ADSORPTIVE REMOVAL OF ACRYLONITRILE USING POWDERED ACTIVATED CARBON

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Abstract

In the present work, acrylonitrile (AN) removal from wastewater was investigated using powdered activated carbon (PAC). The effect of dose, temperature and time of contact was investigated using response surface methodology (RSM) keeping AN concentration 100 mg/l as fixed input parameter. The experimental plan was based on Box–Behnken surface statistical design. Linear and quadratic polynomial equations were developed for proper process parametric study for its optimal performance characteristics. The optimum conditions obtained were: adsorbent dose = 25 g/l, temperature = 30 and contact time = 20 min. The AN removal at optimum conditions was 92±0.8%. The experimental results under optimum conditions were compared with the simulated values obtained from the model. There was good agreement between the experimental and simulated values. The result of Box–Behnken design indicates that the proposed models predict the responses adequately within the limits of input parameters being used. It is suggested that regression equations can be used to find optimum conditions for AN removal.

Keywords: Statistical Design; Response Surface Methodology; Box-Behnken.

JEPS (2008), Vol. **2**, pp. 54 – 62.

Introduction

Acrylonitrile (AN) is a colorless liquid with a sharp, onion or garlic-like odor, which dissolves readily in water. Acrylonitrile is used mostly to make plastics, acrylic fibers, and synthetic rubber. 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 vapors and aqueous effluents and is 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 Services cite 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 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 < 0.2 mg/l [6]. Thus, the concentration of AN in the wastewater to be discharged into surface waters should not exceed 0.4 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. The characteristic of a typical cyanide bearing effluents is given by Kumar et al. [8].

Measurable amounts of AN are found primarily near factories and hazardous waste sites. Exposure to large amounts of AN for a short period of time, as might occur in case of an industrial accident, results mainly in effects on the nervous system. Symptoms can include headache and nausea. At higher concentrations of AN there may be temporary damage to red blood cells and the liver. These symptoms disappear when the exposure is stopped. AN can be smelled at a concentration of 19 mg/l when dissolved in water. In animals, drinking water that contains

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142 mg/l of AN has caused nervous system disorders leading to death [9]. The hazardous rankings of AN has been presented elsewhere [10]. AN induces permanent toxicity [11]. The AN applications, toxic nature and adverse impacts on health are also presented in [9, 12-35]. Removal of AN from aqueous solutions using activated carbons as an adsorbent by adsorption process is currently of great interest.

PAC have been used extensively for the adsorption of a variety of pollutants and toxics from aqueous solutions, as it has a good capacity for the adsorption of various adsorbates because of high surface area, iodine number and fixed carbon etc. Powdered activated carbon (PAC) is more commonly used than granular activated carbon (GAC) to control taste, colour and odor in drinking water treatment. The Physico-chemical and surface characteristic of PAC responsible for adsorption are presented in Table 1. Except the work of Liu et al. [36] wherein the authors used natural zeolite to adsorb AN at high concentrations, no other work is available in literature dealing with the adsorptive removal of AN from wastewaters

Conventional and classical methods of studying a process by maintaining other factors involved at an unspecified 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 a classical method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as Response Surface Methodology (RSM) [37]. 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

The application of statistical experimental design techniques in adsorption process development can result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs [38] and have been extensively used in adsorption process by several investigators [37-46]

The objective of this study is to investigate the feasibility of AN sorption using powdered activated carbon (PAC) and the optimization of process parameters. The study reports important parameters and their interactions, which affect the adsorption process viz. PAC dosage; temperature and time of contact between PAC and AN using Box-Behnken design [47-48]. The optimum parameters thus obtained have been verified experimentally.

Material and Methods

The commercial grade powder activated carbon (PAC) was obtained from HiMedia Research Laboratory, Mumbai. The characterization of PAC was carried out as per the methods presented by Srivastava et al [49]. 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_o =100 mg/l. The required quantity of the adsorbate was accurately weighed and dissolved in a small amount of double distilled water and subsequently made up to 1 litre in a measuring flask by adding double distilled water (DDW). Fresh stock solution as required was prepared every day and was kept at ambient conditions. This was ascertained before the start of each experimental run.

For each experiment, 50 ml of AN solution of known C_o and a known amount of the PAC were taken in a 100 ml air-tight stoppered conical flask. This mixture was agitated at preset temperature in a temperature-controlled shaking water bath at a constant shaking speed 20 rpm. The percentage removal of AN was calculated as:

$$Y = 100(C_o - C_t)/C_o \quad (1)$$

where, C_o is the initial adsorbate concentration (mg/l) and C_t is the adsorbate concentration (mg/l) after time t.

The concentration of AN in the aqueous solution was determined at 196 nm wavelength [50-51] using a high performance liquid chromatography (HPLC) Noval Pack, C_{18} column (size: 3.9 mm x 150 mm) supplied by Waters (India) Pvt. Ltd., Bangalore. Degassed organic 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 peak area versus AN concentration was used for determination of the unknown concentration of AN from a sample.

Box and Behnken [52] have proposed some three-level designs for fitting response surfaces. Box–Behnken design requires an experiment number according to $N = k^2 + k + c_p$, where, (k) is the factor number and (c_p) is the replicate number of the central point. These designs are formed by combining 2^k factorials with incomplete block designs. Box–Behnken is a spherical, revolving design, viewed as a cube and consists of a central point and the middle points of the edges. The resulting designs are usually very efficient in terms of the number of required runs, and they are either rotatable or nearly rotatable. A three-variable Box-Behnken design is presented by [47, 52]. It has been applied for optimization of several chemical and physical processes [53-55].

This design is generally used for fitting the second order model. It is important to second order model to provide good prediction throughout the region of interest. The second order response surface design is rotatable; this means that the variance of the predicted response is the same at all points. Rotatability is a reasonable basis for the selection of response surface design. Because the purpose of RSM is optimization at the location of optimum is unknown prior to running the experiment, it makes sense to use design that provides equal precisions of estimation in all directions [56].

Adsorption Mechanism of AN

PAC contains metal oxides of aluminum, calcium, and silicon on its surface in a small quantity. The presence of these metal oxides in contact with water leads to the development of a surface charge, according to the pH of the solution:

$$H_2O \Leftrightarrow H^+ + OH^-$$

$$M + OH^- \rightarrow MOH$$

$$MOH + H^+ \rightarrow MOH^+{}_2$$

$$MOH + OH \rightarrow M-O^- + H_2O$$

where , M = Al, Ca, or Si. The chemical interaction of AN with PAC may be explained on the basis of the explanation put forth by Weber and Chakravarti, [57] and Zhu et al. [58].

$$AN + H^+ \Leftrightarrow ANH^+$$

$$AN + PAC \Leftrightarrow AN-PAC$$

$$ANH^+ + M^+-PAC \Leftrightarrow ANH^+-PAC+M^+$$

$$H^+ + ANH^+-PAC \Leftrightarrow H^+-PAC + ANH^+$$

$$H^+ + PAC \Leftrightarrow H^+-PAC$$

$$AN-H^+-PAC \Leftrightarrow ANH^+-PAC$$

Results and Discussion

The best performance of a Box-Behnken design depends on some knowledge about the system being optimized. If the values of all the system parameters to be studied are unknown, the projection of the results with the factorial design cannot be optimized. Besides, the total number of experiments required will be excessively large, making the factorial design very complex [59]. Based on the above, preliminary experiments were carried out for the optimization of the adsorption of AN onto PAC at T = 30 ^oC using 100 mg/l AN solution with 20 g/l PAC concentration without adjusting pH of the solution and contact time of 5–360 min. It was observed that for 100 mg/l of AN solutions, the removal of AN from solution after 5 min shaking was 91%. After 285 min, the AN removal increased to 95%. After shaking for 360 min, 96% removal was observed. The difference in the percent removal of AN between these two conjugative contact times is very small.

AN removal by PAC in a batch system usually depends on several factors, such as carbon concentration in the solution, temperature and time of contact between AN and PAC, and the speed of shaking. In the present study, the speed of shaking was kept constant. (20 rpm) The optimization of input parameters in adsorption process using the uni-variate procedure is very tedious, because any variable (parameter) is optimized by varying just one parameter at a time while fixing the others at constant values. Then, the best value achieved by this procedure is fixed and other parameters are varied at a time. The disadvantage of this uni-variate procedure is that the best conditions are not attained, due to absence of interactions among the parameters. It is also not known whether by keeping the values of other fixed variables different, the results would lead to the same optimization. In addition, the total number of experiments to be carried out in the uni-variate procedure is generally much larger than that obtained with statistical design of experiments [60].

In this work, the experiments were designed based on a three level three factors Box–Behnken design. Adsorbent dose (4-36 g/l), temperature (30–60 ^oC) and agitation time (5 to 295 min) were kept as variable input parameters (factors), while AN concentration of 100 mg/l was kept as a constant input parameter. The three factor levels were coded as ˜ 1 (low), 0 (central point) and 1 (high) [52].

Table 1 shows input parameters and experimental design levels used. Response surface methodology 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 [61]. 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 [62]. A manual regression method was used to fit the second order polynomial Eq. (2) 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:

$$Y = \beta_0 + \sum \beta_i A_i + \sum \beta_{ii} A_{ii}{}^2 + \sum \beta_{ij} A_i A_j \quad (2)$$

where β_o = constant, β_i is the slope or linear effect of the input factor A_i, β_{ij} is the linear by linear interaction effect between the input factor A_i and A_i, β_{ii} is the quadratic effect of input factor A_i [63].

Table 1. Physico-chemical and surface characteristics of adsorbent	
Characteristic	**PAC**
Proximate analysis (sample as received)	
Moisture (%)	5.65
Ash (%)	8.74
Volatile matter (%)	4.46
Fixed carbon (%)	81.12
Bulk density (kg/m^3)	562
Carbon pH	5.33
pH_{PZC}	6.50
Heating value (MJ/kg)	4.59
Average particle size	250 mesh
Ultimate analysis (dry basis)(%)	
C	80.25
H	1.658
N	0.158
S	0.052
Chemical analysis of ash (%)	
Insoluble Matter	3.5
Silica	1.5
Ferric & Alumina	3.8
CaO	84.0
Mg	2.0
Surface area (m^2/g)	
BET	798.49
Langmuir	1007.37
t-plot micropore	804.26
t-plot external	203.12
Single point	790.06
BJH adsorption cumulative	192.63[a]
Pore Volume (cm^3/g)	
Single point total pore volume	0.76
t- plot micropore volume	0.25
BJH adsorption cumulative	0.30[a]
Pore size (Å)	
BET Adsorption average pore width	38.25
BJH adsorption average pore diameter	63.39
Functional groups	**PAC (meq/g)**
Carboxylic	0.35
Lactonic	0.60
Phenolic	0.65
Carbonyl	0.45
Phenol number	26
Iodine number	729

The results of the Y (response) of AN onto PAC was measured according to design matrix [64] and the measured responses are listed in Table 2. Analyzing the measured responses by the Design-expert software, the fit summary output indicates that the linear and quadratic model is significant for the present adsorption system.

Table 2. Level of variables chosen			
Variables	Levels		
Coded level	-1	0	+1
w: Dose (g)	4	20	36
T: Temp. (^oC)	30	45	60
t: Time (min)	5	150	295

The test for significance of the regression models, the test for significance on individual model coefficients and the lack of- fit test were performed using the same statistical package. By selecting the manual regression method, which eliminates the insignificant model terms automatically, the resulting ANOVA Table 3 for the reduced quadratic models summarize the analysis of variance of each response and show the significant model terms. Table 3 shows the ANOVA result for the AN-PAC adsorption system, in which it is found that the model F-value of 43.55 implies that the model is significant. The probability p <0.05 indicate that the model terms are significant. In this case, w is highly significant model term, T , t and w^2 are the significant model terms. The model values greater than 0.10 indicate that the model terms are not significant. The value of the lack of fit 8.48 also supports the fitness of the model. There could be 2.82 % possibility of the deviation; this could be large because of noise. The value of the predicted R^2 =0.857 for the same adsorption system is in reasonable agreement with the adjusted R^2 =0.930. The high value of adequate precision, which measures the signal to noise ratio greater than 4 is desirable in support of the fitness of the model. For AN-PAC adsorption system, adequate precision 20.694 indicates an adequate signal. It means that the model can be used to navigate the design space.

The entire adequacy measures are in reasonable agreement and indicate adequate models. The adequate precision compares the range of the predicted value at the design points to the average prediction error. The value of adequate precision is dramatically greater than 4. The adequate precision ratio above 4 indicates adequate model efficacy [65]. Other values, that support the efficacy of the model and the relevant significant terms, are given in the same table.

Table 3. Experimental and predicted values of Y for AN onto PAC

Run order	w	T	t	[a] Y_{AN-PAC}	
				[a] Y_{exp}	[a] Y_{pre}
1	4	30	150	58.75	59.54
2	36	30	150	90.64	89.07
3	4	60	150	45.18	47.92
4	36	60	150	83.86	77.44
5	4	45	5	51.18	51.31
6	36	45	5	80.02	80.84
7	4	45	295	67.87	64.20
8	36	45	295	86.55	93.73
9	20	30	5	80.39	79.62
10	20	60	5	63.72	68.00
11	20	30	295	90.96	92.51
12	20	60	295	81.49	80.89
13	20	45	150	83.5	84.28
14	20	45	150	87.71	84.28
15	20	45	150	84.76	84.28
16	20	45	150	85.21	84.28
17	20	45	150	84.69	84.28

[a] Y_{AN-PAC} is the response (percent removal) corresponding to the AN-PAC system used in the present study. Y_{exp} and Y_{pre} are experimental and predicted responses.

Table 4. ANOVA table for Y_{AN-PAC}

Source	Sum of squares	d.f	Mean square	F-value	p>F[a]
Model	3022.56	5	604.512	43.545	< 0.0001[b]
w	1743.16	1	1743.156	125.567	< 0.0001[b]
T	270.17	1	270.165	19.461	0.0010[c]
t	332.30	1	332.304	23.937	0.0005[c]
w^2	584.15	1	584.145	42.078	< 0.0001[b]
T^2	68.48	1	68.479	4.933	0.0483[c]
Residual	152.71	11	13.882		
Lack of Fit	143.07	7	20.438	8.480	0.0282[c]
Pure Error	9.64	4	2.410		
Cor Total	3175.27	16			

[a] $R^2 = 0.952$, predicted $R^2 = 0.857$; adjusted $R^2 = 0.930$, adequate precision = 20.694

[b] Highly significant

[c] Significant

The ANOVA for AN-PAC system indicates that for the AN concentration input model, the main effect of the dose (w), temperature (T), time (t) and the second order effect of dose (w^2) are the most significant model terms associated with concentration input. Experimental data shows that the temperature induces negative effect for AN removal onto PAC. So the term (T^2) has been removed from the proposed model. However, the model is showing probability value p<0.0483 for (T^2). The final mathematical model eliminating the insignificant terms and interactions, the above empirical model equation may be simplified in terms of coded factors (equ. 3) and actual factors (equ. 4) as determined by Design-expert software is shown below:

$$Y_{AN-PAC,coded} = 84.28+14.76 * w - 5.82 * T + 6.445 * t - 11.76 * w\text{^}2 - 4.027 * T\text{^}2 \quad (3)$$

$$Y_{AN-PAC,actual} = 21.98+2.76 * w + 1.23 * T + 0.045 * t - 0.046 * w\text{^}2 - 0.018 * T\text{^}2 \quad (4)$$

Figs. 1 and 2 shows contour plot and the 3D response surface plots of the effect of w and T on Y holding the value t as a fixed parameter, respectively. The lines in contour plot shows the lines of constant removal for AN. Furthermore, to verify the adequacy of the developed models, confirmation experiments for the AN-PAC adsorption system were carried out using new test conditions, which are within the experimental ranges defined earlier. Using the point prediction option in the software, the response of the validation experiments were predicted using the previous developed models.

The Y is directly related to w, T, t and w^2 for AN-PAC system as given in empirical Eq. (4). It is clear from Eq. (4) that the removal of AN is linear with respect to w, T, t, and quadratic with respect to dose and temperature. This indicates that there is dose-to-dose and temperature to temperature interaction for the AN-PAC adsorption system. The higher percentage removal of AN is obtained with the square of the dose added for AN-PAC system. Further, from the contour plot and 3D graph as obtained from Design-expert software, it is clear that the removal of AN decreases with increase in temperature for AN-PAC adsorption system and hence the model term T^2 has been excluded from the proposed model. Thus, the model equation is reduced into the following form:

$$Y_{AN-PAC,coded} = 84.28 + 14.76 * w - 5.82 * T + 6.445 * t - 11.76 * w\text{^}2 \quad (5)$$

$$Y_{AN-PAC,actual} = 21.98 + 2.76 * w + 1.23 * T + 0.045 * t - 0.046 * w\text{^}2 \quad (6)$$

The reduction of AN removal with temperature indicates that adsorption process is exothermic in nature. Hence, the temperature for AN removal should be low. Since, the most of the AN is removed (91%) within 5 minutes of the start of the sorption process with PAC, the time of contact of AN and PAC must be greater then 5 min for higher removal of AN. The validation experiments were performed based on the optimized predicted values by the proposed model (equ. 6) for the optimal PAC dosage (25 g/l), temperature 30°C and time (20 min) for the AN-PAC sorption processes. It is found that the predicted AN removal is 100.03% as against the actual removal of 92±0.8%. 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.

Conclusion

The objective of the study was to investigate the feasibility of using PAC as possible adsorbent for the sorption of AN from aqueous solution using Box-Behnken design. Box-Behnken design is undoubtedly a good technique for studying the effect of major process parameters on response factor by significantly reducing the number of experiments in the batch study of AN-PAC adsorption system and henceforth, achieving the optimum conditions. This study clearly showed that response surface methodology was one of the suitable methods to optimize the best operating conditions to maximize the AN removal. Graphical response surface and contour plots were used to locate the optimum point. Satisfactory prediction equation was derived for the AN using RSM to optimize the parameters. The optimum conditions for maximum removal of AN from an aqueous solution of 100 mg/L were found. The small deviation from the result may be because of limitation of model developed.

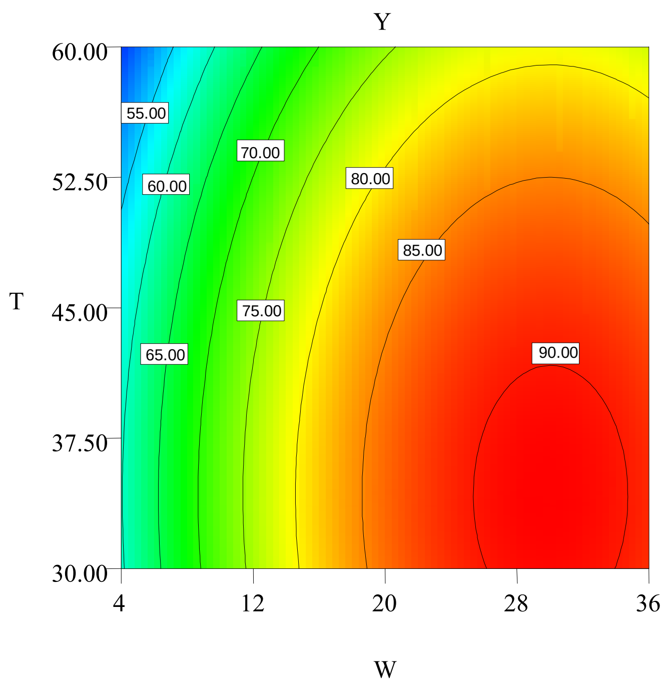

Fig. 1. Contour graph of adsorbent dose versus temperature at holding time 150 min for AN-PAC adsorption system.

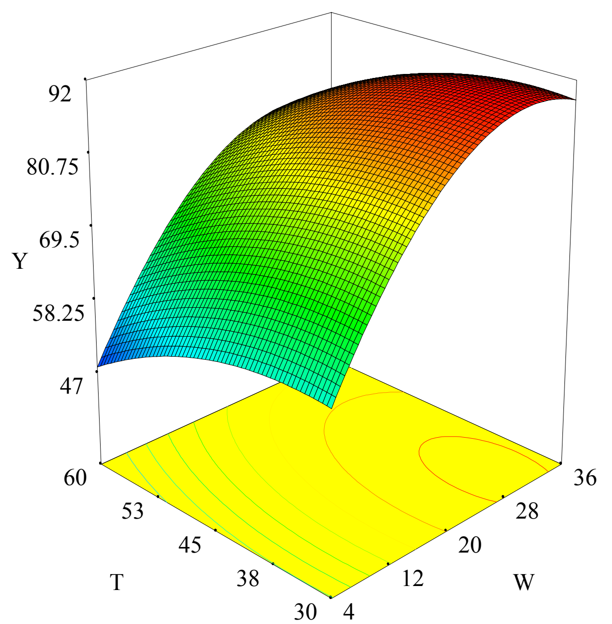

Fig. 2. 3D response surface graph of adsorbent dose versus temperature at optimum condition for AN-PAC adsorption system.

Limitations of DOE

The model estimation performance of the procedure was found to be very sensitive to the relative importance of the effects in the model, with balanced magnitudes of effects yielding the best model estimates. Data generated by first-order models resulted in a better capability of the statistical analysis. If any second-order-quadratic interactions are present in the model, the statistical analysis often fails to identify the right model by either over fitting or under fitting (ANOVA).

No significant change in the effectiveness of the methods in identifying the correct model was observed when systematic low uncertainties in the independent variables and in the response were introduced into the simulations. An explanation is that the systematic errors in the simulation data caused a shift of the whole response surface up or down from the true value, without a significant change in shape. A very large percent of reading type systematic uncertainty in a first-order model could cause a significant warp in the response surface, as could any type of systematic uncertainty in a second-order model with strong curvature, but no effects on the ability of the statistical methods to identify correct models were observed in this study.

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