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Statistical optimization of removal of nitro-body compounds from spent acid of toluene nitration process

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ABSTRACT

The removal of nitro-body compounds from spent acid of toluene nitration process was made by two methods of extraction by ethyl acetate solvent and adsorption by activated carbon particles. In extraction method, three parameters of spent acid sample volume, volume of extracting solvent and the amount of water for dilution of samples were statistically modelled and optimized using mixture design of experiments by Minitab 17 software. In the optimized conditions, the mean of extraction efficiency was obtained 98.5 ± 1.4 wt.% in one step of extraction. Also, the treatment of spent acid for removal of nitro-body compounds by activated carbon adsorbent was optimized using Taguchi method by Minitab 17 software. The optimized values for three variables of shuffle time of mixture, the amount of adsorbent and the dilution times of sample are obtained respectively, 90 min, 0.1 g/L and 10 times by the statistical analysis of Taguchi design. The removal efficiency was resulted 87.5 ± 2.6 wt.% of nitro-body compounds by using activated carbon adsorben. The advantages of proposed methods for the elimination of organic containments in waste acid of trinitrotoluene production process were the safety, simplicity, inexpensive, availability and industrialization.

Keywords: Spent acid; Nitration process; Mixture and Taguchi design; Optimization; Nitro-body compounds

1. Introduction

Trinitrotoluene (TNT) is one of the most commonly used explosives for military and mining applications. In industry, TNT is produced in a three-step process, by nitration of toluene to mononitrotoluene (MNT) with a mixture of sulfuric acid and nitric acid. The MNT is separated and then re-nitrated to dinitrotoluene (DNT). Then, the DNT is nitrated to TNT using an anhydrous mixture of nitric acid and oleum. In this process, main amount of nitric acid is consumed by the manufacturing process, but the diluted sulfuric acid can be re-concentrated and reused [1]. Also, DNT is the main raw materials for the production of toluene diisocyanate (TDI), extensively used in the production of flexible polyurethane foams. It is produced on a large scale, accounting for 34.1% of the global isocyanate market in 2000 [2], and approximately 1.4 billion kilograms were produced in 2000 [3].

The nitration of toluene to form MNT, DNT and/or TNT results in the production of a large stream of contaminated spent sulfuric acid and nitric acid. The success of the recycling of sulfuric acid and nitric acid stream depends on the effective removal of the contaminants mainly MNT, DNT and residual TNT as nitro-body compounds [4,5], because the solidification and energetic characteristics of these compounds can lead to blocking of distillation columns and explosion hazards, that limit the treatment process of acids in the related distillation units. Therefore, a certain amount of organics will normally need to be removed to enable indefinite recycling of the acids with no impact on operation of either the nitration or the acid recovery stages [6]. Due to the mentioned organic contaminants, the spent mixed acid is regenerated industrially in two steps, including purification and concentration. The former aims to abate

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organic compounds and residual nitric acid, and the latter are responsible for adjusting of concentration of sulfuric acid [7]. For purification and thus recycling of sulfuric acid and nitric acid stream in nitration process, the removal of nitro-body compounds is the aims of explosive industries.

The several methods were introduced for elimination of nitro-aromatic compounds from this type of waste acids, such as degradation by hydrogen peroxide or ozone [8], oxidative degradation by potassium permanganate [9], the extraction of dinitrotoluenes and trinitrotoluene by some solvents such as hexane, pentane and benzene [4,10], the converting to high molecular weight, distillation and removal by superheated steam [11], mineralization of dinitrotoluenes and trinitrotoluene of spent acid by Fenton oxidation [12], decomposition by ozonation and photo-ozonation [13], decomposition by electro-Fenton oxidation [14], and also electrochemical destruction process [15]. But, the used solvents show harmful and toxicity effect on environment, and other methods such as Fenton oxidation, ozonation, and electrochemical procedures are significantly expensive for large scale production processes. This research introduce two safe and inexpensive methods for the removal of nitro-body contaminants in the spent acids samples of process of toluene nitration based on the extraction of organic materials by ethylacetate solvent, and their adsorptive by activated carbon particles.

Ethyl acetate is an organic solvent, used as solvent for flavors, fragrances, foods, cosmetics, and personal cares, with median lethal dose for rats, LD_{50} (abbreviation for lethal dose, 50%) near to 5600 mg/kg [16], indicating relatively little risk of toxicity for the ethyl acetate chemical, naturally present in many organisms. In first section of this work, an extreme vertices mixture design methodology were used to study and optimize the effects of mixture components on the response variable by using this solvent for removal of nitro-body compounds. The standard mixture designs of experiments are simplex-lattice, simplex-centroid, and extreme vertices designs. In many situations, that both upper and lower level of components has constraints, the entire simplex design cannot be used, and the extreme vertices designs are most appropriate for these conditions [17–19].

Activated carbon was introduced as green materials [20] and green adsorbent [21]. Carbon adsorption has numerous applications in removing pollutants from air or water streams both in the field and in industrial processes such as: groundwater remediation [22], drinking water filtration [23], air purification [24], dye removal [25], treatment of TNT red water [26], and other processes. The removal of nitro-body compounds by using activated carbon particles was optimized by Taguchi method in the second section of this work. The Full Factorial Design requires a large number of experiments to be carried out as stated above. It becomes laborious and complex, if the number of factors increase. To overcome this problem Taguchi suggested a specially designed method called the use of orthogonal array to study the entire parameter space with lesser number of experiments to be conducted. Taguchi thus, recommends the use of the loss function to measure the performance characteristics that are deviating from the desired target value. The value of this loss function is further transformed into signal-to-noise (S/N) ratio. Usually, there are three categories of the performance characteristics to analyze the S/N ratio. They are: nominal-the-best, larger-the-better, and smaller-the-better [27].

2. Experimental

2.1. Spent acid

A real spent acid of TNT production process was used for study of elimination of organic contaminants. The composition of spent acid was 78.4% of H_2SO_4, 3.6% of HNO_2 and 1.2% of HNO_3 and density of 1.60 g/mL. The amount of nitro-body compounds was obtained 0.45 g in 12.5 mL (~20.0 g) of spent acid that is equivalent of 22500 ppm of COD. The quantitative of COD was used for measurement of nitro-body compounds in spent acid. The HACH test vials (prepared from HACH Company: Water Quality Testing and Analytical Instruments) containing potassium dichromate oxidant, catalyst, masking reagent and diluted spent acid were put into digestion unit [8]. After cooling and cleaning the vials, the COD of diluted spent acid samples was tested by measuring of absorbance at a wavelength of 620 nm in the range of 0–1000 mg/L.

The samples were analyzed to measure the absorbance of diluted spent acid samples by using a UV-Vis spectrophotometer Carry-100.

2.2. Extraction procedure

The solvents of benzene, hexane, cyclohexane and ethyl acetate (all from Merck) were used as extracting solvents in removal of nitro-body compounds of spent acid. In each experiment, 40 mL of deionized water was added to 12.5 mL of spent acid and then, the different volumes (20–100 mL) of extracting solvent was added to diluted spent acid. The samples were stirred for time of 4 min. by a magnetite stirring. The separation of organic and aqueous phases was done by a separating funnel. The residual of organic contaminants in aqueous phase was measured by COD test (n = 3). The extraction efficiency was reported as the percentage of removal of organic contaminants of spent acid.

In this work, after selection of the best solvent for elimination of nitro-body compounds, the MINITAB 17.0™ package software was used for extreme vertices mixture design, analysis of experimental data and optimization of the conditions of extraction. Extreme vertices designs are mixture designs that cover only a sub-portion or smaller space within the simplex. These designs must be used when your chosen design space is not an L-simplex design. The presence of both lower and upper bound constraints on the components often create this condition. The goal of an extreme vertices design is to choose design points that adequately cover the design space [28,29].

Extreme vertices mixture design (3 factors, 2 levels, Table 1) was used in extraction procedure by different amounts of water for dilution of spent acid (X_1), spent acid sample (X_2) and extracting solvent (X_3). Upper and lower limits were also defined for each component based on preliminary experimental results, and also all proportions of components in each formulation were sum to 100.0 *vol*. % for a mixture load of 100.0 mL.

Table 1
The range of parameters for mixture design method in optimization of nitro-body elimination by extraction method

Parameter	Minimum	Maximum
Water for dilution of spent acid, mL (X_1)	40	60
Amounts of spent acid, mL (X_2)	10	20
Extractant solvent, mL (X_3)	30	50

2.3. Adsorption of nitro-body compounds by activated carbon particles

The removal of nitro-body compounds from spent acid was also studied in a batch procedure by adsorbent of carbon active particles prepared by pine tree wood [26], with area and pores volume of 197.0–211.0 m^2/g and 0.149–0.157 cm^3/g, respectively. A known weight of adsorbent (e.g. 0.02–0.10 g) was equilibrated with 10 mL of the spent acid diluted with water (e.g. 0.0–10.0 times) in a polyethylen vessel at room temperature in a thermostatic mechanical shaker for a known period of time (30–120 min). Mechanical shaker is used for all the adsorption experiments for agitating the sample for a desired contact time. After removal of organic contaminants of samples, the carbon particles were separated by centrifuge for time of 20 min at 6000 rpm and the residual of nitro-body compounds was measured by COD test.

The Taguchi L16 orthogonal array design was used to optimization of removal process of nitro-body compounds. The 16 experiments were conducted at different parameters which has sixteen rows corresponding to the number of tests, with three columns at four levels. For the purpose of observing the degree of influence of the process parameters in removal efficiency, three factors, each at four levels, are taken into account, as shown in Table 2. The selected factors were the shuffle time of mixture (X_1), the amount of adsorbent of carbon particles (X_2) and the dilution times of spent acid (X_3).

3. Results and discussion

3.1. Optimization of extraction of nitro-body compounds from spent acid

In the scientific researches, to verify the precision and accuracy of experimental data, using of statistical analysis is very important and necessary. Modeling of data is based on the detail experimental work, planned by standard experimental design and matrix or optimization routes. In order to increase the extraction efficiency of nitro-body compounds from samples, several solvent were used. Fig. 1 shows the extraction efficiency versus volume of solvent for a sample contains 12.5 mL of spent acid and 40 mL of water.

Table 2
The parameters of removal process of nitro-body compounds from spent acid by adsorption using granule carbon particles

Parameter	Code	Levels			
		1	2	3	4
Shuffle time, min	X1	30	60	90	120
Amount of carbon particles, g/L	X2	0.02	0.05	0.08	0.10
Dilution times of spent acid	X3	0	2	5	10

The highest of extraction efficiency of organic compounds of spent acid was obtained by using ethyl acetate as extracting solvent. Also, the optimum amount of extracting solvent was 60 mL for a sample contains 12.5 mL of spent acid and 40 mL of water. The nitro-body compounds in spent acid are 2,3-DNT, 2,6-DNT, 3,4-DNT, 2,4-DNT and 2,4,6-TNT. The polarity of these compounds is due to increasing of extraction efficiency by using ethyl acetate as extracting solvent in comparison of other used solvents [30,31]. The number of stage of extraction was tested and the extraction efficiency of 98% was obtained in three stages with consumption of 20 mL of extracting solvent in each stage. Also, the mixing time of two-phase in extraction process was optimized in 4 min.

The prepared conditions according to Mini tab statistical mixture design were listed in Table 3. Experimental tests were performed according to the matrix proposed by the program Mini tab 17 for optimization of the required volume proportion of three component mixture of water (X_1), spent acid (X_2) and ethyl acetate (X_3). The number of replicates for the whole design was 3 and thus 27 points were obtained for experiments. The experimental and predicted results expressed by the extraction efficiency of nitro-body compounds are summarized in Table 3.

The model for extraction efficiency according to the three factors can be as Eq. (1).

$$Y = b_1X_1 + b_2X_2 + b_3X_3 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 + b_{12(1-2)}X_1X_2(X_1 - X_2) + b_{13(1-3)}X_1X_3(X_1 - X_3) \quad (1)$$

In the regression fitting, with a 95% confidence level, the full cubic models were postulated in Eq. (1) for extraction efficiency response (Y), at the interval of our experiment design (Eq. (2)):

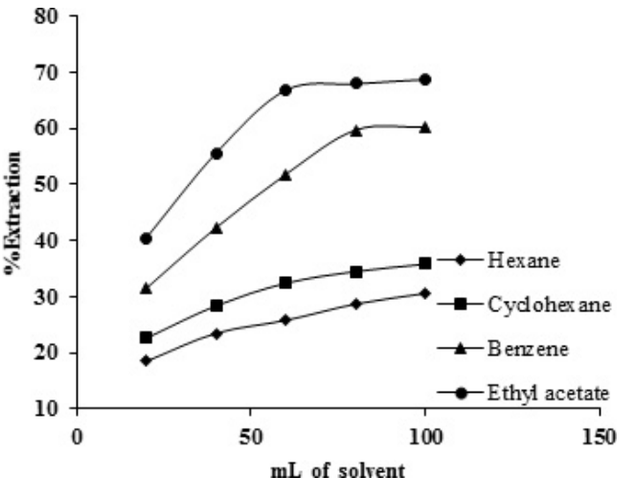

Fig. 1. The effect of solvent on the extraction efficiency of nitro-body compounds from spent acid samples.

Table 3
The extreme vertices mixture design and the related experimental and predicted extraction efficiencies

No. of experiment	Water (X_1), vol.%	Spent acid (X_2), vol.%	Ethyl acetate (X_3), vol.%	Extraction (Y), wt.%	Predicted (Y), wt.%
1	47.50	15.0	37.50	83.33	84.08
2	43.75	12.5	43.75	97.78	98.48
3	48.75	17.5	33.75	47.62	49.89
4	40.00	10.0	50.00	97.22	99.26
5	50.00	20.0	30.00	42.67	44.02
6	40.00	20.0	40.00	62.50	62.28
7	40.00	20.0	40.00	63.90	62.28
8	53.75	12.5	33.75	66.67	68.49
9	43.75	17.5	38.75	73.02	73.24
10	60.00	10.0	30.00	72.22	74.01
11	60.00	10.0	30.00	77.80	74.01
12	50.00	20.0	30.00	46.00	44.02
13	48.75	17.5	33.75	50.80	49.89
14	50.00	20.0	30.00	43.05	44.02
15	40.00	10.0	50.00	100.00	99.26
16	40.00	10.0	50.00	97.22	99.26
17	53.75	12.5	33.75	71.11	68.49
18	40.00	20.0	40.00	61.11	62.28
19	47.50	15.0	37.50	85.20	84.08
20	53.75	12.5	33.75	66.67	68.49
21	43.75	17.5	38.75	73.02	73.24
22	43.75	12.5	43.75	100.00	98.48
23	43.75	17.5	38.75	71.42	73.24
24	48.75	17.5	33.75	52.40	49.89
25	60.00	10.0	30.00	72.22	74.01
26	47.50	15.0	37.50	85.20	84.08
27	43.75	12.5	43.75	97.78	98.48

$$Y = -3.034X_1 + 156.134X_2 + 116.762X_3 - 1.394X_1X_3 - 11.726X_2X_3 + 0.197X_1X_2X_3 - 0.144X_1X_2(X_1 - X_2) + 0.037X_1X_3(X_1 - X_3) \quad (2)$$

where X_1; the amount of water for dilution of spent acid (vol. %), X_2; the amount of spent acid (vol. %), and X_3 is the amount of ethyl acetate (vol. %). The obtained coefficients of Eq. (2) show that the volume of spent acid (sample) and ethyl acetate have the main effect on the extraction efficiency. The predicted values using proposed model (Eq. (2)) were matched with the experimental values. The regression coefficients R^2 and $R^2(adj)$ were obtained 99.22 and 98.93%, respectively, for the response Y. Also, the residual plots for the responses showed that the distribution of the residuals for the response approximately follows the fitted normal distribution and the residuals of the response randomly scatter in the residual plots.

The statistical significance of the ratio adjusted mean square (*adj MS*) due to the regression and adjusted mean square of residual error was tested using analysis of variance (ANOVA). The mentioned ratio allowed the calculation of the Fisher ratios (F-value) for assessing the statistical significance. The residual error measures the amount of variation in the response data left unexplained by the model. According to the ANOVA analysis (Table 4), the model F-values of 343.99 for Y implies that most of the variation in the response can be explained by the regression equation. Also, the related p value is used to judge whether F-ratio is large enough to indicate statistical significance. A p value more than 0.05 indicated that the model could not be considered statistically significant. The p value for the two regressions of Y obtained $p = 0.000$ were lower than 0.05 and means consequently that all terms in the regression equation has significant correlation with the response variable [32].

In the mixture design, the effect of variable changes on the responses can be observed on response trace plots (also called a component effects plots) and the mixture surface plots, presented in Figs. 2 and 3. The response trace plot represents the influence of each element at the center point

Table 4
Analysis of variance for the regression data

Source	DF[a]	Seq SS[b]	Adj SS[c]	Adj MS[d]	F[e]	P
Regression	7	8911.86	8911.86	1273.12	343.99	0.000
Linear	2	7667.25	312.17	156.09	42.17	0.000
Quadratic	2	436.74	521.72	260.86	70.48	0.000
Full cubic	2	794.52	794.52	397.26	107.34	0.000
Residual error	19	70.32	70.32	3.70		
Lack of fit	1	3.43	3.43	3.43	0.92	0.349
Pure error	18	66.89	66.88	3.71		
Total	26	8982.18				

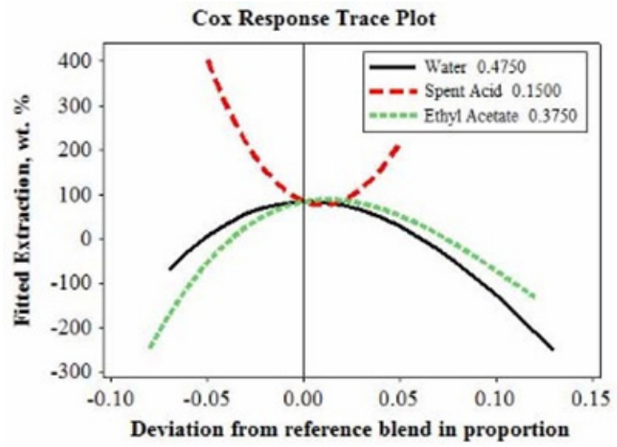

Fig. 2. Response trace plots for the separation of nitro-bodies by ethyl acetate solvent.

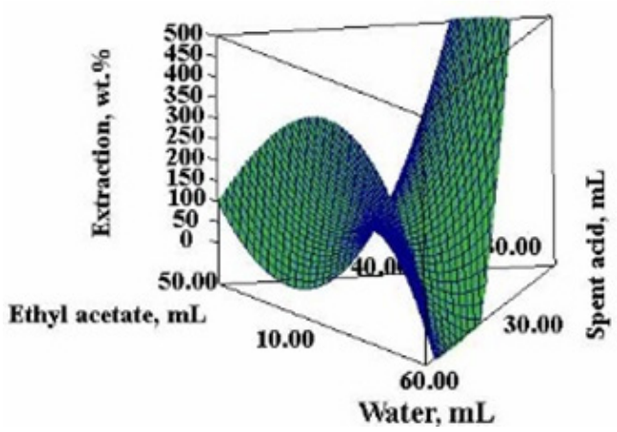

Fig. 3. Response surface plots of water, spent acid and ethyl acetate on the extraction efficiency of nitro-bodies.

of the experimental region on response values. Also, the multi-dimensional plot of Eq. (2) model presented in Fig. 3, shows the effect of various experimental parameters on the extraction efficiency. According to Figs. 2 and 3, the extraction efficiency of nitro-body is relatively improved by increasing in the amount of ethyl acetate and dilution water in the mixture. Furthermore, increasing in the amount of spent acid in the separation mixture leads to decreasing in the separation efficiency of nitro-body compounds. In Fig. 3, the predictions have been also drawn outside of the actual extraction yield. However, in the experimental range, the behavior of extraction efficiency, similar to Fig. 2, is simple and tends to its maximum amount near to center point of mixture design.

Using the Mini tab software, the response optimization calculations were performed to find simultaneously an optimum mixture proportions for higher extraction efficiency (Y responses). Response optimizations recognize the combination of input variable settings that jointly optimize a single response or a set of responses. Here, the maximum responses of 99.9 wt.% extraction efficiency was predicted from the mixture formulation which contained 47.5 *vol. %* water, 14.34 *vol. %* spent acid, and 38.16 *vol. %* of ethyl acetate solvent. The mean desirability of prediction was near to 0.9999. Desirability (d) is a measure of how the solution has satisfied the combined goals for the response, and it has a range of zero to one. One represents the ideal case; zero indicates that one or more responses are outside their acceptable limits. The mean experimental results with five times reproduction in the above optimized conditions show the mean extraction efficiency of 98.5 wt.%, with relative error of 1.4 % for Y.

3.2. Removal of nitro-body compounds from spent acid by activated carbon particles

The removal of nitro-body compounds from spent acid samples was also studied via adsorption by activated carbon particles [26,33]. The optimization of parameters on the removal efficiency such as the dose of adsorbent, the dilution times of spent acid (by addition of water) and shuffle time were done by Taguchi design of experiments. The conditions of experiments, the removal efficiency and the signal to noise for responses are collected in Table 5.

The Fig. 4 shows the main effects plot for means of selected parameters in adsorption process by activated carbon particles. As seen, the removal efficiency (mean of means) is increased with increasing of shuffle time, dose of adsorbent and dilution times. However, the most changes in removal efficiency are observed with shuffle time of sam-

Table 5
Taguchi L16 OA for removal efficiency of nitro-body compounds from spent acid by adsorption using granule carbon particles

Experiment No.	X_1, Shuffle time (min)	X_2, Dose of carbon adsorbent (g/L)	X_3, Dilution times of spent acid	Removal (%)	S/N ratio
1	30	0.02	0	82.5	38.3291
2	30	0.05	2	83.1	38.3920
3	30	0.08	5	85.2	38.6088
4	30	0.10	10	86.0	38.6900
5	60	0.02	2	85.7	38.6596
6	60	0.05	0	85.0	38.5884
7	60	0.08	10	86.8	38.7704
8	60	0.10	5	86.2	38.7101
9	90	0.02	5	88.2	38.9094
10	90	0.05	10	89.5	39.0365
11	90	0.08	0	87.3	38.8203
12	90	0.10	2	88.2	38.9094
13	120	0.02	10	90.3	39.1138
14	120	0.05	5	89.5	39.0365
15	120	0.08	2	89.2	39.0073
16	120	0.10	0	89.1	38.9976

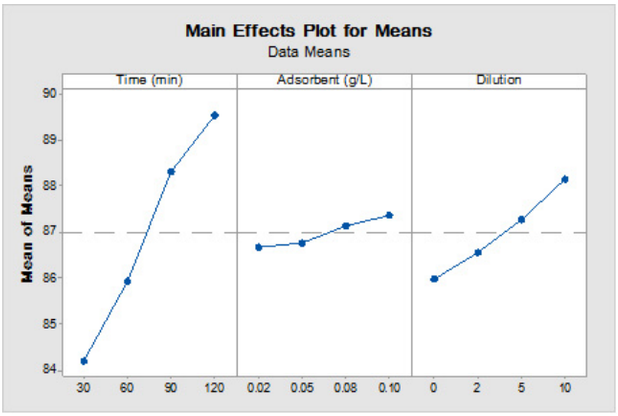

Fig. 4. The main effects plot for means (removal efficiency) of selected parameters (shuffle time, dose of adsorbent and dilution ratio) in removal of nitro-body compounds from spent acid samples by activated carbon particles.

Table 6
Response table for signal to noise ratios, larger is better

Level	Shuffle time (min)	Dose of adsorbent (g/L)	Dilution times
1	38.50	38.75	38.68
2	38.68	38.76	38.74
3	38.92	38.80	38.82
4	39.04	38.83	38.90
Delta	0.53	0.07	0.22
Rank	1	3	2

ples. In Table 6, the responses for signal to noise ratios, larger is better mode [34], is collected. The obtained S/N ratios indicate that the optimum parameters are shuffle time of 90 min, the dose of adsorbent of 0.1 g/L and the dilution times of 10. The predicted removal efficiency is obtained 89.85 wt.% in optimum values of used parameters with S/N ratio of 39.0759. The mean experimental results with five times reproduction in these conditions show the mean removal efficiency of 87.50 wt. %, with relative error of 2.6 %.

The multiple linear regression (MLR) method [35] was used to reliable of coefficients of variables and p-values, the R square of regression and data of ANOVA (analysis of variance) test (Table 7). The R^2 value is 0.9671 that means the fitting of observed values and predicted values of removal efficiencies. The predicted equation for removal efficiency (Y) is as:

$$Y = 80.928 + 0.061X_1\left(Shuffle\ time\right) + 8.946X_2 \left(Dose\ of\ adsorbent\right) + 0.215X_3\left(Dilution\ times\right) \quad (3)$$

The P-value of coefficient's are < 0.05 that indicate in confidence level of 95%, the null hypothesis is rejected and there are a meaningful dependence between variables and response of removal efficiency [36]. Also, the importance of parameters on the response is obtained as: dose of adsorbent > dilution times > shuffle time.

4. Conclusion

In this research, two safe methods can be used for the elimination of nitro-body contaminants in the spent acid

Table 7
The summery output of multiple linear regression (MLR) method on the data of experimental of nitro-body removal by granule active carbon

ANOVA				
Source	DF	SS	MS	F
Regression	3	78.99028	26.33009	117.5793
Residual error	12	2.687218	0.223935	
Total	15	81.6775		
Modelling data				
	Coefficients	Standard Error	P-value	R Square
Intercept	80.92818	0.401623	1.5E-22	0.9671
X Variable 1	0.061167	0.003527	7.32E-10	
X Variable 2	8.945578	3.903033	0.040787	
X Variable 3	0.214758	0.031409	1.8E-05	

samples of trinitrotoluene production process based on the extraction by ethylacetate solvent and adsorption using activated carbon particles.

In the extraction route, the effects of three-component mixture of water for dilution of spent acid (X_1), spent acid sample (X_2) and ethyl acetate solvent (X_3) on the extraction efficiency of nitro-bodies (Y) were modelled and optimized using the extreme vertices mixture designs of experiment. The experimental conditions and statistical tools indicated that the predicted values of extraction are well matched with the experimental values. The validation of proposed model proved with R^2 of 99.22% and $R^2(adj)$ of 98.93% for the response Y. The optimized experimental conditions for the extraction achieved from the mixture 47.5 vol.% water, 14.34 vol.% spent acid, and 38.16 vol.% of ethyl acetate solvent. The mean of extraction efficiency of 98.5 wt.% and relative error of 1.4% is obtained in optimized conditions.

The safe and inexpensive method of adsorption by activated carbon particles can also used for removal of nitro-body compounds in spent acid samples. The method was optimized by Taguchi design of experiments. The mean and relative error, respectively, 87.5 and 2.6 wt.% for removal efficiency of nitro-body compounds are obtained in optimized conditions of shuffle time of mixture, the amount of adsorbent and the dilution times of sample.

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