies the adsorption reaction was a spontaneous adsorption. The negative value of ΔH° indicated the adsorption process was exothermic.

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