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Article

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Abstract: Waste streams with high ammonia nitrogen (NH₃-N) concentrations are very commonly produced due to human intervention and often end up in waterbodies with effluent discharge. The removal of NH₃-N from wastewater is therefore of utmost importance to alleviate water quality issues including eutrophication and fouling. In the present study, vacuum thermal stripping of NH₃-N from high strength synthetic wastewater was conducted using a rotary evaporator and the process was optimized and modeled using response surface methodology (RSM) and RSM–artificial neural network (ANN) approaches. RSM was first employed to evaluate the process performance using three independent variables, namely pH, temperature (°C) and stripping time (min), and the optimal conditions for NH₃-N removal (response) were determined. Later, the obtained data from the designed experiments of RSM were used to train the ANN for predicting the responses. NH₃-N removal was found to be 97.84 ± 1.86% under the optimal conditions (pH: 9.6, temperature: 65.5 °C, and stripping time: 59.6 min) and was in good agreement with the values predicted by RSM and RSM–ANN models. A statistical comparison between the models revealed the better predictability of RSM–ANN than that of the RSM. To the best of our knowledge, this is the first attempt comparing the RSM and RSM–ANN in vacuum thermal stripping of NH₃-N from wastewater. The findings of this study can therefore be useful in designing and carrying out the vacuum thermal stripping process for efficient removal of NH₃-N from wastewater under different operating conditions.

Keywords: ammonia removal and recovery; response surface methodology; artificial neural network

1. Introduction

Nitrogen (N) is an indispensable element for all living organisms and a fundamental component of animal and plant proteins. However, an excess of N caused mainly by anthropogenic activities such as intensive agricultural practices, rapid industrialization, unplanned urbanization, and many others has severe deleterious effects on the environment. Effluents discharged from the industrial and municipal processes and livestock facilities without proper treatment are affecting the waterbodies worldwide through eutrophication, decreasing dissolved oxygen concentration, fish kills, declining aquatic biodiversity and diminishing recreational water usage [1,2]. A recent study reported that potential economic losses due to eutrophication of freshwater resources in the US is around USD 2.2 billion annually [3]. Ammonia nitrogen (NH₃-N), one of the primary nitrogenous compounds, is an indicator of eutrophication and ecotoxicity. Ammonia nitrogen interrupts aquatic enzyme hydrolysis reaction, alters cellular pH, disturbs citric acid cycles and creates neurological disorders in aquatic animals [4,5]. The removal of NH₃-N from waste streams has therefore become a high priority issue and gained great attention in many parts of the world.

For the past few decades, many conventional and advanced technologies have been explored and employed to remove NH₃-N from wastewater [6]. These technologies include biological methods [7–9], breakpoint chlorination [10,11], UV/chlorine [12], ion-
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exchange [13], chemical precipitation [14–16], stripping [17–19], electrochemical oxidation [20–22], and adsorption methods [5,23,24]. Among all the above-mentioned processes, gas and air-mediated stripping with acid-absorption are generally considered efficient technologies for NH₃ removal and recovery. The NH₃ stripped from the system is recovered in the form of ammonium salts (e.g., (NH₄)₂SO₄, NH₄Cl) depending on the acid solution, which can be used as nitrogenous fertilizers. This technology has been improved further and combined with other aids such as heating mantle, microwave, and solar heating [25–27] to facilitate thermal stripping. Ammonia in the wastewater exists in both gaseous (free NH₃) and ionic (ammonium ion, NH₄⁺) forms. In general, the amount and concentration of free NH₃ in total ammonia nitrogen (TAN) increases with the increase in temperature and pH [28]. The thermal stripping process enables the conversion of NH₄⁺ to free NH₃ and then strips the free NH₃ from the wastewater. This system works competently at the boiling temperature and eliminates the need for stripping gas. With the introduction of vacuum in this process, it becomes more efficient in terms of energy consumption [29]. Vacuum decreases the normal boiling point temperature, fortifies liquid–gas phase NH₃ mass transfer and ultimately results in an enhanced NH₃ stripping. However, this process also has a few issues, such as that water vapor from the evaporating flask can either be condensed in the acid solution or leave the system through vacuum exhaust [30]. To tackle this, a closed-system vacuum thermal stripping process using a rotary evaporator was tested in the present study. Rotary evaporators can remove the solvent efficiently from samples through evaporation. Haaz et al. and Akinapally et al. used rotary evaporators to remove COD from process wastewater and pesticide intermediate industrial wastewater, respectively [31,32], while Stall et al. employed a rotary evaporator for extracting polyphosphates in activated sludge collected from wastewater treatment plants [33]. Wang et al. applied a rotary evaporator to simulate humidification–dehumidification process for concentrating biogas slurry [34]. However, none of the studies have reported on a rotary evaporator’s applications in NH₃-N removal from high NH₃ laden waste streams.

Furthermore, in comparison to other NH₃-N removal processes from wastewater, the vacuum thermal stripping is relatively new, and an optimization of the process parameters is therefore needed to ensure effective and efficient NH₃-N removal and recovery. In conventional optimization approaches, values of only a single parameter can be changed at a time which makes the process time-consuming and costly. Moreover, true experimental conditions cannot be optimized by traditional methods as the interactions among the process parameters are not reflected in experimental results [35]. However, response surface methodology (RSM), as an optimization method, considers the effects of independent variables and their interactions, ensures experimental accuracy with minimal experiments, identifies uncertainties, and produces numerical models [36,37]. Optimization studies designed by RSM can adopt different experimental strategies based on full factorial, fractional factorial, Box–Behnken, and Doehlert designs to represent the response surface [38]. Therefore, RSM has widely been used to optimize the operating conditions of water and wastewater treatment processes [35]. Without exception, RSM also has a limitation that non-controllable influencing factors cannot be added in the RSM [39]. Hence, researchers are shifting towards combining RSM with more sophisticated modeling/optimization approaches such as artificial intelligence (AI). As one of the main tools of AI, artificial neural network (ANN) has been gaining more popularity recently due to its ability to process incomplete data and non-linear changes [40]. Artificial neural network produces desired responses by studying processes through alteration of network weight and does not need any precise mathematical descriptions of the phenomena affecting the process. As a result, the non-parametric simulation can be performed more efficiently [41]. Moreover, several studies reported a higher correlation of determination (R²) and lower root mean square error (RMSE) in models developed using ANN compared to RSM [41–44]. Hence, the RSM–ANN approach can better examine the relationship between the independent (inputs) and response (targets) parameters of a system using experimental data.
The present study was focused on the vacuum thermal stripping process for NH$_3$-N removal from synthetic wastewater using a rotary evaporator. Two models, RSM with central composite design (CCD) and RSM–ANN were used to optimize and predict NH$_3$-N removal and its correlation with the input parameters (pH, temperature, and stripping time). Finally, the results obtained from RSM and RSM–ANN models were statistically compared in terms of $R^2$, RMSE, and absolute average deviation (AAD). To the best of our knowledge, this is the first attempt comparing the RSM and RSM–ANN approaches in the vacuum thermal stripping process for NH$_3$-N removal from wastewater.

2. Materials and Methods

2.1. Wastewater Composition

Synthetic wastewater containing high concentrations of ammonia nitrogen (10 g/L) and low carbon to nitrogen ratio was used for all the experiments conducted in this study. O’Flaherty and Gray mentioned some significant advantages of using synthetic wastewater over real wastewater in lab-scale studies which includes availability, easy to store, ensure homogenous loading and data reproducibility, no health and environmental hazards, and less malodorous [45]. The above-mentioned criteria are ultimately beneficial for process development and optimization. The synthetic wastewater used in this study was prepared mixing NaHCO$_3$ 90.06 g/L, (NH$_4$)$_2$SO$_4$ 47.17 g/L, KH$_2$PO$_4$ 9.07 g/L, FeCl$_3$ 0.02 g/L, CaCl$_2$ 0.2 g/L, and MgSO$_4$ 0.22 g/L in deionized water [46]. No additional organic carbon source was added to the synthetic wastewater as the primary focus of the study was to check the feasibility of the employed process in efficient ammonia removal and recovery from wastewater without any losses. All the chemicals used in this research were supplied by Thermo Fisher Scientific, Waltham, MA, USA.

2.2. Experimental Setup

The conventional biological treatment processes require high capital investment and operational cost as well as further treatment prior to discharge into the environment [47]. Increasing operational cost and stringent regulatory standards encourage further research on improved and economical viable treatment technologies [48]. Instead of just removing ammonia from waste streams, coupling thermal stripping to the acid adsorption process to produce ammonium salts can be sustainable, as the recovered ammonium salts have commercial values. In addition, introducing vacuum in the thermal stripping process can reduce the energy consumption by more than 50%, and subsequently, a significant reduction in operating cost can be achieved [29].

The schematic of the vacuum thermal stripping process used in this study for NH$_3$-N removal and recovery is elucidated in Figure 1. All the experiments carried out in this study were performed in closed-system batches and each batch contained 200 mL of synthetic wastewater in 500 mL evaporating flask. The pH of the synthetic wastewater was adjusted to the experimental conditions using a 15 N NaOH solution [25]. A rotary evaporator (Buchi R-100, BUCHI Corporation, New Castle, DE, USA) was used to evaporate the wastewater and condensate the vapors under vacuum. The synthetic wastewater in the evaporating flask was heated using the heating bath. The rotation of the evaporating flask was controlled by a rotary drive unit. Due to continuous rotation, water in the heating bath was agitated and allowed increased heat transfer to the evaporating flask. Moreover, rotation also influenced the surface area of the liquid and mixing inside the flask and ultimately resulted in an improved evaporation rate. After achieving the desired temperatures, a vacuum pump (Gast™ DOA P704 AA, Gast Manufacturing, Inc., Benton Harbor, MI, USA) was turned on. The vapor and stripped (free) NH$_3$ from the evaporating flask entered to the cooling section (condenser) through a vapor duct. The free NH$_3$ was drawn to a 500 mL Büchner flask having 200 mL H$_2$SO$_4$ (2 N) using the vacuum pump [49]. As the thermal energy of the vapor was transferred to the coolant fluid (ice water), it recondensed and deposited in a receiving flask; thus, the issue related to condensation of water vapor in the acid solution was solved. Along with facilitating transportation of the free NH$_3$ ammonia
to acid solution, the vacuum pump also helped to maintain the boiling point vacuum. The
NH_3 stripped from the synthetic wastewater was introduced to the acid solution using a
diffuser and ultimately absorbed by the acid solution. The NH_3-N removal efficiency was
calculated using Equation (1):

\[
\text{Removal efficiency (\%) } = \left( \frac{C_o - C_t}{C_o} \right) \times 100
\]  

(1)

where \(C_o\) represents the initial NH_3-N concentration and \(C_t\) is the NH_3-N concentration at
the time \(t\). The amount of NH_3 recovered as (NH_4)_2SO_4 was quantified theoretically using
the concentration of NH_3-N after stripping [25].

Figure 1. Schematic of the experimental setup.

2.3. Experimental Design
2.3.1. Response Surface Methodology (RSM)

In this study, the CCD of RSM was initially adopted to model the NH_3-N removal
performance from synthetic wastewater through vacuum thermal stripping process using
three independent variables. These data were later used to model the process using artificial
neural network (ANN). The CCD allows the fitting of a quadratic surface with minimum
experiments for the process parameters optimization [50] and assists in identifying the
interaction among the parameters. The CCD also presents sufficient information needed
to test the lack of fit, with a reasonable number of experiments conducted. Moreover, it
enables easy understanding of orthogonal blocking and rotatability, which are the most
important features of an experimental design [38]. The required number of experiments
were calculated using the following Equation (2):

\[
N = 2^k + 2k + c
\]  

(2)

where \(N\) is the required number of experiments, \(k\) represents the number of factors and
\(c\) indicates the number of central points. This resembles to 8 factorial points \(2^3\), 6 axial
points \((2 \times 3)\), and 6 replicates of central points. These central points are very crucial in
measuring experimental errors [51]. A total of 20 experiments were therefore conducted
using the model showed by Equation (2). All the experiments were performed in triplicates
and the mean values were used in data analysis. The obtained data were analyzed using the
software Design-Expert version 13.0.5 developed by StatEase, Inc., Minneapolis, MN, USA.
The developed model adequacy and statistical significance of the regression coefficients
were verified using analysis of variance (ANOVA) test. Response surface contour plots
were used to represent the interaction among the independent variables and their effects
on responses.

In the present study, pH, temperature, and stripping time were the independent
variables, while the NH_3-N removal efficiency was selected as response. Table 1 elucidates
the values of the independent variables along with their coded levels. Furthermore, an empirical model was developed based on the experimental results conforming to the operational parameters. The obtained data were fitted to the following second-order polynomial model (Equation (3)):  

\[
y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{11} x_1^2 + b_{22} x_2^2 + b_{33} x_3^2 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 \quad (3)
\]

where \(y\) is the predicted response, \(b_0\) indicates the offset term, \(b_1, b_2,\) and \(b_3\) are the linear coefficients, \(b_{11}, b_{22},\) and \(b_{33}\) represent the quadratic coefficients, and \(b_{12}, b_{13},\) and \(b_{23}\) denote the interaction coefficients.

2.3.2. Artificial Neural Network (ANN)

Artificial neural network (ANN), as a sophisticated tool for simulation and optimization, has recently gained popularity among the researchers due to its potential of powerful prediction and estimation competencies [52]. In this study, an ANN model was therefore integrated with the RSM for more accurate prediction. The data obtained from the experiment designed by RSM were used to ascertain the optimum ANN architecture.

In the present study, a feed forward ANN having an input layer consisting of independent variables, a hidden layer and an outer layer consisting of response was used (Figure 2). In developing successful ANN architecture, selection of appropriate topology plays an important role. Gadekar and Ahammed stated that the number of hidden layer neurons has direct impact on the ANN performance [39]. In most of the ANN networks, the number of hidden layer neurons varied from 1 to 20 [53–56]. Although hidden layer with large number of neurons shows more flexibility, it also exaggerates the chance of model over fitting simultaneously, whereas in networks with less hidden layer neurons, the learning ability is restricted along with approximate arbitrary accuracy [57]. Therefore, different feed forward networks of various hidden layer neurons were trained (Table S1). The network having the lowest mean square value (MSE) and correlation coefficient (R) value close to 1 was chosen for training. Based on the above-mentioned criteria, the optimum feed forward network topology of 3:5:1 was selected.

![Figure 2. Architecture of the developed ANN model.](image-url)
The details of the ANN architecture used in this study are shown in Table 2. To train the ANN model, the Levenberg–Marquardt (LM) algorithm was applied. A total of 60 experimental results were used to model the network and were divided arbitrarily into training (70%), validation (15%), and test (15%) subsets. Random weights were allotted to each neuron connection between layers to initiate the training process. Weights were altered until nominal error between observed and predicted values for NH$_3$-N removal efficiency was attained. The data were further validated using the validation process once the error between predicted and experimental values reached a smaller level. The testing process was used to assess the generality of the ANN model. After successful validation and testing, the ANN model was applied for prediction. Moreover, a linear regression analysis was performed between the observed and predicted values to examine the trained network response. The toolbox ‘nnstart’ of MATLAB (R2021a) was used to simulate NH$_3$-N removal.

**Table 2.** Network parameters of the ANN architecture.

| Parameters | Details |
|------------|---------|
| Network    | Two-layer feed forward; three inputs, one output and one hidden layer with five hidden neurons |
| Data       | 60; training: 70%, validation: 15%, testing: 15% (all data are selected randomly) |
| Transfer   | Tangent sigmoid (tansig) (between input and hidden layers) |
| Linear (purelin) (between hidden and output layers) |
| Training   | Levenberg–Marquardt backpropagation algorithm (trainlm) |
| Performance| Mean Squared Error (MSE) |

2.4. Statistical Comparison between the Developed Models

The predictive accuracy and estimation capability of the developed RSM and RSM–ANN were compared statistically measuring the $R^2$, RMSE, and absolute average determination (AAD) [58,59]. In this study, the $R^2$, RMSE, and AAD were calculated using Equations (4)–(6):

\[
R^2 = \frac{\left(\sum_{i=1}^{n} (y_{\text{exp}} - \bar{y}_{\text{exp}}) (y_{\text{predict}} - \bar{y}_{\text{predict}})\right)^2}{\left(\sum_{i=1}^{n} (y_{\text{exp}} - \bar{y}_{\text{exp}})^2 (y_{\text{predict}} - \bar{y}_{\text{predict}})^2\right)}
\]

\[
\text{RMSE} = \left(\frac{1}{n}\sum_{i=1}^{n} (y_{\text{predict}} - y_{\text{exp}})^2\right)^{\frac{1}{2}}
\]

\[
\text{AAD} = \left(\frac{1}{n}\sum_{i=1}^{n} \frac{(y_{\text{predict}} - y_{\text{exp}})}{y_{\exp}}\right) \times 100
\]

where $n$ is the number of points, $y_{\text{predict}}$ is the predicted value, $y_{\text{exp}}$ is the experimental value, and $\bar{y}_{\text{exp}}$ and $\bar{y}_{\text{predict}}$ are the averages of the experimental and predicted values, respectively.

2.5. Sampling and Analysis

Samples were collected at the end of each batch experiment. The NH$_3$-N concentration was measured using salicylate method. Testing kit developed by the Hach company was used to quantify NH$_3$-N concentration (Method 8155). The crystals formed under the optimized conditions were harvested through filtration after cooling down the acid solution saturated with (NH$_4$)$_2$SO$_4$ to 4 °C. The scanning electron microscopy (SEM) (Zeiss Supra 35 SEM, ZEISS Microscopy, Jena, Thüringen, Germany) with a Thermo Fisher System 7 Energy-dispersive X-ray spectroscopy (EDS) (Thermo Fisher Scientific, Waltham, MA, USA) was used for structural identification and elemental composition determination of the recovered material.
3. Results and Discussion

3.1. Response Surface Methodology (RSM) Model

Results obtained from the vacuum thermal stripping process using CCD matrix are shown in Table 3. The second order polynomial quadratic equation of the \( \text{NH}_3\text{-N} \) removal was developed using the obtained data in coded form through RSM is given in Equation (7):

\[
\text{NH}_3\text{-N removal (\%)} = 93.58 + 3.35 x_1 + 15.12 x_2 + 4.29 x_3 - 1.18 x_1^2 - 8.06 x_2^2 - 2.08 x_1 x_2 - 1.36 x_1 x_3 - 1.86 x_2 x_3
\]

Table 3. Experimental design with experimental and predicted responses of independent variables.

| Run | Points | Independent Variables | Response (y: \( \text{NH}_3\text{-N} \) Removal Efficiency (\%)) |
|-----|--------|-----------------------|-------------------------------------------------------------|
|     |        | \( x_1 \) | \( x_2 \) (°C) | \( x_3 \) (min) | Experimental Data | Predicted Value |
| 1   | 9.5 (−1) | 67 (+1) | 45 (−1) | Factorial | 91.35 | 94.96 | 91.99 |
| 2   | 10.5 (+1) | 67 (+1) | 45 (−1) | Factorial | 97.42 | 98.95 | 97.02 |
| 3   | 9.5 (−1) | 61 (−1) | 45 (−1) | Factorial | 56.64 | 55.56 | 56.64 |
| 4   | 9.5 (−1) | 61 (−1) | 75 (+1) | Factorial | 69.86 | 70.58 | 69.85 |
| 5   | 10.5 (+1) | 61 (−1) | 45 (−1) | Factorial | 73.21 | 70.40 | 72.81 |
| 6   | 10.5 (+1) | 67 (+1) | 75 (+1) | Factorial | 97.73 | 101.07 | 98.05 |
| 7   | 10.5 (+1) | 61 (−1) | 75 (+1) | Factorial | 81.32 | 79.97 | 80.49 |
| 8   | 9.5 (−1) | 67 (+1) | 75 (+1) | Factorial | 97.46 | 102.53 | 97.03 |
| 9   | 11 (+α) | 64 (0) | 60 (0) | Axial | 96.77 | 97.54 | 97.13 |
| 10  | 10 (0) | 58 (−α) | 60 (0) | Axial | 29.69 | 33.08 | 29.70 |
| 11  | 10 (0) | 64 (0) | 30 (−α) | Axial | 78.18 | 78.68 | 78.19 |
| 12  | 10 (0) | 70 (+α) | 60 (0) | Axial | 99.22 | 93.57 | 98.10 |
| 13  | 9 (−α) | 64 (0) | 60 (0) | Axial | 87.20 | 84.16 | 88.25 |
| 14  | 10 (0) | 64 (0) | 90 (+α) | Axial | 98.58 | 95.82 | 98.56 |
| 15  | 10 (0) | 64 (0) | 60 (0) | Central | 94.18 | 95.58 | 96.48 |
| 16  | 10 (0) | 64 (0) | 60 (0) | Central | 93.03 | 95.58 | 96.48 |
| 17  | 10 (0) | 64 (0) | 60 (0) | Central | 94.38 | 95.58 | 96.48 |
| 18  | 10 (0) | 64 (0) | 60 (0) | Central | 92.02 | 95.58 | 96.48 |
| 19  | 10 (0) | 64 (0) | 60 (0) | Central | 93.31 | 95.58 | 96.48 |
| 20  | 10 (0) | 64 (0) | 60 (0) | Central | 92.63 | 95.58 | 96.48 |

\( x_1 \): pH, \( x_2 \): temperature, \( x_3 \): stripping time.

The model coefficients were estimated using multiple regression analysis and the fitness of the developed model was arbitrated from the coefficients of determination (R\(^2\)). The statistical significance of the developed quadratic equations was evaluated using the ANOVA (Table 4) and found to be highly significant. The observed Fisher’s F-values showed a lower probability value (\( p < 0.0001 \)). The non-significant (\( p > 0.05 \)) lack of fit relative to pure error suggested the validity of the quadratic models [60]. Furthermore, fair high R\(^2\) values between the observed and predicted values for NH\(_3\)-N removal elucidated the goodness of fit and statistical significance of the model. On the other hand, the predicted R\(^2\) value was in reasonable agreement with adjusted R\(^2\) values. Moreover, a lower coefficient of variation (CV) (<5% for both responses) indicated better precision and reliability of the obtained experimental data [61]. The adequate precision indicates the signal to noise ratio comparing the predicted value ranges to the mean prediction error at the design points, and the ratios greater than 4 are preferable [62]. In this study, a high adequate precision value (23.927) was observed, which suggests the adequacy of the developed model. Furthermore, data fitting potential of the developed RSM model were tested by plotting the predicted values against observed data for NH\(_3\)-N removal (Figure 3). The data points were well concentrated around the slope, signifying the close association between predicted and observed values. This implicitly reveals the developed model equation is capable of providing a satisfactory estimation of the studied process [63,64]. Overall, the ANOVA analysis represents the model applicability in predicting NH\(_3\)-N removal from high strength synthetic wastewater using the vacuum thermal stripping process.
Table 4. ANOVA results for the response surface quadratic models.

| Source          | SS     | df  | MS      | F-Value | p-Value  | p-Value  |
|-----------------|--------|-----|---------|---------|----------|----------|
| Model           | 5881.82| 9   | 653.54  | 38.79   | <0.001   | significant |
| $x_1$ (pH)      | 179.04 | 1   | 179.04  | 10.63   | 0.009    |          |
| $x_2$ (Temperature) | 3659.69| 1   | 3659.69 | 217.20  | <0.001   |          |
| $x_3$ (Time)    | 293.82 | 1   | 293.82  | 17.44   | 0.002    |          |
| $x_1^2$         | 35.03  | 1   | 35.03   | 2.08    | 0.179    |          |
| $x_2^2$         | 1634.45| 1   | 1634.45 | 97.00   | <0.001   |          |
| $x_3^2$         | 108.91 | 1   | 108.91  | 6.46    | 0.029    |          |
| $x_1 x_2$       | 58.76  | 1   | 58.76   | 3.49    | 0.091    |          |
| $x_1 x_3$       | 14.87  | 1   | 14.87   | 0.883   | 0.369    |          |
| $x_2 x_3$       | 27.77  | 1   | 27.77   | 1.65    | 0.228    |          |
| Residual        | 168.49 | 10  | 16.85   | 2.92    | 0.132    | not significant |
| Lack of Fit     | 125.53 | 5   | 25.11   | 2.92    | 0.132    |          |
| Pure Error      | 42.96  | 5   | 8.59    | 4.74    | 23.927   |          |

1 SS: sums of squares, 2 df: degrees of freedom, 3 MS: mean squares.

Figure 3. RSM model predicted NH$_3$-N removal versus observed NH$_3$-N removal.

3.2. Effects of Operational Parameters on Ammonia Removal

The regression analysis reports the linear, quadratic and interaction effects of the independent variables on the responses. On the other hand, the 3D response surface and contour plots reflect the main and cross-product effects of independent operational parameters on desired responses [52].

Table 4 shows that the NH$_3$-N removal was mainly governed by temperatures at both linear and quadratic levels ($p < 0.001$). This finding is further confirmed by the perturbation plot (Figure S1). The plot elucidates high steepness with coded factor $x_2$ (Temperature), which indicates the primary factor for NH$_3$-N removal. At lower temperatures, the NH$_3$-N removal efficiencies remain low, whereas higher removal efficiencies were observed at higher temperatures. NH$_3$-N from wastewater is removed in the gaseous form (free NH$_3$). With the increase in temperatures, NH$_3$ saturation concentrations decrease and the amounts of free NH$_3$ in the system increase. Moreover, introduction of vacuum accelerates vapor current and liquid turbulence, improves mass transfer of NH$_3$ and ultimately enhances the removal efficiency [25,65,66]. Other factors that contribute significantly towards NH$_3$-N
removal were the linear terms of pH and stripping time ($p < 0.05$) and quadratic term of stripping time ($p < 0.05$) (Table 4), while no interactive effect of the independent variables was observed (Figure 4A–C). Tao and Ukwuani used thermal stripping acid-absorption for NH$_3$ removal and recovery from digested and undigested liquid dairy manure and reported similar amount of NH$_3$-N removal at pH 9 and 11 from liquid dairy manure [25]. They observed that with the increasing temperature the free NH$_3$ concentration in the feed increased sharply at pH 9, but at pH 11 a little variation in free NH$_3$ concentration was found. In another study, Ukwuani and Tao stated that depending on the temperature (50 to 100 °C) and vacuum pressure (16.6 to 101.3 kPa) it might take 180 min to achieve 93.3 to 99.9% NH$_3$-N removal efficiencies after 60 min of temperature ramping time [30]. This study also showed less significant effect of pH and stripping time compared to temperature on NH$_3$-N removal, which are in line with earlier findings [30,67].

![Figure 4. Three-dimensional surface and contour plots for NH$_3$-N removal: (A) temperature $\times$ pH, (B) time $\times$ pH, and (C) time $\times$ temperature.](image)

### 3.3. Process Optimization and Validation

The main purpose of the process optimization was to figure out the optimal values of the independent variables (pH, temperature and stripping time) for maximum NH$_3$-N removal. To determine the optimum conditions, the desired favorable conditions for responses and independent variables can be chosen from the available options. In this study, the desired goal for NH$_3$-N removal was set as ‘maximum’ whereas for operational independent parameters were set as ‘within the range’. Equal weightage was allocated for all the variables and response. The optimal conditions for NH$_3$-N removal are presented in Table 5. For validation, optimized conditions were experimentally tested in quintuplicate and compared with the predicted values. Under the optimized conditions, a NH$_3$-N removal of 97.84% was obtained while the RSM and RSM–ANN model predicted values were 99.44 and 97.39%, respectively. The experimental value is well within the range of 95% low and high confidence interval (Table 5). The overlay plot also showed the similar phenomenon (Figure 5). The shaded yellow region in the overlay plot elucidates the optimum area as a design space. The selected value for NH$_3$-N removal was 99.98%, at the pH, temperature, and stripping time of 9.7, 65.7 °C and 60 min, respectively, and is indicated by a flag (Figure 5).
Table 5. Predicted and observed values under optimum conditions for validation of models.

| Parameters 1 | Optimum Conditions | Response (NH\textsubscript{3}-N Removal Efficiency (%)) |
|--------------|---------------------|-----------------------------------------------------|
|              | Predicted Values    | Observed Value | 95% CI Low | 95% CI High |
|              | RSM | RSM–ANN | RSM | RSM–ANN | RSM | RSM–ANN |
| x\textsubscript{1} | 9.6 | 99.44 | 97.39 | 97.84 ± 1.86 | 93.91 | 89.76 | 104.99 | 105.02 |
| x\textsubscript{2} (°C) | 65.5 | 60.5 | 65.5 | 65.617 |
| x\textsubscript{3} (min) | 59.6 | |

\(1\) x\textsubscript{1}: pH, x\textsubscript{2}: temperature, x\textsubscript{3}: stripping time.

Figure 5. Overlay plot showing the optimal region with a stripping time of 60 min.

3.4. Ammonium Sulphate Recovery and Characterization

Recovery of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} has mostly been conducted in liquid forms [68,69]. However, (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} recovered in crystals has several benefits compared to a solution [25]. In this study, the theoretical production of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} was calculated as 38.01 ± 0.63 g/L under the optimum conditions. The (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} was recovered in solid state and the structure was found to be irregular, rectangular, and orthorhombic under SEM analysis (Figure 6A). Ammonium sulfate having similar crystal shapes were reported in earlier studies [70,71]. Studies also stated that factors such as crystal harvesting method, the saturation conditions and final acid content can alter the content and shape of the (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} crystals [30,71].

Ammonium sulfate is mainly used as an inorganic fertilizer for alkaline soils. Upon application in the soil, the S (as SO\textsubscript{4}\textsuperscript{2–}) is released and forms H\textsubscript{2}SO\textsubscript{4}, thus lowering the pH of the soil, whereas N contributes to the plant growth. The EDS analysis revealed the elemental composition of the recovered (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} (Figure 6B), which contained 21.3% N, 52.3% O and 26.4% S. These values are comparable with the commercially available (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, thus highlights the potential of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} recovery from waste streams and its application as a fertilizer source.
3.5. Response Surface Methodology (RSM)–Artificial Neural Network (ANN) Model

Figure 7 elucidates the experiment and RSM–ANN predicted values of the target response in all subsets of network validation. In all the cases, data points were concentrated closer to the regression line, which is conducive to the reliable precision and accuracy of the RSM–ANN model prediction [52]. Moreover, the linear regression analysis between experimental and RSM–ANN predicted NH$_3$-N removal showed higher R$^2$ values in comparison to RSM (Figure 7). This signifies the adequate prediction and estimation capabilities of the trained ANN model used in this study [53,55,72]. The NH$_3$-N removal efficiency of 97.39% was obtained using the RSM–ANN model under the optimum conditions, which was close to the experimental values and further confirmed the model validity.

3.6. Model Comparison

A comparison between the RSM and RSM–ANN models was performed to demonstrate their predictive and estimation capabilities. Figure 8 presents the residual distribution patterns of the two models. The fluctuations of the residuals based on the RSM–ANN model are smaller and more consistent compared to that of RSM model.
The performance of the developed ANN and ANN–RSM models were further compared statistically. Table 6 shows the statistical comparison of the RSM and RSM–ANN models for NH₃-N removal. In terms of RSME and AAD values, the lower the better, while a higher R² value denotes the better fitting of the model [73]. In this study, the two models indicated good quality predictions, while the RSM–ANN demonstrated a clear advantage over RSM for both prediction and estimation capabilities. Previous studies also reported the superiority of RSM–ANN over RSM [39,42,74,75]. In RSM, a standard experiment design is needed to predict and explain the interactive effects of independent factors on the target responses, while no standard experimental design is required for model development in ANN [59]. Moreover, the ANN is flexible in nature and allows to add new experimental data to generate a trustable model [52,76]. Therefore, the RSM–ANN model would be more reliable and rational to interpret the data on NH₃-N removal using the vacuum thermal stripping process.

Table 6. Comparison of RSM and RSM–ANN models.

| Parameters                                | RSM     | RSM–ANN |
|-------------------------------------------|---------|---------|
| Coefficient of determination (R²)         | 0.972   | 0.998   |
| Root mean square error (RMSE)             | 4.215   | 1.221   |
| Absolute average deviation (ADD)          | 0.340   | 0.143   |

4. Conclusions

In this study, the vacuum thermal stripping process for NH₃-N removal using a rotary evaporator was presented. The effect of independent variables (pH, temperature and stripping time) on NH₃-N removal was modeled using RSM and RSM–ANN. The developed second-order polynomial equations using RSM predicted competently the effect of independent variables on the responses, while the relatively smaller differences in predicted and experimental values were observed in the RSM–ANN model. The obtained NH₃-N removal efficiency of 97.84% under the optimized conditions of pH 9.6, temperature 65.5 °C and time 59.6 min was well within the range of the 95% low and high confidence intervals for both models. Comparison between the models based on R², RMSE and AAD elucidated a better prediction capability of the RSM–ANN model. The results of the study thus can be used as a prediction guide of the vacuum thermal stripping process for NH₃-N removal under different experimental conditions and will encourage further studies on vacuum thermal stripping of ammonia from real wastewater.
Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/pr9112059/s1, Table S1: Feed forward networks with different hidden layer neurons, Figure S1: Effect of independent variables on NH3-N removal at RSM conditions of pH (9–11), temperature (58–70 °C), and time (30–90 min).

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