Application of Response Surface Methodology (RSM) to Optimize COD and Ammoniacal Nitrogen Removal from Leachate using Moringa and Zeolite Mixtures

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Abstract: This paper reported the optimization of COD and NH_3-N reduction from a stabilised leachate by zeolite (ZE) and moringa oleifera leaf powder (MP) mixture using response surface methodology (RSM) and central composite design (CCD). Quadratic polynomial equations were obtained for the removal process. An initial experiment was conducted to establish the optimum mixed ratio between ZE:MP and resulted in a ratio of 24:16. Independent variables investigated in the subsequent optimization experiments include pH ,dosage and contact time. The results revealed that the optimal reduction of COD and NH_3-N from landfill leachate was considerable at pH 5.9 , optimal time of 113 minutes and $100gL^{-1}$ of adsorbent dosage with desirability value of 0.917. The upper limits for the actual versus predicted reduction were 70.14 against 69.13% and 86.94 against 86.55 % respectively for COD and NH_3-N which defined that the experimental values were relatively close to the predicted values. The study also revealed that ZE:MP mixture has a very high potential for the remediation of COD and NH_3-N from a stabilized leachate.

Keywords: zeolite, moringa, RSM ,optimization , leachate, COD and NH_3-N.

1. Introduction

Sanitary landfills are designed waste conservation systems encompassing high-technology processes and applied to dispense with the solid waste generated from municipal or industrial activities. In developed nations, waste disposal does not only rely on sanitary landfills but extended to concept of waste minimization such that the waste that reaches the landfill is eventually minimized. Sanitary landfills in developing countries are susceptible to problem of technological and economic constraints. landfills are predominantly built of layers of accumulated solid waste and overlaid with soil or other types of blanket materials. Landfills constitute a problem in waste disposal because they produce leachate. Leachate is generated from the biochemical reaction that occurs within the waste deposit as it undergoes physical, biological, and chemical decomposition under aerobic and anaerobic conditions[1-3]. It usually comprise of dissolved pollutants, unstable organic acids, toxicant heavy elements, and high density of organic matter, chemical oxygen demand (COD), ammonia nitrogen as well as biochemical oxygen demand (BOD), and may pose a critical threat to the environment and to public health if necessary control is not applied prior treatment; resulting in soil contamination and water bodies especially the rivers, lakes and groundwater that hold 0.016%, 1.5%, and 22.3%, of the earth's freshwater respectively. Virtually all prevailing leachate treatments incorporate high-technology processes. Such processes are considered to contribute to high initial and operational cost, generation of waste residue, and less adaptability to a wide variety of pollutants, among others. Selecting and designing a suitable leachate treatment system are difficult because of the dissimilarity in the amount and characteristics of leachate produced from landfill to landfill, especially as the landfills age [4-6]. Inconsistencies between landfill leachates are due to their hydrogeological conditions, locations, and environmental contributors. Hence, landfill leachates from different landfills and their respective treatment must be processed appropriately per the characteristics of each site [7,8]. Leachate treatment is necessary to prevent ground and surface water pollution although pollutant level generally decreases with landfill age.

The application of natural plant for cleansing of contaminated soil and water known as phytoremediation, has attained increasing recognition due to the added cost-effective and lesser side effects than chemical or other approaches [9,10]. Numerous plant species have been identified and examined for their potential in reducing

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different pollutants. Among them is the reknown *Moringa oleifera*, which is known by numerous regional names as; murunga (Sri Lanka), zogale (Nigeria), ben aile (Cambodia), la mu (Taiwan), Kelor (Malaysia) mulangai (India) among others [9-11]. The emerging challenge is in the application of biosorbents and their mixtures for the treatment of landfill effluents.

The response surface methodology (RSM) with a multivariate function of the polynomial equation model is very eminently effective to relate the experimental data set of the optimisation system. The factorial design of the response surface analysis provides reliable information about the adsorption process interactions and saves time and materials significantly as opposed to the conventional linear optimization technique. The conventional linear optimization involves changing a parameter and fixing other variant parameters constant which is more commonly referred as one-factor-at-a-time. The methodology of RSM it assesses several variables by operating the regression statistical analysis on the independent variables to establish the most desirable overall factor surface [12-14]. Through the representation of the surface model, responses on the basis of the combined factors can be determined [14-16].

In this work, the effect of dosage, contact time, and pH on zeolite and *Moringa oleifera* leaves powder mixture, on COD and ammonia removal from leachate was examined. RSM was used in designing the experiment, developing models and to assess the most favourable conditions.. The outcome of the investigation can be used to determine the efficacy of the mixture in the remediation of contaminants from wastewater and possibly will substitute activated carbon in the wastewater treatment industry.

2. Materials and method

2.1 Leachate sampling

The leachate sample was procured from Simpang Renggam municipal landfill located at $N1^0$ 53 41.64 latitude and $E1^030$ 22 34.68 longitude in Kluang District of Johor. Uncontaminated 20-L high-density polyethylene bottles was utilised to manually collect the leachate at site in accordance to the method outlined by [17-18]. And then the leachate was characterized within 24 h according to the standard methods for the examination of water and wastewater [19].

2.2 Preparation of Adsorbent media

Moringa leaves was harvested from experimental plantation under the center of advanced research for integrated solid waste management (CARISMA) of the Faculty of civil and environmental engineering, universiti Tun Hussein. The leaves were washed clean with distilled water and oven dried at 38ºC for 24 hours, then the leaves were pulverized to powder using mortar grinder model Fritsch. The moringa powder (MP) was sieved using 0.150mm sieves. Natural zeolite (Mechastone brand) was obtained from Pt. Anugerahalam Sdn. Bhd., Parit Raja,

Malaysia at a retail price of about 0.4RM per kilogram. The zeolite (ZE) was then powdered using the grinder and then sieved to 0.150mm particles size.

2.3 Adsorption experiments

Seven runs (for the mix ratio) and twenty (parameter optimization) runs were conducted in the current study. For each run, 100 mL of the raw leachate with an initial COD and NH₃-N concentration of 1,763 and 573 mg/L respectively was introduced into a 250 mL Erlenmeyer flask [17]. Initial experimentation was carried to determine the optimum mix ratio between moringa and zeolite media according to the design obtained by RSM using 150 rpm shaking speed on an orbital shaker (model Daiki) at a defined dosage (40g), pH 7 and varied mix ratio according to the RSM design.

Further optimisation was performed using acquired optimized mix ratio and raw leachate solution at 150 rpm agitation speed using the RSM selected pH, dosage and contact time. After some RSM suggested time interval, samples were then taken from the flasks, filtered using 0.45 µm filter membrane and analyzed for residual COD and NH₃-N content [17]. The COD and NH3-N were assessed by the closed reflux and Nessler Method respectively using atomic adsorption spectrophotometer (Model HACH DR6000). The effect of pH was studied by adjusting the pH of the leachate solutions using HCl and NaOH [18]. Experimental results were calculated as percentage removal of COD and NH₃-N according to equation (1).

$$\%Removal = [(C_i - C_f)/C_t] \times 100 \qquad (1)$$

Where C_i and C_f are the initial and final COD(mg/L) and NH₃-N(mg/L) concentration respectively.

2.4 Design of experiment

The Design Expert (version 7.0) Software was used to ascertain the number of experiments to be assayed for the optimization of three components (independent variables) comprising contact time (A), pH (B) and dosage (C) on the removal of COD and NH₃-N (dependent parameters). Table 1 shows the Codes, ranges and levels of the different independent variables of contact time, dosage and pH by the RSM design. The quadratic equation model of the response *Y* derived for predicting the optimum conditions is a function of the levels of independent variables expressed according to Equation (2):

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i.x_i + \sum_{i=1}^{k} \beta_{ii}.x_i^2 + \sum_{t_i=j}^{k} \sum_{j}^{k} \beta_{ij}.x_i.x_j + .. + e \quad (2)$$

where *i* represents the linear coefficient, *j* the quadratic coefficient, β as the coefficient of regression, *k* is for the amount of factors studied and optimized by the experiment while *e* stands for the random error [20,21].

Table 1. Codes, ranges and levels of independent variables of Contact time, dosage and pH in RSM design

Factor	Code	Low	High
ContactTime	A	5	120
Dosage	B	0.5	10
pH	C	5	8

3. Results and Discussion

3.1 Optimum mix ratio

The ooptimization solutions by the RSM for mixing ratio between MP and ZE in the removal of COD and ammonia is shown in figure 1. The interaction between the various mix ratios of the MP and ZE indicated that the removal of COD and NH3-N increased with the increase in zeolite quantity and corresponding reduction in MP in the mixture probably due to the accumulation on the binding sites of the adsorbent by the adsorbate up to a certain maximum limit when there are no further available sites (optimum condition) after which the removal becomes significantly diminished. The optimum was obtained at ratio 24(ZE):16(MP) which corresponds to 49.18% and 55.14% COD and NH_3-N removal respectively (see table 2).The Values of "Prob > F" is 0.0003 and 0.0042 for COD and NH_3-N respectively, which is less than 0.05 indicating that the model terms are significant.

3.2 Central composite design (CCD)

In this investigation, three significant factors, contact time (A) adsorbent dose (B) and pH (C) were designated as independent variables and analysed. Whereas the removal of COD (Y_{COD}) and ammonia (Y_{NH3-N}) were selected as the dependent variable (response) in order to observe the comprehensive components which have the capacity to influence a reduction of COD and NH_3-N. The percentage reduction as a response to each experimental state was analysed using the RSM as presented in Table 3.The percentage removals ranged from 47.15% to 70.14% and 60.43% to 86.94% for COD and NH_3-N respectively. Accordingly, the software package using the function of multiple regression analysis technique offered a quadratic model, the models were selected going by highest order polynomials [22-25]. The quadratic model used for the removal of COD (Y_{COD}) and NH_3-N (Y_{NH3-N}) was represented as follows:

$$Y_{COD} = 69.13 + 2.07*A - 0.41*B - 2.31*C + 0.57*A*B - 2.07*A*C + 0.99*B*C - 2.03*A^2 - 1.47*B^2 - 6.45*C^2 \quad (3)$$

$$Y_{NH3-N} = 82.62 - 1.99*A + 1.72*B + 3.74*C + 3.70*A*B - 2.50*A*C - 0.59*B*C - 0.64*A^2 - 0.50*B^2 - 5.73*C^2 \quad (4)$$

3.2 Statistical analysis

3.2.1 Analysis of variance

The regression coefficients for reducing COD and NH_3-N in the leachate at the end of the adsorption process are presented in Table 4. The calculation of the regression coefficients of the linear and quadratic, as well as the interaction between the factors in the model, was conducted using the least square method. The effect of each independent factor was considered significant at P-value <0.05 and 95% of the confidence level. From Table 4, the F-value of the COD model was found to be 267.15, whereas the F-value for NH_3-N was 110.75. Low error probability value [(Prob > F) < 0.0001] demonstrated that the generated models are statistically significant for representing the observed experimental data. Model with higher coefficient of determination value, R^2 (R2 = 0.9959 for COD and R^2 = 0.9901 for NH_3-N) can have high levels of multi collinearity which authenticate the obtained regression models. It can be seen that the standard deviation and coefficient of variation of the model are quite low and acceptable. A high adjusted R^2 value of 0.9921 for COD and 0.9811 for NH_3-N show the models are adequate to predict the removal in different process condition. The validity of the models was demonstrated by the "Lack of Fit F-value" of 0.62 (COD removal) and 0.4 (NH_3-N removal) implying the Lack of Fit is not significant and the models fit well to predict the removal. The results also found that one of the examined factors (time) have a positive significant linear effect on the reduction of COD (see equation 3), while dosage and pH have a negative significant effect which means that the increasing of dosage and pH affects or reduces the efficiency of the adsorption process. In contrast, for NH_3-N, two factors (dosage and pH) have a positive significant effect on the removal and contact time exhibits negative effect, indicating as the contact time increases (see equation 4), adsorption decreases depending on the behaviour of the adsorbent to adsorbate interaction [6,20,21].

Other significant model terms are A, B, C, AB, AC, BC, A^2, B^2 and C^2 are attained because of the interactions in system by the variable factors. Considering table 4. all the terms are significant for COD removal and A, B, C, AB, AC and C^2 are significant for NH3-N removal. This can be recognized base on the P-values less than 0.05 which implies the significant variable quantity at 95% confidence limit. Significant terms are having larger F value while the insignificant terms have smaller F value, and apparently the variable having the most significant effect in the removal of COD were the quadratic term C^2 (F value = 1731.24) followed by the liner term pH (F value = 210.03) and quadratic A^2 (F value = 99.81). Similarly for NH3-N removal the most significant terms are the quadratic term C^2 (F value = 516.73) followed by the linear terms pH (F value 208.35) and AB (F value = 119.29). Hence, as suggested by the ANOVA pH and contact time were the most instrumental operating factors for COD and comparatively for NH_3-N removal pH and the coupled contact time and dosage term are influential in the study.
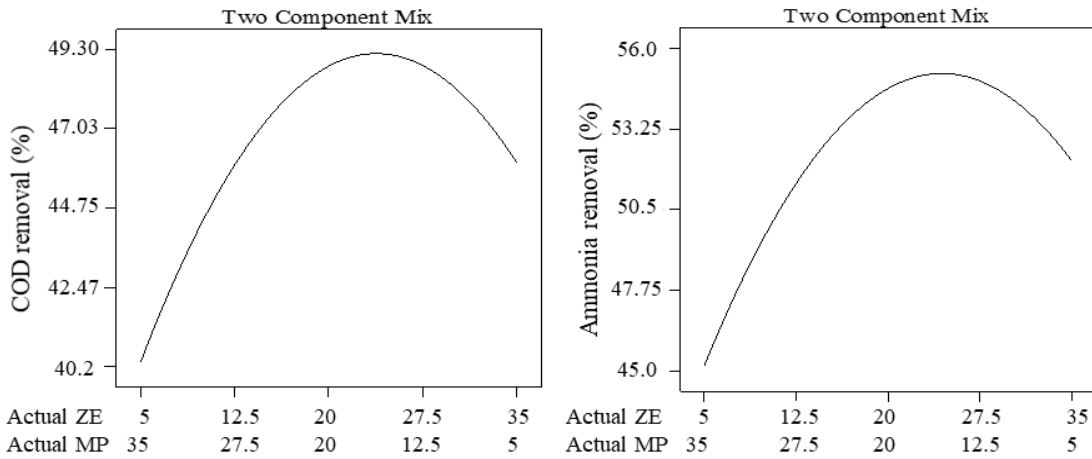
Figure 1. Optimization solutions response for mixing ratio between MP and ZE by the removal of COD and ammonia.

Table 2. Mixing ratio optimization solution between moringa leaf powder and zeolite

Solutions Number	ZE (g)	MP (g)	COD (%)	Ammonia (%)	Desirability	
1	24	16	49.18	55.14	0.966	Selected

Table 3 CCD of two variables and their responses.

Run	Factor 1 A:Contact Time mins	Factor 2 B:Dosage mg/L	Factor 3 C:pH	Response 1 COD (%) Actual	Predicted	Response 2 NH$_3$-N (%) Actual	Predicted
1	62.5	13.24	6.5	64.25	64.28	84.42	84.1
2	62.5	5.25	3.98	54.54	54.77	60.43	60.12
3	120	10	5	65.19	64.8	77.75	78.53
4	62.5	5.25	6.5	68.5	69.13	81.26	82.62
5	62.5	5.25	6.5	69.33	69.13	81.96	82.62
6	120	10	8	57.87	58.03	79.97	79.82
7	5	10	8	56.95	56.89	80.87	81.42
8	62.5	5.25	9.02	47.15	47.01	72.93	72.7
9	62.5	5.25	6.5	70.14	69.13	83.79	82.62
10	120	0.5	5	66.48	66.47	66.67	66.51
11	62.5	5.25	6.5	68.36	69.13	81.49	82.62
12	159.2	5.25	6.5	66.72	66.89	77.98	77.45
13	5	10	5	55.2	55.38	70.45	70.13
14	5	0.5	5	59.55	59.32	72.35	72.89
15	34.2	5.25	6.5	68.46	67.62	83.61	83.45
16	62.5	5.25	6.5	68.98	69.13	83.74	82.62
17	5	0.5	8	56.54	56.86	86.94	86.55
18	62.5	2.74	6.5	65.59	65.66	78.53	78.31
19	120	0.5	8	55.98	55.73	69.46	70.17
20	62.5	5.25	6.5	68.75	69.13	83.23	82.62

Table 4 ANOVA for Response Surface Quadratic Model of COD and NH$_3$-N

Source	Sum of Squares		Mean Square		F Value		p-value	
	COD	NH$_3$-N	COD	NH$_3$-N	COD	NH$_3$-N	COD	NH$_3$-N
Model	832.19	912.63	92.47	101.4	267.15	110.75	< 0.0001	< 0.0001
A-Contact Time	1	36.83	39.79	36.83	114.96	40.23	< 0.0001	< 0.0001
B-Dosage	2.29	40.53	2.29	40.53	6.62	44.26	0.0278	< 0.0001
C-pH	72.69	190.77	72.69	190.77	210.03	208.35	< 0.0001	< 0.0001
AB	2.58	109.22	2.58	109.22	7.44	119.29	0.0213	< 0.0001
AC	34.28	50	34.28	50	99.04	54.61	< 0.0001	< 0.0001
BC	7.88	2.81	7.88	2.81	22.77	3.07	0.0008	0.1104
A^2	34.55	3.44	34.55	3.44	99.81	3.76	< 0.0001	0.0811
B^2	31.26	3.6	31.26	3.6	90.31	3.93	< 0.0001	0.0755
C^2	599.21	473.12	599.21	473.12	1731.24	516.73	< 0.0001	< 0.0001
Residual	3.46	9.16	0.35	0.92				
Lack of Fit	1.33	2.61	0.27	0.52	0.62	0.4	0.6909	0.8323
Pure Error	2.13	6.55	0.43	1.31				

	COD	NH$_3$-N
Std. Dev.	0.59	0.96
Mean	62.73	77.89
C.V. %	0.94	1.23
R-Squared	0.9959	0.9901
Adj R-Squared	0.9921	0.9811
Pred R-Squared	0.9874	0.9568
Adeq Precision	53.176	39.049

Fig. 2 demonstrates the plot of the predicted values alongside the actual values, the predicted values were distributed systematically near to the actual responses and this has demonstrated the generated regression models can effectively explain the correlation between the independent variables and the response for the contaminants removal. The data are distributed consistently in a straight line thus the error is insignificant within the bounds of operating parameters.
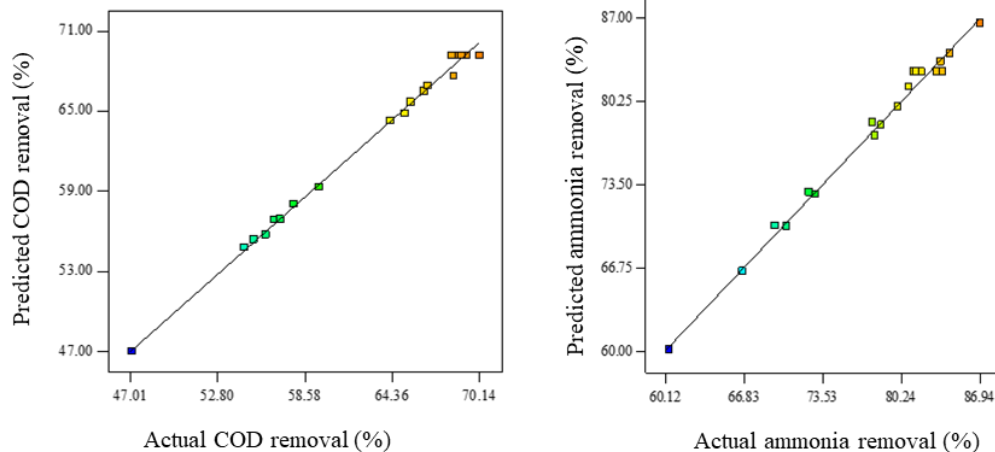

Fig.2 Predicted versus actual values plot for COD and NH$_3$-N removal

Figs. 3 presents the 3D response surface plots for the removal of COD and NH$_3$-N parameters respectively as a function of contact time and dosage while pH was set as actual factor (pH value 6) by the RSM. It can be observed that all of the parameters feature the highest level at the middle region. From both figures, NH$_3$-N constituted the better removed variable in the removal process than COD. Similar behavior was observed by Moideen [20] and Daud [24].

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3.2.2 Process optimization

The RSM statistical optimization process was employed to evaluate the optimal response conditions in the space of the controlling factors by taking into consideration the Model F-value that is presented in the model. The lesser and upper bounds of the sequence for all the parameters are enclosed in this optimization process as shown in Fig. 4. The desirability function was administered to suggest an effective method to achieve optimum reaction conditions. Aided by the Design Expert software, varying sets of different optimum operating variables and corresponding parameter removals are generated. The desirability of the optimum solutions is established as 0.917 to represent the accurateness between the experimental results and recommended solutions.
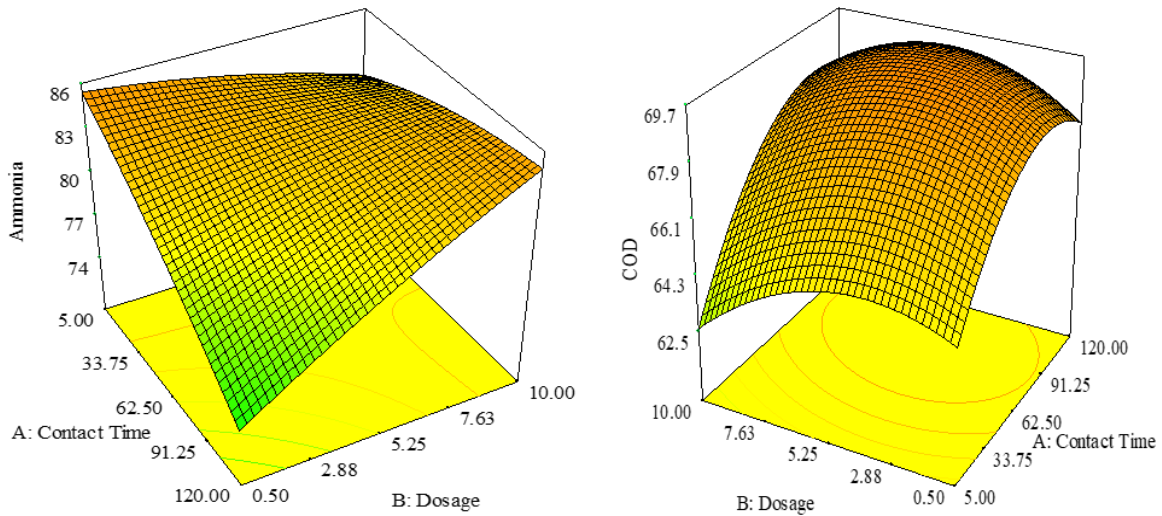
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Fig. 3 Response surface plot for NH$_3$-N and COD removal
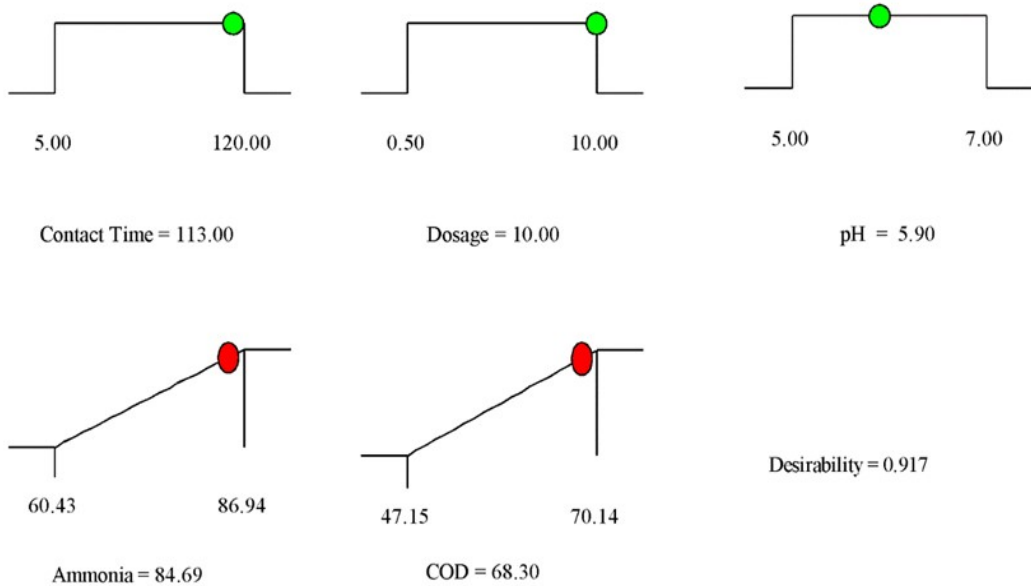

Fig. 4 Numerical optimization solution

4. Conclusion

According to the limit criterion for maximization of contaminants removal, the numerical RSM optimization technique was applied to produce several optimum operational process conditions. The optimization of the process parameters improved the optimum adsorption of the response factors. Based on the data obtained from the analysis, ZE:MP mixed ratio was 24:16, pH was 5.90, dosage 100g/L and the contact time 113 minutes were suggested to be the optimum condition for COD and NH$_3$-N removal. Under the optimum operating conditions, the actual versus predicted parameter removal can achieve around 70.14% and 86.94% for actual COD and NH3-N removal respectively and 69.13% and 86.55% for the predicted COD and NH3-N removal respectively. RSM is more reliable in predicting the nonlinear relationship between the process variables and response.

Acknowledgement

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