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An artificial neural network approach to determine the rheological behavior of pickering-type diesel-in-water emulsion prepared with the use of β-cyclodextrin

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Abstract−With the use of β-cyclodextrin (β-CD), Pickering-type diesel-in-water emulsions were prepared based on the inclusion complex formed between diesel and β-CD which acted as an emulsifier. By using the artificial neural network (ANN), the rheological behavior of the emulsions was characterized using three input variables: diesel-to-water ratio, β-CD concentration, and shear rate and one-output variable as shear stress. Gradient descent (GD), conjugate gradient (CG), and quasi Newton (QN) were used as three different methods in the feed-forward back-propagation algorithm for network training. Hyperbolic tangent sigmoid and pure linear were the transfer functions used for transforming information between input and output through one hidden layer containing ten neurons. By dividing the experimental data into three sets of training, validation, and testing, the QN method in predicting shear stress was found to have performed better than the other two network learning techniques (R^2=0.994 and MSE=0.006).

Keywords: β-Cyclodextrin, Diesel-in-water Pickering-type Emulsion, Rheological Behavior of Emulsion, Artificial Neural Network, Feed-forward Back-propagation Learning Algorithm

INTRODUCTION

Emulsion, as a mixture of two immiscible liquids, has been defined as a significantly stable suspension of particles of a particular size of one liquid dispersed within the other liquid that has different sizes of particles [1]. The term "stability" intends to show the emulsion capacity by keeping its properties unchanged with time, and emulsion resists the physicochemical changes that may occur with time [2]. Interest in applications of emulsions is, therefore, the subject of kinetic stability: for instance, though emulsions with small-sized droplets are kinetically more stable than the ones with large-sized particles, both types of emulsions are thermodynamically unstable [2]. Attention is particularly directed toward the preparation of emulsions without the use of emulsifiers, mainly because of some adverse effects observed in the use of surfactants (such as skin irritation, environmental issues, etc.) [3,4]. The use of Pickering-type emulsions in this respect has attracted great interest, wherein solid particles of colloidal dimensions, by being dispersed in a mixture of the two immiscible liquids, play the role of the emulsifier [5]. The reduction in surface tension is important and thus the stability of the emulsion can be ensured. The wetting characteristic of the surfaces of solid particle determines the type of emulsion and may form when the contact angle of the adsorbed solid particles in the water phase is lower than 90^o. The preference of the system then is the formation of the oil-in-water (O/W) emulsion [5,6].

The property of emulsification of cyclodextrins (CDs), which are starch derivatives with a cyclic structure produced by the catalytic action of the microbial cycloglucanotransferase (CGTase), has attracted considerable interest. The key role played by CD can be attributed to its unique property as possessing both hydrophilic-hydrophobic characters, and this behavior was found to be related to the special arrangements of the glucose moieties inside and outside the CD molecule [7,8]. During an emulsion preparation, CD by accepting a particular molecule in its interior structure (preferably nonpolar in nature) can form an inclusion complex (IC). The IC performs as solid particles covering the organic droplets of one immiscible liquid in emulsion preparation. In this way, the IC molecules stabilize the emulsion [9]. The characterization of the IC formed between β-CD and diesel has been described in our previous work [10].

A point to be further noted is the quality of a particular product made with the use of emulsions (pharmaceuticals, health products, food items, etc.). This certainly relates to the rheological characteristics of the emulsion, where product quality reflects the efficiency of the production process. The artificial neural network (ANN) method in the model prediction process is preferred over the statistical approach. For instance, the necessity of having prior knowledge about the data is not considerable in the ANN methodology. The superiority of the NN in reporting results with greater accuracy is also related its ability of using a large number of data points (such as 171 values in the present study) [11].

The present work was undertaken to study the rheological properties of diesel-in-water emulsions prepared with the use of β-CD as emulsifier (i.e., the Pickering-type emulsion) using the ANN methodology. In this manner, it was possible to predict the model for the relationships between the inputs and output within the range of the variables used here in this study. The three inputs were the diesel-to-water ratio (at three ratios), the β-CD concentration (at three levels), and the shear rate as related to shear stress (output variable) measured at 19 levels.

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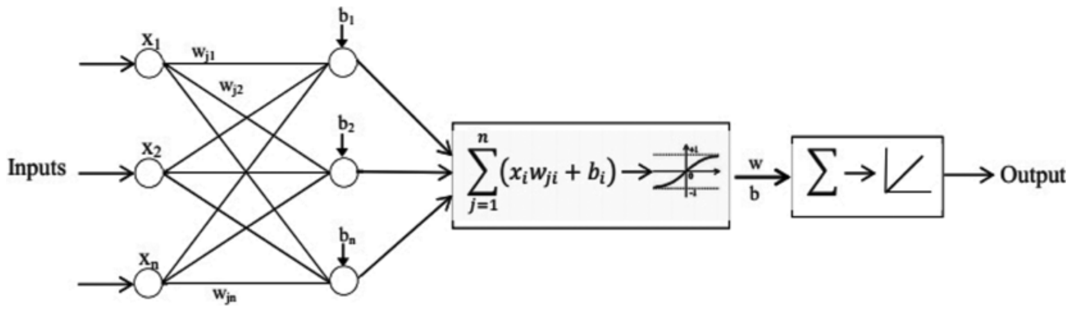


Fig. 1. Schematic diagram of a typical three layer neural network used in the present study where the inputs are x_1 as the diesel-to-water ratio, x_2 as the β-CD concentration, and x_3 as the shear rate. The output neuron is the shear stress.

MATERIALS AND METHODS

1. Materials

The diesel fuel used in the present study was obtained from the Tehran Oil Refinery Company (TORC). Some of its specifications are as follows: 826.2 kg/m^3 as a density at 15 °C, 2.5 cSt as the kinematic viscosity at 37.8 °C, and 0.826 as the specific gravity [10]. β-CD (Sigma-Alderich-C4767), and all other reagents used in this study were of the analytical grade and purchased from a local supplier.

2. Preparation of Emulsion

Diesel-in-water emulsions were prepared at room temperature by mixing these two immiscible fluids in the presence of β-CD using the HO4 Edmund Buhler 7400 Tubingen homogenizer (Germany), where the speed and time of the homogenization were set at 11000 RPM and two minutes, respectively. Details of the preparation of the emulsion are given elsewhere. Three levels of β-CD and three ratios of diesel-to-water were examined [12].

3. Rheology Measurements

All the tests regarding steady state measurements involved using a Brookfield DV-II+ pro rotational viscometer, which was equipped with a SC4-18 spindle. The measured data was shear stress obtained at the different applied shear rates; it ranged from 3.96 to 264 s^{-1}. The values of shear stress obtained by applying shear rate were within the range of 3.96 to 264 s^{-1}—these were confirmed by repeating the readings at each shear rate for five times. The average value of these readings was obtained.

4. ANN Analysis

MATLAB software (version 8.1.0.604) was used for the development of the ANN. The focus of the present study was on a common ANN structure involving three types of layers: the input layer having the predictor variables, one hidden layer containing the constructed variables (neurons), and the output layer made up of the response variable. As mentioned above, three neurons that corresponded to the three inputs were the diesel-to-water ratio at the three levels (40 : 60, 45 : 55, and 50 : 50), the β-CD concentration at three levels (0.75, 1, and 1.25 w/v%), and the shear rate as related to shear stress (the output variable) measured at 19 levels. Therefore, the output layer, which consisted of one neuron for shear stress, was measured at the 19 different levels of shear rates by considering the three levels of the two other input variables. The dataset containing 171 data points for the inputs and the corresponding output values was obtained experimentally. Fig. 1 schematically shows complete interconnections of the neurons involved in the NN. A multilayer feed-forward ANN (MLFFANN) with back propagation (BP) was the overall algorithm used for the training of the NN. By following the default values of the software and according to the concept used by the network, the data obtained was divided into training data (70%), validation data (15%), and testing data (15%). The importance of using an appropriate training pattern is to make the ANN able to learn. The tangent sigmoid (tansig) function was used to transfer information from inputs to the hidden layer, while the transfer function from the latter to the output neuron was described linearly (purelin). Statistical parameters like the coefficient of determination (R^2) and the mean squared error (MSE) were used to compare the results of the present study in terms of the extent of the difference between the NN predicted and actual value of the output [13].

RESULTS AND DISCUSSION

ANN can acquire and store knowledge that is experientially obtainable. This inherent ability shows a unique characteristic of the network in handling complex phenomena mathematically. BP, as the overall algorithm used in this study for the NN training, has many variations (mainly based on the weights/bias). Gradient descent with momentum BP, conjugate gradient BP, quasi-Newton BP, and Levenberg-Marquardt BP were used in this respect. The learning process was initiated by randomly assigning weights/bias to the neurons. The adjustment of the weights occurred at the end of each cycle of information passage (epoch). These weight modifications continued till the network gained the ability to reach a single point in the weight space (without the oscillation usually seen in the online BP model), where the difference between the actual and the corresponding expected values of the output (error) reached the smallest value. Selecting the optimal number of the neurons in the hidden layer is, therefore, of great importance—this was conducted in the present study by the trial and error method by considering the presence of nine to 16 neurons in that layer. Table 1 shows adequacy in the selection of ten neurons, wherein the minimum error function in the minimal number of epochs was with a high rate of reduction of initial error during the training phase of the network. The intensity of the information discharge from the inputs to the output layer depends on the optimal number of the

Table 1. MSE*, R^{2*}, and iterations values in the topology optimization

Number of neurons	R^2	Best validation MSE at epoch	Epochs
9	0.924	18	24
10	0.992	74	80
11	0.963	17	23
12	0.969	7	13
13	0.957	5	11
14	0.986	70	76
15	0.987	79	85
16	0.987	38	44

*$\mathrm{MSE}=\frac{\Sigma(y-\hat{y})^2}{N-1}$ and $R^2=1-\frac{\Sigma(y-\hat{y})^2}{\Sigma(y-\bar{y})^2}$ y and $\hat{y}$ are the actual (or observed) and ANN-predicted values of the response variable respectively: $\bar{y}$ is the mean value of the response and "N−1" is the number of degrees of freedom

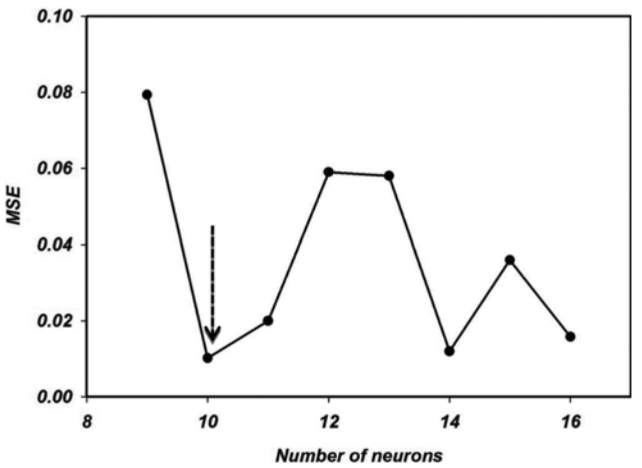


Fig. 2. Selection of number of neurons in the hidden layer for the determining shear rate-shear stress relationships of the O/W emulsions.

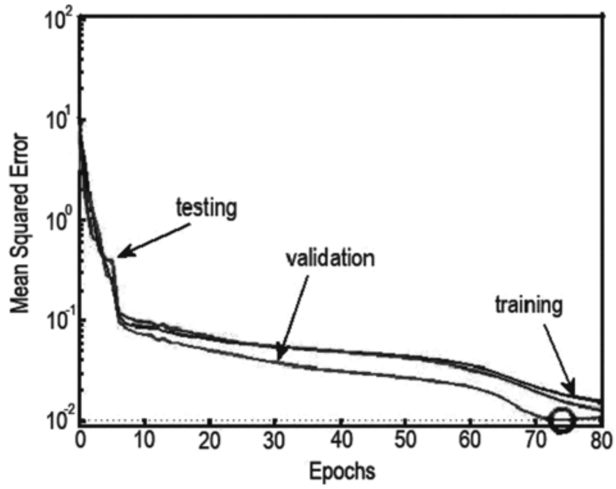


Fig. 3. Network performance during training.

neurons in the hidden layer. The results presented in Table 1 and Fig. 2 indicate that increasing the number of neurons beyond ten did not lead to a considerable improvement in terms of decreasing MSE and increasing R^2 values. Thus, topology 3,10,1, which showed the lowest MSE and the highest R^2 values with 74 iterations, was selected (Table 2). To validate the quality of the network generalization, 15% of the data was used and training continued till the MSE of this phase was reduced to the MSE level of the validation step. This indicates that the network could learn. After the network training and for comparing the actual values of the output with the values obtained through the neural network process, an adequate R^2 value for a linear regression fit showed the qualification of the trained network for recognizing the pattern between the inputs and output in this study (Figs. 3 and 4). Of further note were the different training functions used in the present study under the FFBP as the overall learning algorithm. The number of epochs for gradient descent (GD) (traingdm version) and conjugate gradient (CG) (traincgp version) compared to quasi Newton (QN) (trainbfg and trainlm versions) were lower. However, the results of QN methods in terms of R^2 values, which indicated the error between inputs and the output, were better (Table 2).

The trend of nonlinear relationships between inputs (O:W ratio and β-CD concentration) and shear stress of the O/W emulsion as the output is easy to follow by considering the three-dimensional response surface diagrams presented in Fig. 5. The convex and symmetric surfaces are indicative of the presence of optimum conditions. The plots in that figure are dome-shaped, showing a linear trend of change in the axis of β-CD concentration, while the

Table 2. Comparison of training functions used under the overall FFBP learning algorithm in the present study

Algorithm	Training function	Best validation MSE at epoch	MSE	Epochs	R^2 (training)	R^2 (validation)
GD	Traingd	1000	0.214	1000	0.885	0.868
	Traindgm	2	0.262	8	0.886	0.878
	Trainrp	150	0.108	156	0.936	0.952
CG	Trainscg	34	0.219	40	0.901	0.897
	Traincgp	20	0.228	26	0.872	0.889
	Traincgf	78	0.049	84	0.936	0.983
QN	Trainbfg	33	0.097	39	0.958	0.970
	Trainlm	38	0.006	44	0.994	0.994

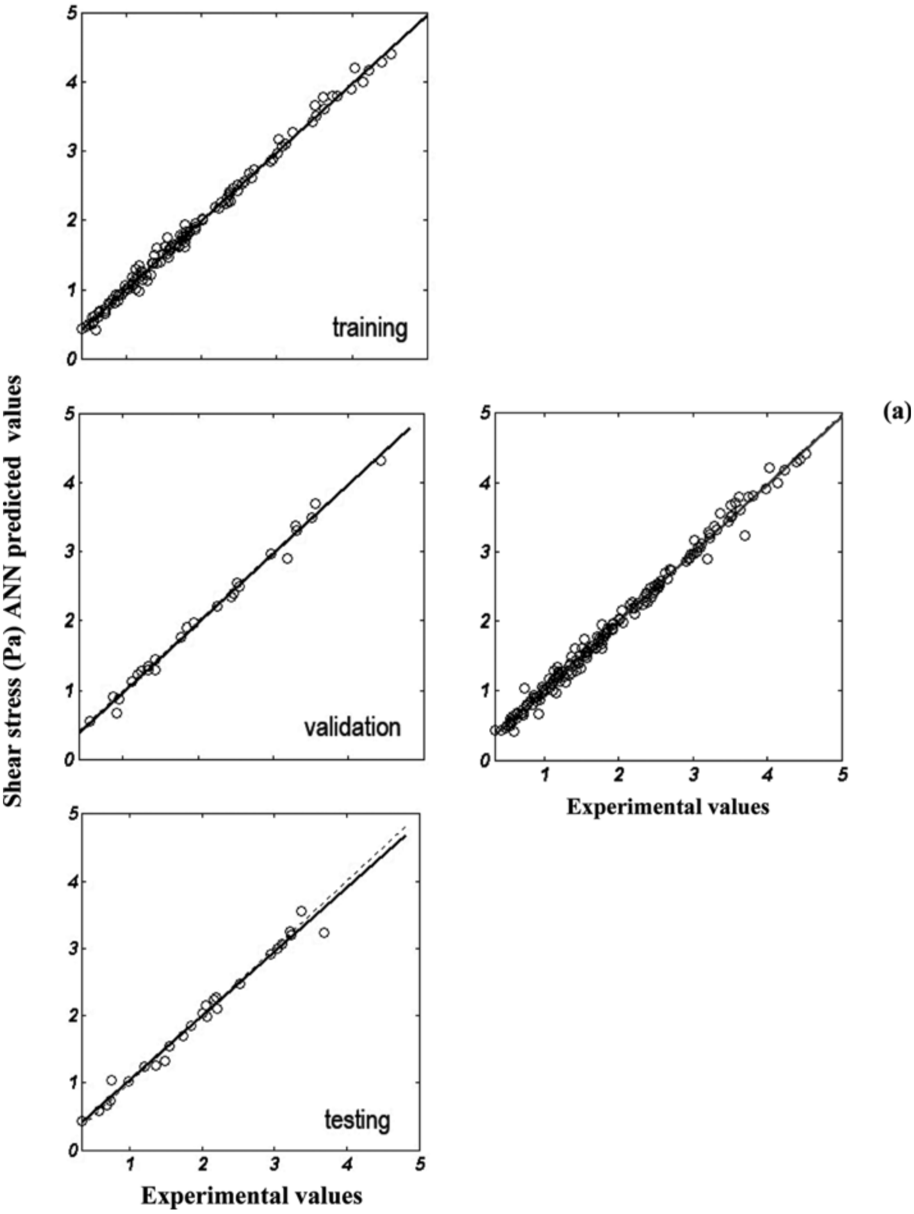


Fig. 4. Parity plots of shear stress of the prepared O/W emulsion, obtained from different stages of the ANN model of 3,10,1 configuration. The relevant plot for the NN prediction, considering all the three stages of the network learning is also shown (a).

trend in the axis of O:W ratio shows an increase in τ to some extent. Again, τ decreases after that as the diesel-to-water ratio increases beyond 0.4 level.

For characterizing the flow behavior of fluids and treating flow data obtainable over a range of shear rates, several flow equations have been reported in the literature. Based on our previous work and among six rheological models used in that emulsion study, two models were found to be satisfactorily able in describing the relationship between the shear stress-shear rate as the plots in Fig. 6 show the results [12]. According to the three-parameter Sisko (1958) equation, originally proposed for the determination of the viscosity of greases, two flow units (Newtonian and non-Newtonian) are involved in describing shear stress: $\tau=a\gamma+b\gamma^n$. In many other dispersal systems, the Sisko equation was also used to fit experimental flow data [14]. Note that the Casson equation is explained as $\tau^{1/2}=\tau_0^{1/2}+k\gamma^{1/2}$, where the flow curve as a straight line is obtainable by plotting the square root of shear stress against the square root of shear rate [15]. The goodness of the fit results obtained for the model-fitted data describing the shear stress-shear rate relationship for the O/W emulsions prepared in the ratio of 45 : 55 of diesel-to-water with the use of β-CD at 1.25 w/v% was highly satisfactory (Fig. 6).

CONCLUSIONS

* ANN was used to characterize the flow behavior of the prepared diesel-in-water emulsion where, with the use of β-CD as an emulsifier, a Pickering-type emulsion was considered.

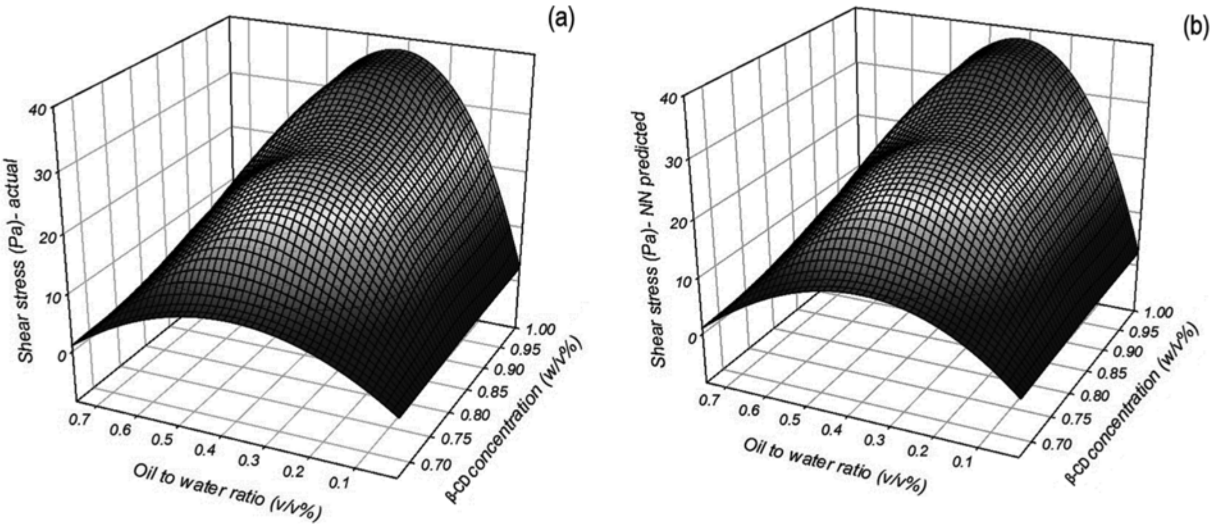
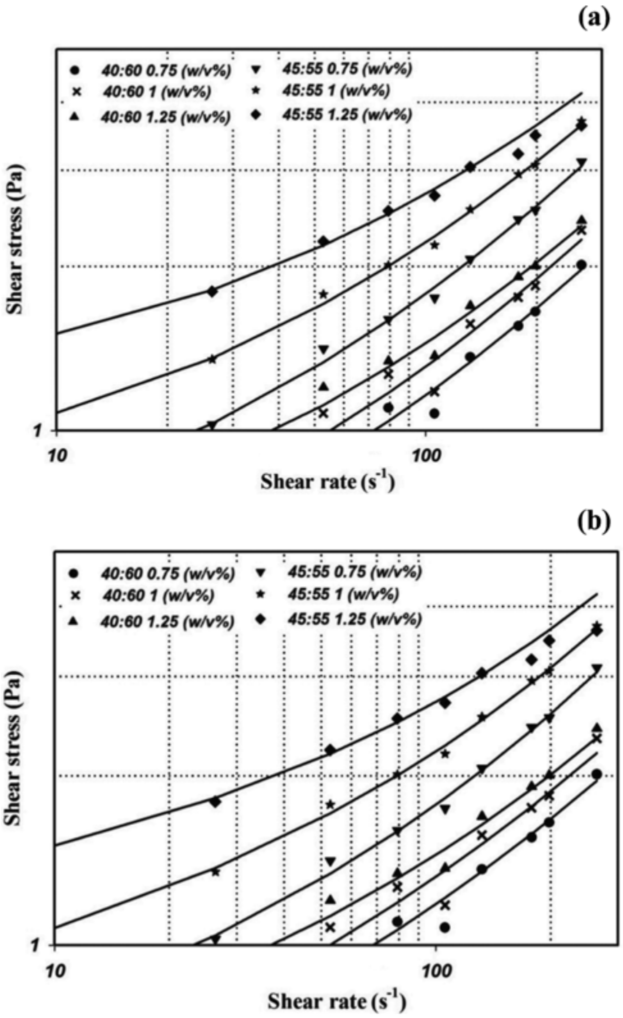


Fig. 5. Actual against ANN modeled surfaces for the shear stress of the O/W emulsion as function of oil-to-water ratio and β-CD concentration. (a) τ As the experimental values; (b) τ as the model-predicted values.



(a)

	R^2	RMSE
●	0.958	0.0973
×	0.971	0.0926
▲	0.987	0.0635
▼	0.993	0.0615
★	0.996	0.0544
◆	0.997	0.0459

(b)

	R^2	RMSE
●	0.985	0.0609
×	0.976	0.0896
▲	0.988	0.0614
▼	0.993	0.0614
★	0.996	0.0541
◆	0.996	0.0511

Fig. 6. Plots of shear stress as function of shear rate for the diesel-in-water emulsions prepared with the three ratios of diesel to water ratios and three levels of β-CD concentrations. The two rheological models used to fit the data: (a) Casson model, (b) Sisko model (see the text for details).

* The quantitative evaluation of the emulsion was in terms of the shear rate-shear stress relationship, and thus the three controllable factors in this study were the diesel-to-water ratio, the β-CD concentration, and the shear rate.

* MLFF with BP was the overall algorithm used for training the network with one hidden layer, optimized for its number of neurons, and the architecture finally was 3,10,1.

* By adjusting the connection weights, the network was trained by examining three different learning algorithms (GD, CG, QN).

* The transfer functions used to transform the information from inputs to the neurons in the hidden layer and from this layer to the output layer in this study were hyperbolic tangent sigmoid and pure linear respectively.

* Two statistical parameters (R^2, MSE) were used for evaluating the network performance based on the determination of error and the quality of the ANN prediction. The values indicated that the knowledge-distributing capacity of the network was satisfactory (R^2=0.994, MSE=0.006).

* Study on the shear stress-shear rate flow behavior of the O/W Pickering emulsion was based on using some selected models, and the fitting of the two models (Casson and Sisko equations) on the experimental data obtained through ANN was adequate.

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