Optimization of Process Conditions for the Concentration of Isopropyl Alcohol – Water Solution Using Response Surface Methodology

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ABSTRACT
Potato starch was used as an adsorbent in concentrating isopropyl alcohol – water solution. Response surface methodology statistical technique was used to optimize the reaction conditions which were; temperature, time, adsorbent/ solution ratio and the initial concentration of the isopropyl alcohol – water solution, with the final concentration of the isopropyl alcohol water solution as the response. Based on the sequential model sum of squares, a quadratic vs 2F1 model was developed. The significant factors on the experimental design response were identified from the analysis of variance (ANOVA). The optimal conditions obtained for the concentration reactions were temperature of 35^{o}C, time of 40mins, adsorbent/solution ratio of 1:4 and initial concentration of 40% which resulted in final concentration of 43.369%.

Keywords- ANOVA, Adsorbent/Solution ratio, CCD, Concentration, Isopropyl Alcohol-Water Solution, Optimization, RSM, Temperature, Time.

INTRODUCTION

Isopropyl alcohol is one of the most widely used solvent in the pharmaceutical company. It also serves as a basic substance for a lot of organic synthesis. ISA is a major ingredient in "gas dryer" fuel additives. In significant quantities, water is a problem in fuel tanks, as it separates from gasoline, and can freeze in the supply lines at cold temperature. The presence of water in fuels, even at very small concentration is quite undesirable, so that its separation from isopropyl alcohol solution become a serious technological problem, especially taking into account the azeotropic liquid – vapors equilibrium relation. The traditional way to overcome the azeotropic problem is the azeotropic distillation. Unfortunately, it is high energy consuming separation technology. Therefore, the development of other economically more effective separation methods which will be alternative to the distillation or which will be coupled with the conventional distillation or fermentation processes is a quite perspective research direction [1] Starch and its derivatives represent a cheap and environmentally safe source of raw material for the preparation of low-cost adsorbents [1].

This biopolymer represents an interesting alternative as an adsorbent because it is an abundant, renewable and biodegradable raw resource [1]. Starch is the only qualitatively important digestible polysaccharide and has been regarded as nutritionally superior to low molecular weight carbohydrate or sugar [2]. Starch, cellulose, hemicelluloses and starch – based materials have affinity for water [3] and are able to be regenerated at temperature of 80^{o}C and lower [4].

The aim of this present work is to investigate the possibly of dehydrating isopropyl alcohol water mixtures using potato starch and to establish experimentally the influence of some process parameters and to optimize the process conditions.

2. EXPERIMENTAL DESCRIPTIONS

2.1 Materials

Potato used in this research work was obtained at a local market in Abakpa Enugu, Enugu State Nigeria. The Isopropyl alcohol used was of analytical grade and was obtained from De-cliff integrated services main market Enugu, Enugu state Nigeria. Distilled water used was bought from Pymotech research centre and laboratory Enugu.

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2.2 EXPERIMENTAL METHOD

A.STARCH EXTRACTION

Starch was extracted from tubers using a slight modification an in [2].

Tubers were manually peeled, cut into smaller pieces, soaked in 0.2% sodium metabisulfite for 5 mins, and the juice was extracted at a low speed for 5 min. The resulting starch slurry was filtered using a screen (200 microns) and then passed again through a 100 micron screen. The filtrate was collected and allowed to settle unhindered over night. The white starch fraction was collected, resuspended in distilled water and allowed to settle. This process was repeated three times to eliminate sulphite residue. The resulted starch was dried to a constant weight.

It was finely ground and sieved through a 212μm mesh size, packed in polythene bags and stored at room temperature.

2.3 DEHYDRATION ANALYSIS

Wide ranges of concentration were prepared for the production of calibration curve. The experimental conditions were used according to the design matrix in ''table'' 1. The flasks containing the solution and the adsorbent were corked and left to stand in a thermo state water bath with an accuracy of ± 0.1^{o}C for the specified time interval. At the end of each time interval, the refractive index of the fluid phase was measured using Abbe refractometer. The end concentration of the sample was obtained from the calibration curve.

2.4 DESIGN OF EXPERIMENT

DOE is a preplanned approach for finding cause and effect relationship. The purpose of statistically designing an experiment is to collect common relationship between various factors affecting the process towards finding the most suitable conditions [5]. It is essential that an experimental design methodology be economical for extracting maximum amount of complex information, a significant reduction in experimental time, saving both material and personnel cost [6].

CCD is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments and also to analyze the interaction between the parameters. In CCD, each variable is investigated at two levels and as the number of factors increase the number of runs for a complete replicate of the design increases rapidly. This kind of design provides equally good predictions at points equally distant from the later, a very desirable property for RSM. The center points are used to

determine the experimental error and the reproducibility of the data. Rotatable designs are most efficient and recommended for K=3. The properties of Hartley's and orthogonal designs are worse (though they require less experiments), but they may be used when it is necessary to keep a minimal number of design points [5].

To determine the effect of various operating parameters CCD has been used.

Central composite design (CCD) was used to study the individual and synergetic effects of the four factors towards the response. It is a method that helps to prune unnecessary experiments and checkmate whether or not there is synergy amongst the factors [7]. CCD is characterized by three operations namely: 2n axial runs, 2^n factorial runs and six center runs. The total number of experiment is $2n + 2n + n_c$

Where n is the number of factors, n_c is the number of center points. The value of rotatability α, which depends on the number of points in the design of the factorial portion, was obtained from the following ''(1)''

$$A=N_p^{1/4} \quad (1)$$

Where $N_p = 2^k$ is the number of points in the cube portion of the design. k is the number of factors.

2.5 BUILDING EMPIRICAL MODEL

In the first step of RSM, a suitable approximation is introduced to find true relationship between the dependent variable and the set of independent variables, that is, the single-response modeled using the RSM correspond to independent variables. Then a mathematical model in the form of a second – order polynomial is formed to predict the response as a function of independent variables involving their interactions. Generally the behavior of the system is explained by the following quadratic equation.

$$Y = bo + \sum_{i=1}^{n} bixi + \sum_{i=1}^{n} biix^2ii + \sum bijxixj \quad (2)$$

Where Y is the predicted response, bo the offset term, bi the linear effect, bii the squared effect, bij the interaction effect and X_i and X_j represent the coded independent variables.

Multiple regression analysis technique was used to evaluate the coefficient of the model.

Table 1: Experimental Design matrix with the predicted and experimental values

Std	Run	Type	Temperature (oC)	Time (Mins)	Adsorbent /Solution Ratio	Initial Concentration (%)	Experimental value (%)	Predicted value (%)
16	1	Factorial	45.00	80.00	1:4	40.00	43.00	42.73
6	2	Factorial	45.00	40.00	1:4	20.00	21.333	20.89
19	3	Centre	40.00	60.00	1:3	30.00	28.00	29.34
2	4	Factorial	45.00	40.00	1:2	20.00	22.00	20.99
18	5	Centre	40.00	60.00	1:3	30.00	28.00	29.34
1	6	Factorial	35.00	40.00	1:2	20.00	21.667	21.64
3	7	Factorial	35.00	80.00	1:2	20.00	17.500	18.21
20	8	Centre	40.00	60.00	1:3	30:00	28.667	29.34
8	9	Factorial	45.00	80.00	1:4	20:00	21.333	21.04
7	10	Factorial	35.00	80.00	1:4	20:00	20.667	19.03
4	11	Factorial	45.00	80.00	1:2	20:00	20.667	21.14
15	12	Factorial	35.00	80.00	1:4	40:00	43.000	43.30
9	13	Factorial	35.00	40.00	1:2	40:00	44.00	43.58
13	14	Factorial	35.00	40.00	1:4	40:00	45.500	44.73
12	15	Factorial	45.00	80.00	1:2	40:00	44.000	42.50
11	16	Factorial	25.00	80.00	1:20	40.00	42.00	42.15
5	17	Factorial	35.00	40.00	1:4	20.00	21.667	22.46
17	18	Centre	40.00	60.00	1:3	30.00	28.667	29.34
14	19	Factorial	45.00	40.00	1:4	40.00	42.00	40.58
10	20	Factorial	45.00	40.00	1:2	40.00	39.00	40.34
27	21	Axial	40.00	60.00	1:3	10:00	9.1667	9.38
28	22	Axial	40.00	60.00	1:3	50:00	52.222	53.01
30	23	Centre	40.00	60.00	1:3	30.00	30.48	28.667
23	24	Axial	40.00	20.00	1:3	30:00	30.00	30.48
29	25	Centre	40.00	60.00	1:3	30.00	29.667	27.61
26	26	Axial	40.00	60.00	1:5	30:00	29.333	30.70
24	27	Axial	40.00	100.00	1:3	30:00	28.667	29.20
22	28	Axial	50.00	60.00	1:3	30:00	27.333	28.39
21	29	Axial	30.00	60.00	1:3	30:00	29667	29.62
25	30	Axial	40.00	60.00	1:1	30:00	30.00	29.64

3. RESULTS AND DISCUSSION

CCD was used to develop a polynomial regression equation in order to analyze the correlation between the concentrating variables to the final concentration of the isopropyl alcohol water solution.

''Table'' 1 shows the complete design matrixes together with the response values obtained from the experimental work and that predicted by the model.

Runs at the center points were conducted to determine the experimental error and the reproducibility of the data. According to the sequential sum of squares, the model was selected based on the highest order polynomials where the additional terms were significant and the models were not aliased. For this study, the quadratic vs two factor interaction model was selected by the software.

The final empirical equation model for the final concentration of the isopropyl alcohol in terms of coded factors is shown in ''(2)'', below.

$$Y = 29.15 - 0.11A - 0.4B + 0.46C + 10.56D + 0.66AB - 0.28AC - 0.29AD + 0.39BC + 0.19BD + 0.60CD + 0.56A^2 - 0.094B^2 + 0.44C^2 + 0.52d^2 \quad (3)$$

Y is the final concentration of the isopropyl alcohol water solution, A is the Temperature in ^oC, B is the time in mins, C is the adsorbent/solution ratio and D is the initial concentration of the isopropyl alcohol water solution in %.

The coefficient with one factor represent the effect of the particular factor, while the coefficients with two factors and those with second order terms represent the interaction between two factors and quadratic effect, respectively.
The positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The quality of the model developed was evaluated based on the correlation coefficients, R^2 value. The model developed was best at low standard deviation and high R^2 statistics which is closer to unity as it will give predicted value closer to the actual value for the response.

R^2 of 0.9909 and standard deviation of 1.34 indicated that the predicted value of the final concentration would be more accurate and closer to its actual values.

Model summary statistics focuses on the model maximizing the adjusted R – squared and the predicted R – squared. The predicted R – square of 0.9538 is in reasonable agreement with the adjusted R – squared of 0.9818.

Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 43.240 obtained from this study indicated an adequate signal. This means that the model can be used to navigate the design space.
The adequacy of the models was further justified through analysis of variance (ANOVA).

TABLE 2: ANOVA TABLE

Source	Sum of Squares	df	Mean Square	F – Value	Prob>F
Block	13.64	1	13.64	-	-
Model	2724.90	14	194.64	108.68	<0.0001
A-TEMP	0.30	1	0.30	0.17	0.6903
B-Time	3.76	1	3.76	2.10	0.1694
C-ADS/Solution	5.04	1	5.04	2.82	0.1155
D-Initial Concentration	2678.77	1	2678.77	1495.79	<0.0001
AB	6.89	1	6.89	3.85	0.0700
AC	1.27	1	1.27	0.71	0.4148
AD	1.36	1	1.36	0.76	0.3980
BC	2.38	1	2.38	1.33	0.2686
BD	0.56	1	0.56	0.31	0.5842
CD	5.84	1	5.84	3.26	0.0925
A^2	8.66	1	8.66	4.84	0.0452
B^2	0.24	1	0.24	0.14	0.7178
C^2	5.24	1	5.24	2.92	0.1094
D^2	7.52	1	7.52	4.20	0.0596
Residual	25.07	14	1.79	-	-
Lack of fit	23.43	10	2.34	5.72	0.0537
Pure error	1.64	4	0.4	-	-

Statistical analysis obtained from the analysis of variance (ANOVA) for response surface quadratic model is shown in ''table'' 2. The value of "P>F" indicated that the model is significant which is desirable as it indicated that the terms in the model have a significant effect on the response. The P-value of 0.0001 indicated that there is only a 0.01% chance that a "model F – value" this large could occur due to noise. Generally P – value lower than 0.01 indicated that the model is considered to be statistically significant at the 99% confidence level [5]. Values greater than 0.1000 indicated the model terms are not significant. In this case, D, AB, D^2 are significant model terms.

The "lack of fit F – value" of 5.72 implied that the lack of fit is not significant. There is only a 5.37% chance that a "lack of fit F – value" this large could occur due to noise.
From the statistical results obtained, it was shown that the above model were adequate to predict the final concentration within the range of variable studied.

''Fig'' 1 shows the predicted values versus the experimental values for the dehydration capacity. As can be seen, the predicted values obtained were quite close to the experimental values, indicating that the model developed was successful in capturing the correlation between the final concentration and the dehydration variables.

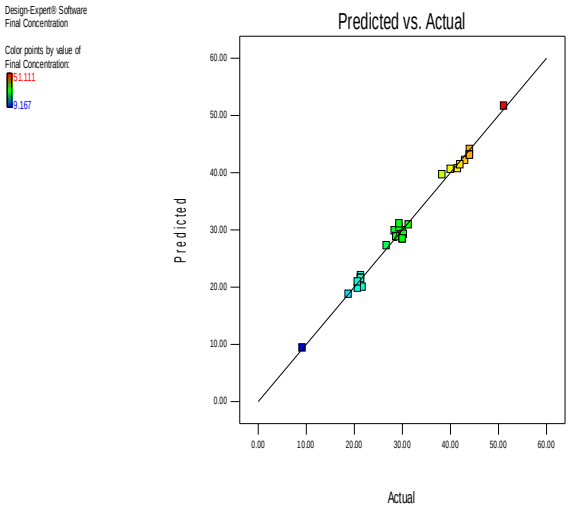


Fig. 1 Predicted vs Actual values for the final concentration.

EFFECT OF PROCESS PARAMETERS

The effects of individual variables on the uptake of water were discussed by response surface one factor plot in ''fig''2, while the interaction between variables is shown in ''fig''3 in the form of three – dimensional response surface and contour plots.

INFLUENCE OF INDIVIDUAL FACTORS

The individual effect of Temperature (A), Time (B), adsorbent/solvent ratio (C) and initial concentration of the solution (D) towards the final concentration of the solutions were plotted in ''fig'' 2 from the graph it showed that temperature (A), Time (B) and adsorbent/solvent ratio (C) had no effect on the final concentration. This meant that any increase or decrease on the factor will have little or no effect on the response. Initial concentration (D) had a positive effect on the response. This showed that as the initial concentration is increased the final concentration of the solution also increases.

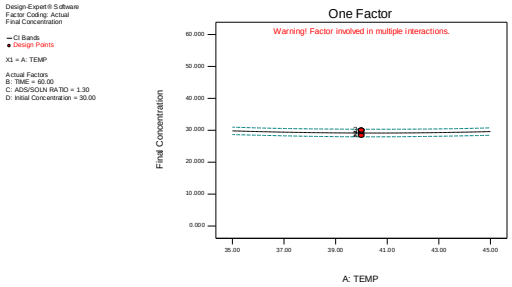


Fig (2a). Temperature Effect.

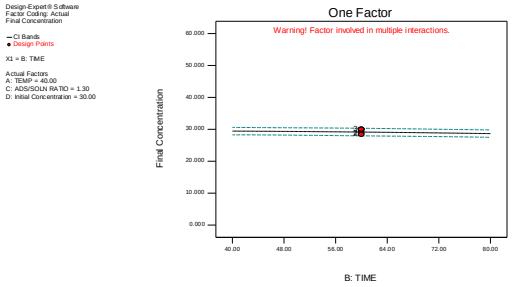
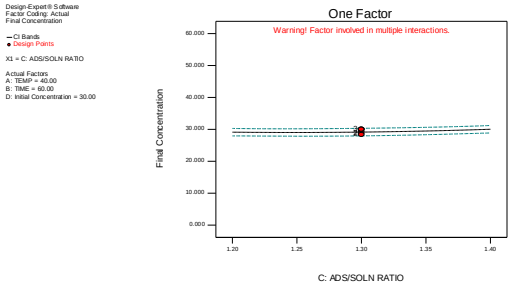


Fig (2b). Time Effect



Fig(2c). Adsorbent/Solution ratio Effect

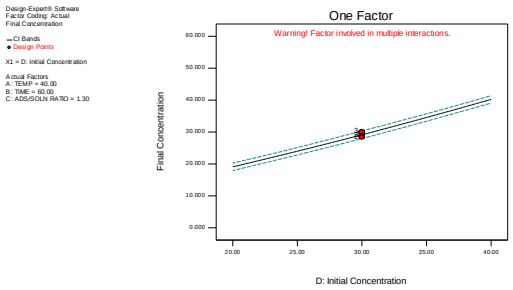


Fig (2d). Initial Concentration Effect

However, the interaction effects must also be considered as the individual effect plot does not give information regarding the significant interactions involved.

INFLUENCE OF INTERACTION EFFECT

Three dimensional and contour plots for interaction effect of initial concentration (D) with other factors are shown in ''fig'' 3.

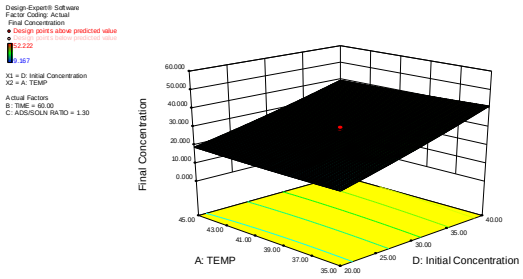
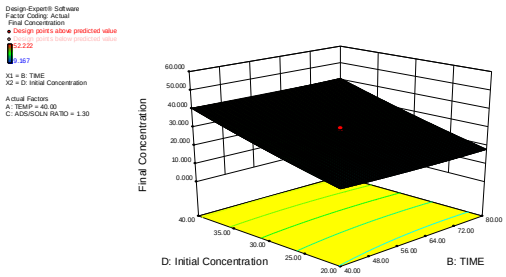
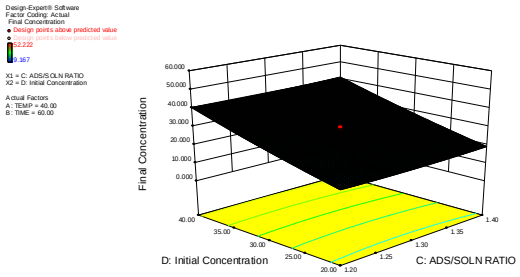


Fig (3a). Temperature Effect



Fig(3b). Time Effect



Fig(3c). Adsorbent/Solution ratio Effect

The contour and 3 dimensional plots showed that as initial concentration is increased with any value of the other factors, the final concentration increased.

PROCESS OPTIMIZATION

In the dehydration of isopropyl alcohol, relatively high concentration is expected when the factors are varied inter-changeably. To obtain the best conditions that will give the highest concentration using the model, optimization was done using Design expert software 8.0.1 version. With the aim of maximizing the response, the condition that gave the highest desirability of 0.812 was selected. The optimal final concentration of 43.968% was obtained using Temperature of 34^{o}C, Time of 40 mins, adsorbent/solvent ratio of 1:4 and initial concentration of 40%.

CONCLUSION

A central composite design was conducted to study the effects of four dehydration variables which where, the temperature, time, adsorbent/solution ratio, and initial concentration of the isopropyl alcohol water solution on the final concentration of the isopropyl alcohol solution A quadratic vs 2FI model was developed to correlate the dehydration variables to the final concentration of the isopropyl alcohol solution.

Through analysis of the response surfaces derived from the models, time, temperature and adsorbent/ solution ratio were found not to have significant effect on the response, while the initial concentration of isopropyl alcohol was found to have significant effect on the response. Process optimization was carried out and the optimum dehydration conditions were obtained at temperature of 35^{o}C, time of 40 mins , adsorbent/solution ratio of 1:4 and initial concentration of 40% with the predicted response of 43.369%.

The potato starch was found as promising adsorbent for water uptake from the solution.

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