# Modeling and Experimental Prediction of Wastewater Treatment Efficiency in Oil Refineries Using Activated Sludge Process

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## Abstract

In this study, activated sludge process for wastewater treatment in a refinery was investigated. For such purpose, a laboratory scale rig was built. The effect of several parameters such as temperature, residence time, effect of Leca (filling-in percentage of the reactor by Leca) and UV radiation on COD removal efficiency were experimentally examined. Maximum COD removal efficiency was obtained to be 94% after final testing. An artificial neural network (ANN) was applied to evaluate the effect of operational parameters on the efficiency as the next step. A two-layered ANN provided the best results, using Levenberg–Marquardt back propagation learning algorithm (trainLM) in which tansig and purelin used as transfer functions in the hidden and output layers. Furthermore, the application of three neurons in the hidden layer caused to gratify network training while overfitting was hindered. ANN model, provided a good estimation for correlation coefficient and the mean square error (MSE) which calculated 0.997 and $0.5 \times 10^{-3}$ respectively.

**Keywords**: Wastewater treatment, COD Removal, Activated sludge, Artificial neural network

## Introduction

To avoid problems resulting from industrial waste disposal into the environment, wastewater treatment plants have been established. Usually the amounts of contaminants in the oil refinery effluent are different. Various physical and chemical methods are applied to remove dissolved organic pollutants in activated sludge biological treatment, especially those causing degradation such as COD and BOD [1].

Nowadays, the common biological methods are showed to be high efficient and effective for the biodegradation of organic compounds in large industrial scale. In recent years, biological treatment methods have been considerably developed and widely expanded. To have a successful treatment, an efficient, convenient and optimal contaminated environmental condition is prepared using appropriate microorganisms, oxygen and nutrients [2].

One of the most common biological methods is the activated sludge wastewater treatment. In a laboratory scale continuous flow system, a separator is used to reduce oil level from an activated sludge. Natural microbial growth in an aerobic tank is applied. COD removal efficiency of petroleum hydrocarbon solids by an activated sludge treatment during a residence time of 20 days holds a value of 98 to 99% [3]. Freire et al. [4] studied the COD removal from wastewater and sewage sludge in a SBR for various percentages of contaminations. In a mixture of 45% and 35% effluent COD, the removal efficiency varies from 30 to 50%. They have investigated the effect of salinity on the removal of COD effluent. In saline water tanks, aerobic wastewater treatments with rod-shaped micro-organisms are dominant, that is for growing microbes.

Palmer et al. [5] used rotating biological surfaces for oilfield produced water treatment. BOD removal efficiency of oil and gas, were found as 74% and 94%

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respectively. Microorganism's inactivity can increase the filtration efficiency.

In another study, Zhao et al. [6] used a commercial microorganism B350 and B350M groups. A pair of BAF reactors was examined. The results indicated that a hydraulic residence time of four hours with a loading volume of 1.07 KDOCg/B350M, leads to an exciting value of TOC removal from waste oil that is 78% and 94% for B350, 86% and 64% for B350M, respectively.

In biological oxidation, harmless bacteria, algae, fungi and protozoa to organic materials and ammonia compounds to water and carbon dioxide, nitrates and nitrites are converted [5], but had no effect on TDS [7].

The dominant mechanism for the removal of hydrocarbons in biological treatment is the biodegradation of particles by microorganisms such as bio-coagulation. Absorbing particles of activated sludge are soluble and insoluble. Bacterial surface-active compounds, such as surfactants and emulsifiers produce a soluble hydrocarbon and biologically active bacteria which increase the mass transfer [8]. Biodegradation of petroleum complex feature combinations such as the normal alkenes is simpler than larger molecules. Biologically active molecules attached to the microorganisms remains in the aeration. These compounds are removed along with the excess sludge contaminants. However, such mixtures of hydrocarbons and microorganisms are a source of hazardous materials.

Gallagher [9] studied biodegradation of organic acids in wastewater under anaerobic conditions and in the presence of petroleum acids in a Fixed Film Bio reactor with a volume of 0 59L. The results showed that petroleum acids are properly biodegraded in anaerobic conditions. In another unique technology for wastewater treatment, sandy beds were applied to remove hydrocarbons as well as heavy metals pollutants. Other researches refer to sand bed filtration of 800 $m^2$ which utilizes for treatment of 20$m^3$/day wastewater. The results show that over 98% of hydrocarbons were removed by above-mentioned method [10]. In a similar unit, 3000 $m^3$/day wastewater was treated in order to reduce the total concentration of hydrocarbons by a mean value of 96%. Concentrations of Metals were decreased by 78% for aluminum, barium, chromium, copper, zinc and by 40% for iron, lithium, manganese, lead, arsenic, cadmium, cobalt, molybdenum, nickel, cerium and vanadium [11].

The present work is conducting for modeling the effect of four important operational parameters (i.e. temperature, residence time, Leca Percentage of the reactor and UV radiation) on percentage of COD removal in activated sludge equipped with UV ray for Kermanshah refinery wastewater treatment. Also the application of a three-layered ANN with different repartitioning neuron numbers in a hidden layer is investigated. The corresponding calibration iteration is also determined using the simple and commonly used trial and error method in the application herein.

## 2. Materials and methods

### 2.1. Chemicals

Nitrogen and phosphate fertilizers; as source of nitrogen and phosphor are used throughout the experiments. Furthermore, for COD test, powdered potassium dichromate, silver sulphate, mercuric sulfate, sulfuric acid (98 wt%) and potassium hydrogen phthalate standard were used for calibration charts.

### 2.2. Equipment

Devices used in this research include a pH meter for pH monitoring during the experiments, oven for ensuring 150°C temperature in COD test, spectrophotometer for reading the amount of absorption and an aquarium pump with a maximum capacity of 14L/min for aerating the tank in the biological reactor. Figure 1; illustrates a schematic presentation of the experimental setup used in this work.

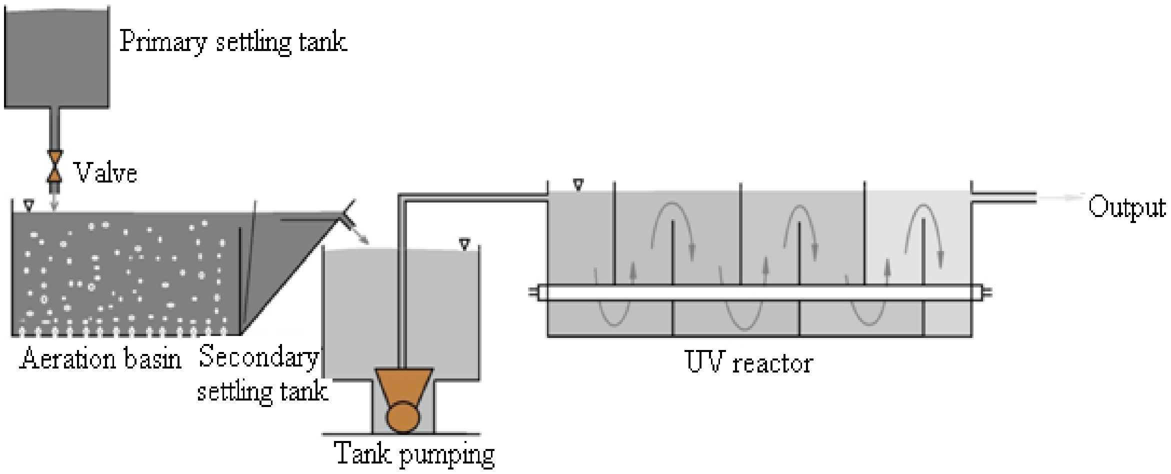

**Figure1: A schematic diagram of the experimental setup**

Primary settling chamber is a plastic tank with a volume of 6L which is used for the primary raw wastewater settling with a valve to create different residence time throughout the experiments. Reactor used in this study consists of a cubic Plexiglas tank with a volume of 12L and an additional 8L settling tank. The two parts are separated by a partition with vertical tilt and height of 13cm apart. Furthermore, in various stages a 10, 20, 30 and 40% of the aeration basin volume filled by Leca beads which consider as biofilm support so that leads to the higher surface area, lower density, and lower prices.

The main causes of lightness of Leca aggregates are air into and out of them. The air in terms of grain size between 73 to 77% occupies the entire space. These grains with very high surface area of 525 $m^2/m^3$, are a suitable environment for microbial growth.

Pumping tank or a secondary settling tank with a volume of 6L, was used for the settling wastewater and creating different residence times in order to study the effects of UV radiation time on COD removal efficiency. UV reactor with a volume of 14L which equipped with the six baffles situated at the bottom of the reactor. The effluent of the reactor is passed through the UV reactor. Baffles are constructed so that the wastewater can lead plug into the UV reactor.

## 2.3. Methods

For reactor operation, the sludge of Kermanshah refinery was used. Up to 50% of the volume of the reactor was filled up with the sludge then water was fed into the reactor after that aeration establishment. The reactor was operated for 24 hours and thereafter the aeration was off until sludge is settled. Sludge supernatant was then removed from wastewater. For the next step of the operation, the reactor filled up with combining two parts water per part wastewater. Then in order to provide a source of nitrogen and phosphorus, nitrogen and phosphate fertilizers were used, respectively. Optimum conditions for microorganism growth, the ratio of C: N: P of 100:5:1 was set [12, 13].

The reactor was aerated for three days, and the results were recorded every 12 hours. During the next three days, reactor was operated with the effluent consist of two sections of wastewater per one section of water. In the final step, the refinery wastewater without any dilution was fed to the reactor for accustomed of activated sludge to refinery effluent. The samples were taken from the reactor, and COD was determined. For operation of reactor as the continuous process, wastewater was fed up to the reactor from primary settling tank and offloaded to secondary settling tank continually.

### 2.4. Calculation of nutrients

Nutrients are an important component in the operation of a wastewater treatment unit, specifically, the two macronutrients nitrogen and phosphorus. They are critical building blocks for bacterial growth and reproduction, as well as energy transfer.

The content of the individual nutrients in wastewater should correspond to the needs of the bacteria in the activated sludge, and there should be a balanced relationship between C, N and P. This is crucial to the effectiveness of the biodegradation processes. During aerobic wastewater treatment, the C: N: P ratio should be in the range between 100:10:1 and 100:5:1[12].

#### 2.4.1. Nitrogen

For treatment of wastewater, nitrogen is present in organically bonded form (organic N) or as ammonium nitrogen ($NH_4$-N) form. During biological wastewater treatment, organic N is converted to $NH_4$-N by the bacteria in the activated sludge. This $NH_4$-N and the $NH_4$-N from the inflow are converted to nitrite, which in turn is converted to nitrate (nitrification).

In this study, the fertilizer was used as a nitrogen source. 5kg nitrogen per 100kg COD removed by N ($COD_r$) is required. First, the required mass of pure fertilizer was calculated:

$$N_{req} = Q.\left(\frac{COD_r}{R_N} - C_N\right).\frac{M_A}{M_N} \quad (1)$$

Where $N_{req}$ is Nitrogen requirements (kg/ day), Q is inflow to the system ($m^3$/ day), $COD_r$ is COD removal, $COD_i$- $COD_f$, (mg/ L), $R_N$ = 100:5:20, $C_N$ (Wastewater nitrogen inputs) = 4.2 mg/ L, $M_A$ (nitrogen fertilizer molecular weight) = 60.06, $M_N$ (N molecular weight) = 14.

Then Kg solution fertilizers to be calculated by using the following equation:

$$AA_{req} = \frac{N_{req}}{0.46} \quad (2)$$

Where $AA_{req}$ is nitrogen fertilizer mass needed for solution. Since nitrogen fertilizer used contains 46% nitrogen so the denominator number is considered as 0.46.

#### 2.4.2. Phosphorus

The P load in the wastewater treatment unit is made up of orthophosphate-phosphorus ($PO_4$-P), polyphosphates and organic phosphorus compounds. So the fertilizer was used as a phosphorus source.

1 kg phosphorus by P per 100 kg COD removal ($COD_r$) is required. First, the required mass of pure fertilizer was calculated:

$$P_{rreq} = Q.\left(\frac{COD_r}{R_P} - C_P\right).\frac{M_B}{M_P} \quad (3)$$

Where $P_{req}$ is phosphorus requirements (kg/ day), Q is the inflow to the system ($m^3$/ day), $COD_r$ is COD removed, $COD_i$- $COD_f$, (mg/ L), $R_P$ = 100:1:100, $C_P$ (Wastewater phosphorus inputs) = 3.5 mg/ L, $M_B$ (Phosphate fertilizer molecular weight) = 132.07, $M_P$ (P molecular weight) = 31.

Then Kg solution fertilizer Phosphate to be calculated by the following equation:

$$BB_{req} = \frac{N_{req}}{0.50} \quad (4)$$

Where $BB_{req}$ is mass of Phosphate fertilizer solution needed (Kg/ day). Because Phosphate fertilizer used contains 50% Phosphate the denominator number is considered as 0.50.

As the phosphate fertilizers contain nitrogen, thus in the beginning of the calculations, obtaining the amount of phosphate fertilizer in the nitrogen fertilizer input to the system, seems to be required. The effect of nitrogen fertilizer needed in the calculation process.

Characterizations of fertilizers used in this study are listed in Table 1.

**Table 1: Characterization of fertilizers**

| pH (Solution of 1% at a temperature 20° C) | Molecular weight | Chemical formula | Density (g/mL) at a temperature 20° C | Solubility in 100 g of water at a temperature 20° C | color | Properties ⇦<br>fertilizer ⇩ |
|---|---|---|---|---|---|---|
| 8 | 132.07 | $H_9N_2O_4P$ | 1.619 | 69 g | Grayish green | Ammonium phosphate |
| 7.2 | 60.06 | $CH_4N_2O_2$ | 1.336 | 51.6 g | White | Nitrogen |

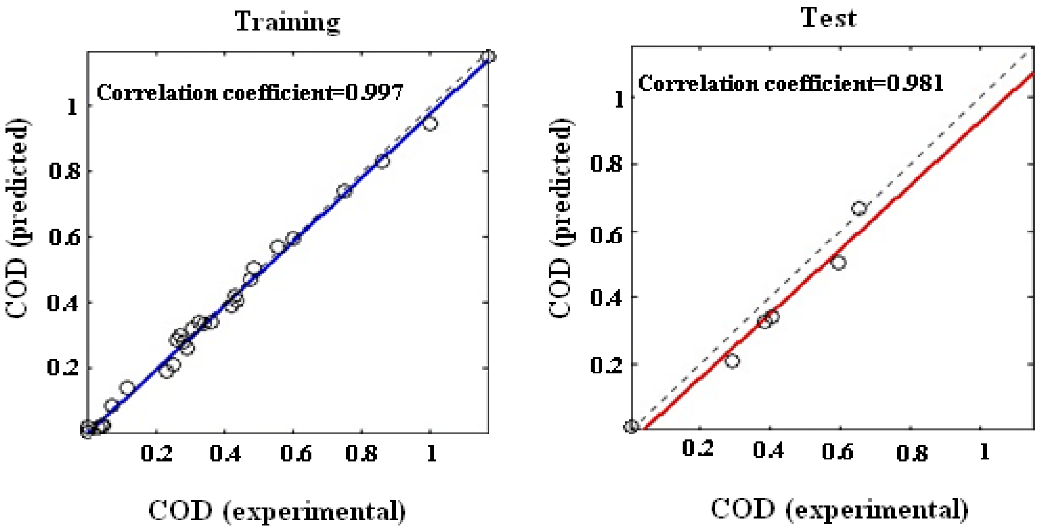

**Figure 2: Regression plot of training and test sets with 3 neurons in hidden layer**

To measure the COD, 5220D method was used [14], (closed reflux, colorimetric method).

### 2.5. Artificial neural network (ANN)

Artificial neural network is an information-processing system that has certain characteristics in common with the biological neural system. Therefore, ANN is composed of many simple elements called neurons. Neurons are interconnected by the weight coefficients that can be used for training ANN for solving a particular problem.

Artificial neural network (ANN) architecture is based on concept's neurons, transfer functions, layers and their connections. Therefore, to the design of an ANN for a specific application, the designer uses the number of neurons, arranges in layers; determines number of layers and types of communication, inputs weight and transfer functions to adjust.

Multi-layer feed forward back propagation network, which is one of the most common ANN architecture, was used in this work. In the ANN, multiple layers of which different numbers of neurons by non-linear transfer functions are connected to predict both the linear and nonlinear relationship between input and output vectors [15].

The number of layers and neurons is usually determined by trial and error. By convention, MATLAB neural network toolbox, the hidden layer is not an ingredient output layer. For the ANN, the first layer is the input layer (independent variables), and the last layer is the output layer (dependent variables). One or more neurons can be placed in the hidden layer. Selection of algorithm and the transfer function appropriate is essential in designing optimal ANN models, here tansig and purelin were used as the transfer functions in the hidden layer and output layer, respectively, and the algorithm used, is the LM algorithm.

Feed forward network is often one or more hidden layer with sigmoid neurons and following output layer neuron which is linear. Multiple layers are of neurons with nonlinear transfer functions to allow the network to learn nonlinear and linear relationships between input and output vectors. In linear output layer, the network allows values outside the range of 1 - to 1 to produce [16]. For the network, the suitable notation is used in two-layer networks [17]. MATLAB software version 2008a was used in the work, and all programs were run using a personal computer.

**Table 2: Effect of the number of neurons in hidden layer on ANN performance**

| Number of neurons in the hidden layer | correlation coefficient | MSE |
|---|---|---|
| 2 | 0.978 | $3.8\times10^{-3}$ |
| 3 | 0.997 | $0.5\times10^{-3}$ |
| 4 | 0.983 | $1.1\times10^{-3}$ |
| 5 | 0.771 | $1.1\times10^{-2}$ |
| 6 | 0.968 | $1.9\times10^{-3}$ |
| 7 | 0.839 | $4.6\times10^{-3}$ |
| 8 | 0.972 | $4.7\times10^{-3}$ |
| 9 | 0.686 | $7.1\times10^{-2}$ |
| 10 | 0.972 | $3.0\times10^{-3}$ |

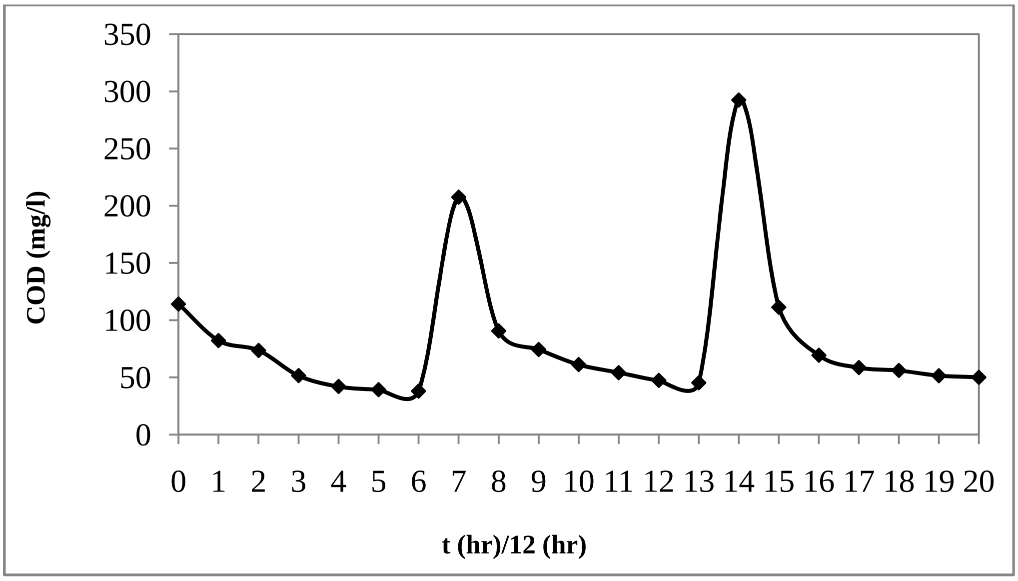

**Figure 3: Variation of COD in the batch period of performance at T=20°C, pH=7.1- 7.8**

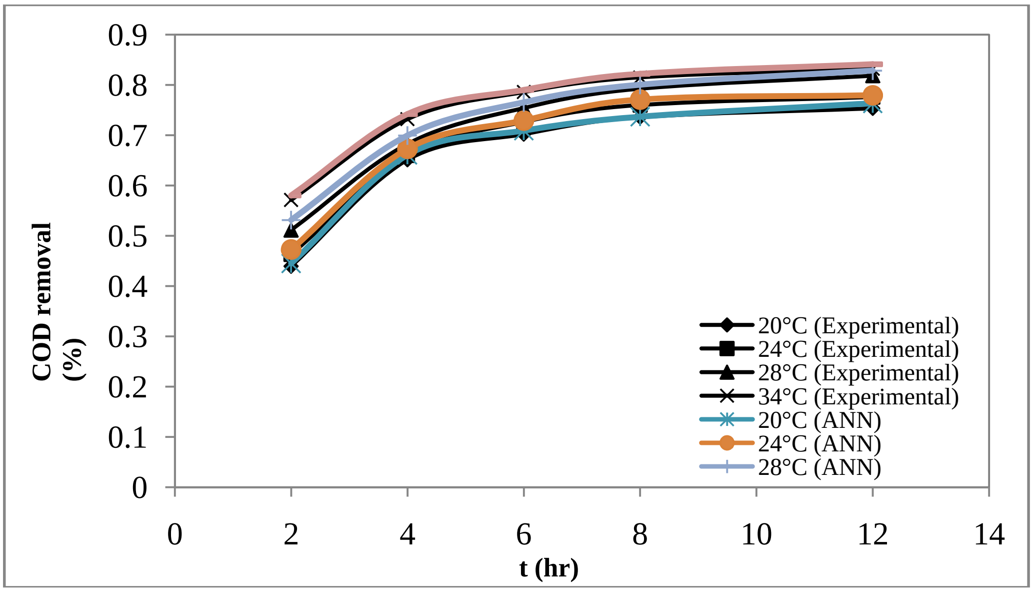

**Figure 4: Effect of temperature on percentage of COD removal at pH=7.1- 7.8 without Leca and UV radiation**

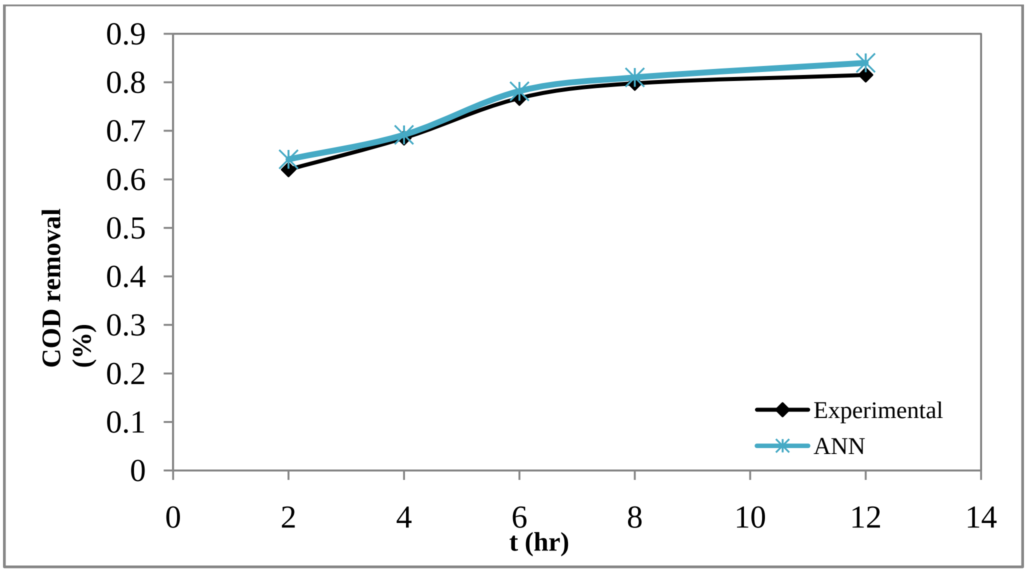

**Figure 5: Percentage of COD removal versus residence time at T=34°C, pH=7.1- 7.8 without Leca and UV radiation**

## 3. Result and discussion

### 3.1. Modeling results with ANN

In order to prediction of the COD removal by using of the ANN model, 70% of the data were used for training purpose. The rests of them were arranged as testing and validation data. The network training database included 28 data sets. To evaluate the capabilities of the ANN model, the new value of COD was introduced into the model. Here, a comparison was made between the COD values estimated by ANN models and their corresponding actual values, which is shown in Figure 2. The output follows the targets very well and the correlation coefficient is over 0.997. Therefore, in this case, the network response is satisfactory. In this work, input variables are temperature, residence time, Leca loading (Percentage valume of the reactor filled by Leca), and UV radiation. COD values are experimental and introduced to the networks as output variable (network response).

The performance of the LM algorithm with different number of neurons in the hidden layer is depicted in Table 2. There is no general and accurate method for the determination of the optimum number of neurons in the hidden layers, and this is determined just by trial and error. The optimum number of hidden layer neurons was determined to be 3 for this network.

## 3.2. Description of experimental aspects

### 3.2.1. Variation of COD removal in the batch period of performance

The batch process was operated during nine days. The reactor operated with the effluent COD of 114.12 mg/ L, and by injecting phosphate and nitrogen source and air into the system, every 12 hours over the three days sampling was done and COD were recorded. During the second three days the COD effluent was 207.54 mg/ L. During the second three days, COD changes were similar to the first three days. Finally, the system operation in the third three days of Kermanshah refinery DAF unit was started which stats by COD effluent of 292.4 mg/ L. Microorganisms in activated sludge are acclimatized with the effluent and the COD. In fact, the 9-day period led to the sudden shock of the high COD of wastewater which induced to elimination of contaminant and microorganisms were grown step by step with the COD encounter (figure 3).

### 3.2.2. Effect of Temperature

In the present work, the effect of the temperature on COD removal was investigated. Four temperature values of 20, 24, 28 and 34°C by a tubular heater a temperature control was provided. The effect of temperature in batch state for biological reactors was studied so that at each of the temperatures studied after 2, 4, 6, 8 and 12 hours of high reactor sample operation and the COD was measured. In figure 4, it can be seen that the temperature increases the efficiency of COD removal performance of the reactor, especially in the early hours.

These experiments not only for studying the effect of temperature even also for determining the effect of residence time was done.

### 3.2.3. Effect of residence time

In Figure 5, the effect of residence time on the COD removal efficiency in biological reactor by activated sludge at 34°C and at residence time of 2, 4, 6, 8 and 12 h is illustrated. As shown in this figure, the COD removal efficiency increased with increasing residence time. However, to increase the residence time at a fixed flow rate the volume of the tanks should increase and it has a high cost. Therefore selection of a residence time in which economic cost in terms of performance to provide standard output it is necessary. Here the residence time of eight hours as the optimal time is selected, and further studies will be used continuously since then.

### 3.2.4. Effect of Leca

In order to study the effect of Leca on the COD removal efficiency, a series of experiments were carried out at various Leca filling between 0 and 40% of the total volume of the biological reactor. During the four experiments that were conducted continuously, temperature set as 34°C, the hydraulic residence time considered as eight hours and a pH range was selected between 7.1 and 7.8. As shown in Figure 6 s the increasing in volume of Leca leads to COD removal efficiency improvement. However, increasing of Leca filling led to reduce volume of wastewater in biological reactor but the effect of COD reduction was more receivable.

### 3.2.5. Effect of UV radiation

In the present research, the effect of UV radiation was investigated. The treated wastewater in reactor which filled by LECA (40%) was fed to UV reactor. The revealed results in Figure 7 indicate that increase in the residence times led to a increasing in the COD removal efficiency. According to Figure 7, in UV reactor for hydraulic residence time more than two hours, the COD removal was not changed. When both biological and UV reactor were operated as continuously at 34 °C, residence time of 8 hours and percentage of Leca filling 40% for a biological reactor, and hydraulic residence time of 6 hours for UV reactor, the overall efficiency of COD removal was achieved about 94%. Meanwhile, COD removal efficiency in biological unit of Kermanshah refinery was obtained 75.8%.

## 4. Conclusions

This work represents the treatment of refinery wastewater by combination of activated sludge and UV raddiation processes. The effect of several parameters such as temperature, residence time, Leca presence, and UV radiation on the efficiency of COD removal were examined experimentally, and the following results are obtained:

- In the bioreactor the COD removal efficiency increased by any increment in temperature.
- Percentage of COD removal was grown with any increase in residence time.
- With increasing congestion of Leca, percentage of COD removal improved.
- In UV reactor, with increasing in hydraulic residence time up to two hours the COD removal was increased but increasing more than two hours was not more effective.
- Then, the results of the COD test by an Artificial neural network (ANN) were modeled. ANN model, provided good estimation with correlation coefficient and the mean square error (MSE) of 0.997 and $0.5 \times 10^{-3}$ respectively.

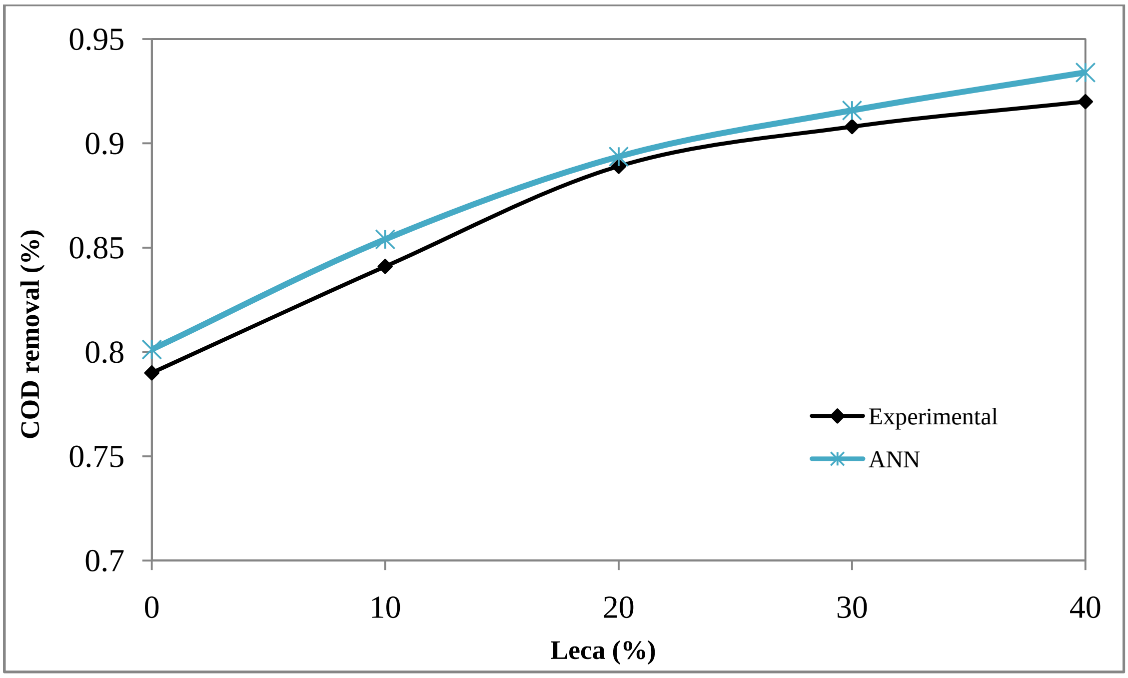

**Figure 6: Percentage of COD removal versus Leca filling percentage at T=34°C, pH=7.1- 7.8 without UV radiation**

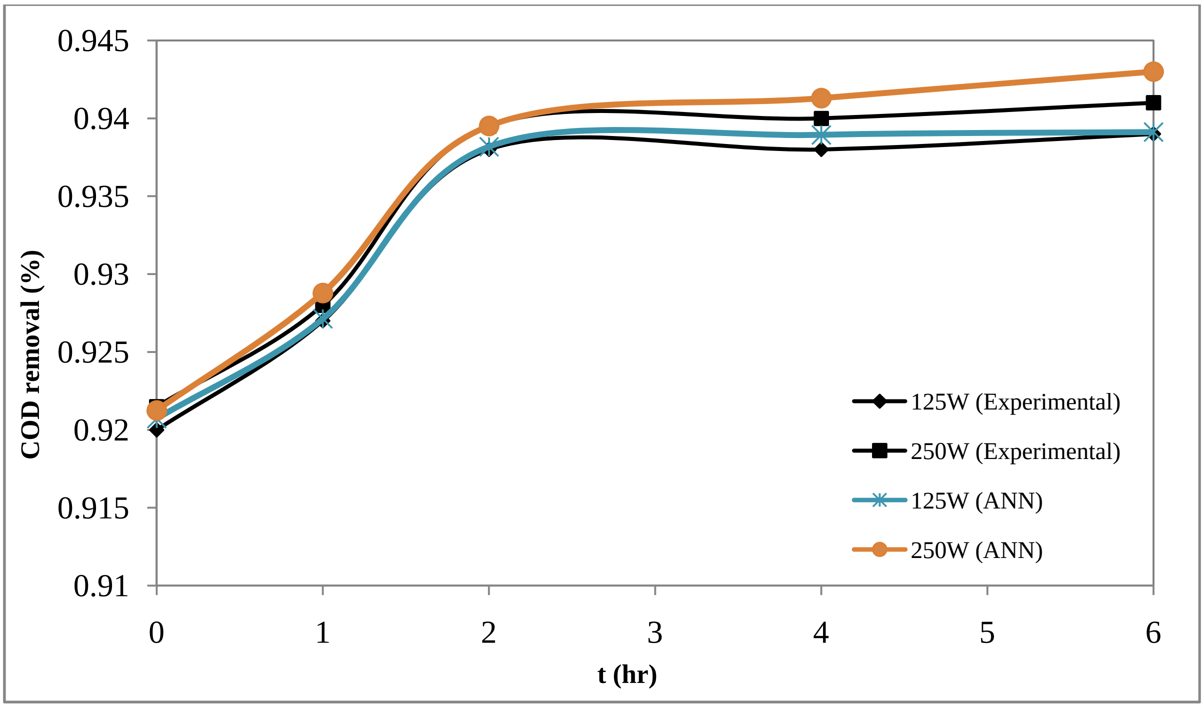

**Figure 7: Effect of UV radiation on percentage of COD removal at T=34°C, pH=7.1- 7.8 and Leca 40%**

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