Modeling of Ammonium and COD Adsorption in Aqueous Solutions Using an Artificial Neural Network

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Abstract – This paper illustrates the application of the artificial neural network for adsorption of ammonium NH$_4^+$ and COD from fish farm by rice straw as low cost carbonaceous. The effects of input parameters (contact time, pH, initial concentration of NH$_4^+$ and COD, adsorbent dosages, and temperature) are studied to optimize the conditions for maximum removal of NH$_4^+$ and COD. The artificial neural network with a single hidden layer with ten nodes trained with Levenberg-Marquardt algorithm predicted the removal efficiency of NH$_4^+$ and COD from aqueous solution accurately.

Keywords – adsorption; artificial neural networks; modeling; ammonium.

I. INTRODUCTION

The presence of chemical oxygen demand (COD) and ammonium (NH$_4^+$) in water is a major concern due to their adverse effect on life. The discharge of NH and COD in the environment are worrying for both toxicological and economically reasons. Wastewater from fish farms and agricultural drainage are some of the sources for NH$_4^+$ and COD effluents [1, 2]. Therefore, it is necessary to treat the wastewater containing COD and NH$_4^+$ for reusing it in fish farms. A count of physical and chemical processes such as oxidation, denitrification, chemical coagulation and adsorption has been widely used to treat wastewater containing those pollutants. Moreover, the adsorption has been found to be superior compared to other techniques for wastewater treatment in terms of its ability to remove pollutants, ease to implement, where it does not require skilled labor for employment, and the possibility of applying it in small areas. The activated carbons are considered expensive for treating wastewater due to limited extraction, sources nonrenewable and relatively expensive raw materials like coal, which is unacceptable in pollution control applications. Therefore, in recent years, researchers have been interested in production of active carbon from cheaper and renewable precursors such as agricultural residues [3, 4, 5, 17].

Rice straw is a major concern in the pollution of the environment due to lack of recycling it or benefit from it, but it ends up burned to get rid of it. The rice straw possesses the structure and properties that make from it a good biochar as one of the carbon precursors. For that, obtaining the biochar from rice straw was used in this study for adsorption NH$_4^+$ and COD [6-9].

Many of the previous studies examined the effect of one or two parameters at a time and did not discuss the effect of six parameters on the efficiency of adsorption. The effect of these six parameters on the adsorption process can be studied using artificial intelligence techniques like an artificial neural network, which can be efficiently carried out to predict NH$_4^+$ and COD removal from input factors. Moreover, the ANN is able to describe the interactive effect between variables, as well as the relationship of each variable with outputs to give the target result. In addition, it is capable of solving complex and
highly nonlinear relationships between several variables [10, 11, 12, 13].

The main objectives of this research study are to (i) find the performance of biochar obtained from rice straw for removal of COD and NH\textsubscript{4}+ from wastewater of fish farms in a batch adsorption process, and (ii) obtain a predictive model of ANN for prediction of the adsorption of COD and NH\textsubscript{4}+.

II. METHODS AND MATERIALS

Preparation of adsorbents. Biochar obtained from rice straw was used for NH\textsubscript{4}+ ions removal and reduction of COD from the aqueous solution. Rice straw was collected from the local area near Kafr el-Sheikh, Egypt and transported to Rostov-on-Don in Russia for studying in the laboratory of Don state technical university. Firstly, the rice straw (RS) was washed with tap water to remove dust. The rice straw was soaked for 24 h with 1M of NaOH to remove cellulose, lignin and silica also for activating the surface of RS with a negative charge. After treating RS with NaOH, it was washed four times with distilled water for adjusting pH with 7 - 8. Finally, it was washed with distilled water three times and dried at 120°C. During drying, the RS was produced as activated rice straw by NaOH (RS\textsubscript{NaOH}). The biochar of rice straw (RS\textsubscript{600}) was produced by pyrolysis of the RS\textsubscript{NaOH} in the oven at temperature from 500°C to 600 °C for 1 h. The RS\textsubscript{600} was characterized by infrared spectral analysis (FT-IR).

Adsorbate. The adsorbate is divided in two groups:

1 - The first group is ammonium chloride with different concentrations of ammonium (3, 8, 12, 18, and 25 mg/l) was obtained from the Aquatest company in Rostov on don city, Russia.

2 - The second group is wastewater with COD concentration from 150 to 1000 mg was withdrawn from fish farms.

Experimental setup. Batch experiments were carried at different parameters as follows: room temperatures (25 ± 5 °C, 35 ± 5 °C and 45 ± 5 °C), the amount of the bio-char adsorbent, in g/L (1 to 4), different contact time, in min (0 to 120), pH (2 to 10), where the pH was adapted in the solution by adding HCl or NaOH solution as required, initial NH\textsubscript{4}+ concentration, in mg/L (3 to 25) and initial COD concentration, in mg/L (150 to 1000). Different values of parameters were selected to simulate verities of wastewater in fish farming under normal and abnormal environmental conditions. The influence of those factors on the removal of NH\textsubscript{4}+ ions and COD were evaluated and optimized by a 14 full factorial experimental design (fourteen model, each model contains 12 readings from time 0 to 120 min). The design of the matrix and interaction of the six studied factors were listed in (Table 1). The removal of NH\textsubscript{4}+ and COD on biochar obtained from rice straw was investigated by adding different doses of adsorbate to 250 ml of a solution in flasks in different conditions as shown in table 1. Those flasks were placed in a shaker at 120 r/min for a suitable amount of time to ensure mixing adsorbent with the solution. During mixing processes the samples were extracted from the flasks for analysis every 10 min. The samples passed through membrane filters 0.22 μm and using the device “Expert 001 pH meter-ionomer”, the residual concentrations of contaminants were measured. The removal efficiency of NH\textsubscript{4}+ and COD were calculated by (Eq.1):

\[
\text{% NH}_4^+ \text{ or COD removal} = \frac{C_0 - C_e}{C_0} \times 100
\]  

where C0 (mg/L) is the initial concentration of NH\textsubscript{4}+ or COD; Ce is the concentration of NH\textsubscript{4}+ or COD at time taken as the sample in the solution after adsorption (mg/L).

Artificial Neural Network (ANN) Modeling. An artificial neural network (ANN) is a simulation of human neural networks; for that principle, it is called a black box, the ANN has recently gained the high confidence to apply it in the modelling of nonlinear problems like adsorption [14]. ANN consists of interconnected processing elements called as nodes or neurons acting in exact harmony to solve a specific problem. A basic ANN architecture is shown in Fig. 1 where inputs are indicated by x1, x2, … xn and for each input there weight coefficients are indicated by Wx1, Wx2, … Wxn. Every input is weighted, then we summed those in an intermediate layer, and then by a transfer function the output is calculated [14, 15, 16]. The input layer takes data from an experimental data then transfers them to the network for processing.

### TABLE I. FACTORIAL DESIGN AND TOTAL DATA FOR ANN MODELING

<table>
<thead>
<tr>
<th>No. test group</th>
<th>Initial NH\textsubscript{4}+ [mg/L]</th>
<th>Initial COD [mg/L]</th>
<th>Adsorbate [g/L]</th>
<th>Temperature [°C]</th>
<th>Contact time [min]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>0</td>
<td>2.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 2.0</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>0</td>
<td>2.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.5</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>0</td>
<td>2.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 10.0</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>0</td>
<td>2.0</td>
<td>35 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>0</td>
<td>2.0</td>
<td>45 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>6</td>
<td>12</td>
<td>0</td>
<td>1.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>7</td>
<td>12</td>
<td>0</td>
<td>4.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>0</td>
<td>2.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>0</td>
<td>2.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>10</td>
<td>18</td>
<td>0</td>
<td>2.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>11</td>
<td>25</td>
<td>0</td>
<td>2.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>150</td>
<td>2.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>1000</td>
<td>2.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>1000</td>
<td>1.0</td>
<td>25 ± 5</td>
<td>0</td>
<td>120, 7.50</td>
</tr>
</tbody>
</table>

The next layer is a hidden layer that receives information from the input layer and generates information to an output layer after processing. All generated data are sent to the output layer. In the output layer all data is converted by transferring functions to a net output value. The target is compared with the net output value by calculating mean square error (MSE) value. The MSE is calculated from (Eq.2). The resulting error is distributed by back propagation from the output layer to the input layer, so that the weights and biases of the network are adjusted again. This step is repeated until the network approaches the target values with the acceptable error.
Accordingly, the number of iterations is determined to reach the optimal case:

$$\text{MSE} = \frac{\sum_{i=1}^{N}(t_i - a_i)^2}{N}$$ (2)

where $t_i$ is target output; $a_i$ is predicted outputs; and $N$ is the number of points. The optimum design of a neural network is central for its perfect application. The neural network has several parameters such as network architecture, network type, input selection, training algorithms, activation functions, neural network weight, bias value, number of iterations momentum rate and data-set partitioning ratio, which influence the model [10]. However, all transfer functions and algorithms may not be applicable for all the processes. Selecting a transfer function, a suitable training algorithm and the number of neurons in each layer is a very sensitive parameter for the design of a network as they have a control and influence in network training time, training performance, and its generalization abilities. Training of the ANN is sensitive to the number of hidden layers and neurons in these layers. A few numbers of neurons in the hidden layer may be better than the several numbers of neurons, or the opposite may be true, because excessive numbers of neurons in the layer are better in fitting data but may lead to excessive installation that may be the cause for the loss of generalization capability of the network. On the other hand, few numbers of neurons in the hidden layer may not fit the data, and subsequently the network may not be able to learn. Subsequently if the model does not agree with the experimental results, then the output value will be haphazard and wrong data. A trial-and-error method was implemented to find the most suitable network model [11, 12].

![Cell pattern of Artificial Neural Network (ANN).](Fig. 1.)

![Artificial neural network (ANN) configuration.](Fig. 3.)

In the present study, an artificial neural network (ANN) with 6-10-2 was configured. The network consists of three input layer with six input elements (initial concentration of NH4+, initial concentration of COD, the amount of adsorbent, temperature, contact time and pH), one hidden layer with ten nodes or neurons that are selected by the trial and error method, and an output layer with two output elements (% NH4+ adsorption and % COD adsorption). Each element of the 6-length input vector (P6x1) is connected to each neuron input through a 10 x 6 weight matrix (W10x6). The inputs are weighted and summed up (W6x3 P6x1), and then an eleven-length bias (b6x1) is added. The net resulted from input (U11x1 = Σ W10x6 P6x1 + b10 x1) is transformed in a nonlinear manner through transfer functions. The logistic transfer function (Eq.3) squashes the output into the range from 0 to 1 as the neuron’s net input goes from zero to positive infinity. The last layer is used as a linear transfer function (Eq.4) for function fitting:
\[
f(x) = \tanh(x) = \frac{e^x - e^{-x}}{1 + e^{-x}}, \quad 0 \leq f(x) \leq 1
\] (3)

\[
f(x) = x, \quad -\infty \leq f(x) < +\infty .
\] (4)

III. RESULTS

Bio-char characterization. The FT-IR spectra of the rice straw before and after adsorption of NH\textsubscript{4}\textsuperscript{+} and COD are shown in Fig. 3. Before adsorption, the presence of strong peaks at 3436.73 cm\textsuperscript{-1} can be attributed to the presence of hydroxyl groups (\textnormal{-OH}), as a result of chemical activation of raw rice straw. The band that appeared at 2920 cm\textsuperscript{-1} is due to stretching vibrations of aliphatic acids in the (\textnormal{-CH\textsubscript{3}}) group. Furthermore, the appearance of bands at 1634.60 cm\textsuperscript{-1} is due to stretching vibrations of carbonyl group at (C=O). In addition, the appearance of less prominent bands at 1323.75 cm\textsuperscript{-1} is probably due to carboxylate group (\textnormal{-COO}) stretching. The appearance of carbon in different groups is attributed to the carbonization of rice straw. After adsorption, the vibrational mode of NH\textsubscript{3}\textsuperscript{+} at absorption bands 3420 cm\textsuperscript{-1} and 3222 cm\textsuperscript{-1} which were assigned to antisymmetric stretch of vibrational mode of (N-H), and symmetric stretch of vibrational mode of (>N-H) respectively, while their bending vibrations was observed at 1625 cm\textsuperscript{-1}. The two bands appeared at 2929 cm\textsuperscript{-1} and 2843 cm\textsuperscript{-1} were attributed to antisymmetric stretch (str. asym) and symmetric stretch (str. sym.) of vibrational mode of (>CH\textsubscript{3}) respectively, the band observed at 1426 cm\textsuperscript{-1} was assigned to the bending of vibrational mode of organic moiety (H-C). Change of the FT-IR curve and appearance of both (N-H) and (H-C) groups refer to the achievement of the adsorption process and removing the NH\textsubscript{3}\textsuperscript{+} and COD in the solution.

Effect of input parameters on adsorption behavior. As presented in Fig. 4, input parameters influence adsorption processes or removal efficiency of pollutant (chemical oxygen demand (COD) and ammonium NH\textsubscript{4}\textsuperscript{+}). The influence of contact time on the removal efficiency of adsorbate NH\textsubscript{4}\textsuperscript{+} is drawn in Fig. 4-A, in which the amount of adsorption of adsorbate is increased with increased contact time durations until 90 min. That is supposedly due to the larger surface of functional groups of adsorbents at the beginning for the adsorption of NH\textsubscript{4}\textsuperscript{+}. Moreover, the surface adsorption sites go into saturation case then the adsorbate is transported to interior sites of the adsorbent particles, in this case, the adsorption efficiency is slowed down until saturation is achieved. Increase in the concentration of NH\textsubscript{4}\textsuperscript{+} ion from 3 mg/L to 25 mg/L resulted in decrease removal efficiency of NH\textsubscript{4}\textsuperscript{+} from 55.5 % to 36.00 %. On the contrary, an increase in COD concentration from 150 to 1000 mg/L resulted in increase in removal efficiency of COD from 76.67% to 90.44%. Moreover, the ability of the adsorption of chemical oxygen demand, which achieved efficiency removal of COD by 76.67%, is better than ammonium adsorption on biochar obtained from rice straw, which achieved efficiency removal of NH\textsubscript{4}\textsuperscript{+} by 55.56 % in the same conditions of the experiment. Adsorption of ammonium on biochar occurs as a result of chemical adsorption and physical adsorption. Chemical adsorption occurs due to the presence of the functional groups with negative charges on the surface of biochar. However, the behavior of physical adsorption on the pores is poor. However, with increasing NH\textsubscript{4}\textsuperscript{+} concentration, the active sites of functional groups with a negative charge on biochar surface could be saturated by NH\textsubscript{4}\textsuperscript{+}, there are few active free sites that reduce adsorption efficiency if the ion concentration in solution is increased. In contrast, with increasing chemical oxygen demand (COD), the removal efficiency of COD is increased, since too much of COD is adsorbed by physical adsorption and only a little of it is absorbed by chemical adsorption. Physical adsorption efficiency increases with the increased of adsorbate concentration in the solution because it causes high pressure on the adsorbent surfaces, resulting in the creation of adsorption sites. Otherwise, the removal efficiency of adsorbent increases with increase pH from 2 to 8.5 because at low pH level the concentration of ion hydrogen [H\textsuperscript{+}] which has a positive charge is increases, as a result, competition for active sites increases between adsorbents and hydrogen ion on the surfaces of functional groups. Moreover, with the high pH level more than 8.5 the adsorption of NH\textsubscript{4}\textsuperscript{+} decreases due to converting ions NH\textsubscript{4}\textsuperscript{+} to NH\textsubscript{3} (Fig. 4-E). The amount of adsorbents and temperature have a direct relationship with the adsorption efficiency. Increasing of the adsorbent amount creates a better chance to adsorption on the functional groups and pores (Fig.4-C). On the other hand, at a higher temperature, ions have high kinetic energy that makes them fast and active to find adsorption sites (Fig.4-D).

Modeling of Artificial Neural Network (ANN). An artificial neural network displayed in Fig. 2 was generated by MATLAB program by the neural network toolbox "nntool" as shown in Fig. 5. The 52 models of ANN were tested with a different number of neurons and layers to find the optimal number of neurons and hidden layers by observing the MSE mean squared error and comparing the predicted values of test data with targeted values. We found the optimal value of ANN (to obtain optimal performance while not over-fitting) at a single-hidden layer with 10 neurons with structure 6-10-2. The input matrix consists of 126 columns and 6 rows, and the target matrix also consists of 126 columns and two rows as a result of the input matrix. In the training process we employed 70% of input and target data, where the ANN program randomly divides the data of input and target into 3 groups (70 % for training, 15 % for validation and 15 % for testing.). The Levenberg–Marquardt (LM) training algorithm was used, where LM is one of the fast training methods for training moderate-sized neural networks. The LM algorithm is designed to approach second-order training speed without computing the Hessian matrix. Moreover, the LM algorithm has better performance than the other methods for function approximation problems. A screenshot of training progress was illustrated in Fig. 5, the training of network stopped after 56 seconds due to the validation check number, which was 100, because the progress of training not achieved the target of a gradient value 1e\textsuperscript{-5}, but gradient achieved value 0.225 at 100 epoch (training stops when any of these conditions occurs: the maximum amount of time is exceeded, the maximum number of epochs (validation check number) is reached, the performance gradient falls below min. grad, performance is minimized to the goal).
Fig. 4. FT-IR spectra of biochar before and after adsorption.

Fig. 5. Effect of input parameters on removal efficiency.

Fig. 6. Proposed ANN structure.
The plot in Fig. 6 shows the value of the mean squared error, versus the iteration number of training. The best validation performance was 3.78 at epoch 0. After epoch 0 the test curve had increased as the curve of validation increased, which reveals that the test and validation curves are very similar.

IV. CONCLUSION

The influence of six independent variables like pH, contact time, NH$_4^+$ concentration, COD concentration, temperature and the amount of adsorbent dosage on the removal of ammonium NH$_4^+$ and COD from aqueous solution by biochar obtained from rice straw are studied systematically in a batch study. The current work demonstrates successful removal of NH$_4^+$ ions and COD from the aqueous solutions with maximum removal efficiency of 70.83 % and 90.44 %, respectively. A suggested artificial neural network (6-10-2) with six inputs (pH, contact time, NH$_4^+$ concentration, COD concentration, temperature and amount of adsorbent dosage) was capable of predicting removal efficiency of NH$_4^+$ ions and COD with acceptable accuracy with R 0.9. This network can be used to predict and control water quality of the fish plant under changing conditions.

Acknowledgment

The first author is very grateful to the Ministry of Higher Education of Egypt represented by Kafr-el-sheikh University, and Don State Technical University for providing financial support for this research.

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