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Prediction of Oil Sorption Capacity on Carbonized Mixtures of Shungite Using Artificial Neural Networks

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Abstract: Using the mixture of carbonized rice husk and shungite from the Kazakhstan Koksu deposit and the experimentally determined oil sorption capacity from contaminated soil with oil originating in the Karazhanbas oil field, a set of Artificial Neural Network (ANN) models were built for sorption predictions. The ANN architecture design, training, validation and testing methodology were performed, and the sorption capacity prediction was evaluated. The ANN models were successfully trained for capturing the sorption capacity dependence on time and on a carbonized rice husk and shungite mixture ratio for the 10% and 15% oil-contaminated soil. The best trained ANNs revealed a very good prediction capability for the testing data subset, demonstrated by the high coefficient of the determination values of R^2 = 0.998 and R^2 = 0.981 and the mean absolute percentage errors ranging from 1.60% to 3.16%. Furthermore, the ANN sorption models proved their interpolation ability and utility for predicting the sorption capacity for any time moments in the investigated time interval of 60 days and for new values of the shungite and rice husk mixture ratios. The ANN developed models open opportunities for planning new experiments, maximizing the sorption performance and for the design of dedicated equipment.

Keywords: modeling; artificial neural networks; sorption; crude oil; shungite; rice husk; carbonization

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1. Introduction

During the exploration, production and transportation of oil, environmental pollution occurs to varying degrees. Soil pollution with oil and oil products affects not only human health, but also the growth of vegetation and the biological environment.

Many soil remediation methods have been developed, but a fast, environmentally friendly and economical method is required to eliminate and minimize the hazardous effects of crude oil. One review [1] discusses various methods of soil remediation to remove crude oil. The effectiveness of these methods depends on a number of factors, such as the amount of oil spilled, the depth of the oil penetration into the soil, the type of oil and contaminated soil, the age of the soil and the degree of contamination [2]. Bioremediation technology is considered efficient, inexpensive, does not require any technical skills to operate and, in most cases, does not have a negative impact on the ecosystem.

Despite the obvious advantage of bioremediation for oil-contaminated soils, its application is limited due to the poor adaptation of native or inoculated microorganisms and plants in heavily contaminated soils. Additional acceleration of bioremediation can be created by introducing natural adsorbents into the soil [3]. The positive effect of the adsorbents is explained by a decrease in the soil toxicity for microorganisms and plants due to the predominantly reversible adsorption of toxic oil components and especially their oxidation products, a decrease in the soil hydrophobicity with a subsequent increase in their water-holding capacity, localization of water-soluble components in the treated soil layer and the presence of some adsorbents.

In the articles [4,5], bioremediation is considered together with the processes of adsorption and photocatalysis to reduce the level of pollutants. The soils treated with sorbents maintained a neutral pH, increased moisture and reduced soil phytotoxicity. The carbon-based sorbent showed the maximum efficiency.

One of the main technologies with the advantages of ease of operation and relatively low cost for the decontamination of the ecosystem is the adsorption process. Adsorption is a surface phenomenon and is widely used in the treatment of water, soil and air emissions [6]. The main adsorbents include activated carbon, metal oxides, carbon nanotubes, zeolite, clay, mesoporous silica, polymer resin, organometallic frameworks and some agricultural wastes [7].

The adsorption properties of activated carbon are due to a large surface area, microporous structure and a high degree of surface reactivity [8]. The mechanism of adsorption by the activated carbon is usually due to its micropores present in carbon, or weak van der Waals forces, which can attract impurities [9].

In the study [10], coal was proposed as an adsorbent for the removal of mineral oil from wastewater. The mineral oil adsorption increased as the pH values deviated from seven and equilibrium was reached after 10 h under static conditions, removing more than 99% of the mineral oil.

Article [11] considers the synthesis and adsorbing properties of natural sorbents for oil spill response. Non-biodegradability is the main disadvantage of these materials since landfilling is not desirable from an environmental point of view and incineration is very expensive.

Rice husks and other biodegradable plant products are economical, technically feasible and environmentally acceptable for use in oil spill cleanup technology. Rice husk is a by-product of rice production and one of the main adsorbents for removing contaminants. Agricultural wastes play a large role as an alternative material for obtaining valuable carbon materials due to their low cost and abundance compared to conventional sources of carbon materials.

In the article [12], the addition of the carbonized rice husk improved several soil properties, mainly related to the pH and cation exchange capacity.

The thermal and chemical modification of rice husks [13] led to the efficiency of phenol removal from aqueous solutions at the level of 36–64% and 28%, respectively. The thermally treated adsorbents had a larger surface area (24–201 m^2/g) than chemically treated ones (3.2 m^2/g).

In [14], the highest gasoline adsorption capacity was shown by the activated carbon from the rice husk activated with H_3PO_4 at 450 °C for 2 h, which had a Brunauer–Emmett–Teller (BET) surface area of 336.35 m^2/g.

The rice husks were converted into carbon materials by heat treatment in the presence of an inert gas at 500 °C and 800 °C for 2 h [15]. The materials showed a porous structure and a significantly high content of the carbon element.

For the adsorption of toluene from water, biochar was proposed, which was obtained by the gasification of pine wood [16]. In [17], coffee shells were chosen as a raw material for the production of activated carbon by the chemical activation of KOH. The optimum carbonization temperature for coffee shells is 923 K.

To obtain a microporous carbon material that effectively adsorbs iodine and organic compounds, peat carbonization under the action of microwave radiation was used [18]. It was shown that, as a result of carbonization, the content of the charged surface areas decreased due to the destruction of the functional organic compounds, porosity appeared and the adsorption properties of the carbon material improved.

Recently, it has also become relevant to solve the problems of environmental pollution with the help of environmentally friendly processes based on natural mineral and biological components. In [19], it was shown that shungite rocks are characterized by sorption activity for cationic and anionic complexes and are differently able to sorb pollutant components, including heavy metals, from water.

The adsorption capacity of bentonite clay and shungite of the Koksu deposit for the purification of mine wastewater from heavy metal ions was studied [20]. It was established that the most effective method for modifying sorbents is mechanical activation.

The use of activated shungite steam treated and modified with nanosilver provided an increase in the efficiency of cleaning from harmful impurities [21].

A new catalytic adsorption material based on shungite was developed for the restoration of soils contaminated with toxic components of rocket fuel [22]. The index of soil detoxification at the concentration of the analyzed decomposition products from 0.1 mg/kg to 3.21 mg/kg was from 81.1 to 98.8%.

The spectrum of the new modeling approaches, using group methods of data handling [23] and building data-driven models—such as evolutionary polynomial regression, M5 model tree, gene-expression programming and multivariate adaptive regression spline [24]—have shown good potential and they complement the mature neural networks-based modeling methodology.

The use of Artificial Neural Networks (ANNs) to model the adsorption process has expanded significantly over the past decades. These ANNs models are used to correlate and predict the adsorption kinetics of a wide range of adsorbents and adsorbates. ANNs overcome some of the shortcomings of traditional adsorption models, especially in terms of providing better predictions under different operating conditions. Many models are mainly applied to adsorption systems with only one contaminant, which indicates the importance of extending their application to predict and model the adsorption systems with multiple adsorbates.

The review [25] analyzes and describes the data of modeling the adsorption of organic and inorganic water pollutants using ANNs. The results showed that this ANN tool has significant potential for developing robust models of multicomponent adsorption systems that can exhibit antagonistic, synergistic and non-interacting adsorption behaviors simultaneously.

The modeling of the multisystem dynamic adsorption of organic pollutants on activated carbon was carried out using the ANN method [26]. The results showed that the optimized ANN was obtained with a high correlation coefficient, R = 0.997, standard error RMSE = 0.029 and mean absolute deviation MAD (%) = 1.810 at the generalization step.

The study [27] developed multilayer ANN models to predict the total yield and surface area of the activated carbon produced from various biomass feedstocks using pyrolysis and steam activation. The trained ANN models showed high accuracy ($R^2 > 0.9$) and good agreement with the independent experimental data.

Multilayer perceptron artificial neural networks (MLP-ANN) and multiple linear regression (MLR) models have been applied to predict the dynamic adsorption of a complex adsorbent–adsorbate system in the solid–liquid phase [28]. The statistical results showed a correlation coefficient of R = 0.991 with a mean square error of RMSE = 0.0521 for the MLP-ANN model and R = 0.80 with RMSE = 0.237 for the MLR model.

Paper [29] presents a numerical study regarding mass prediction using a long short-term memory (LSTM) algorithm with two hidden layers for three sorbents in fixed fluidized beds. The results obtained by the developed LSTM network algorithm and experimental tests were in good agreement with the results above R = 0.95.

An ANN and least squares support vector machine (LS-SVM) were used to model the adsorption of methylene blue by a composite of zinc sulfide nanoparticles with activated carbon [30]. The mean square error (RMSE) values corresponding to the methylene blue test set were 0.00013 and 0.00071, while the corresponding coefficient of the determination (R^2) values were 0.9996 and 0.9983 for the LS-SVM and ANN models, respectively.

The neural model has shown excellent predictive ability when modeling the data obtained for the removal of Pb(II) and Cd(II) from the aqueous solution [31]. The modeling of the trained ANN showed that an increase in the initial content of Pb(II) and Cd(II) ions led to a significant increase in the adsorption capacity, and Cd(II) had a higher adsorption due to a strong interaction with the adsorbent surface.

The prediction of the process of adsorption of alkyl polyglucoside (APG) and alkyl ether carboxylate (AEC) was studied using a modified extended Langmuir model (MEL) and an ANN [32]. It was shown that in a heterogeneous adsorption system with an uneven distribution of surfactant molecules, both monolayer and multilayer adsorption takes place, which was in good agreement with the simulation results.

The aim of the present work was to build artificial neural network models and test their aptitude to predict the oil sorption capacity of the mixture consisting of carbonized rice husk and shungite from the Koksu deposit of the Republic of Kazakhstan, targeting the cleaning of oil-contaminated soils from the Karazhanbas oil field. This work is original by proposing an efficient methodology for the ANN model design, training and evaluation of the sorption capacity prediction performance and for building dedicated ANN models able to describe the complex oil sorption phenomena using the carbonized rice husk and the Koksu shungite mixture.

2. Materials and Methods

Valorizing the high potential of the mixture consisting of the carbonized rice husk and shungite from the Kazakhstan Koksu deposit to perform the oil decontamination of the polluted soil was the primary motivation of the present research. As a result, the first step of the research was to prepare and characterize both the sorbent mixture and the oil-contaminated samples, find the appropriate sorption conditions and then determine the sorption capacity of the different sorbent mixtures of the oil-contaminated samples. As this high sorption capability was clearly proven and the data base of experiments was created during the first research step, the second step of the research was aimed at building ANN based models for describing the complex sorption process.

The fundamental approach of modeling the sorption capability of this novel mixture was to consider the most important factors that influence the sorption capacity, as they are also revealed in the literature [33]. The ratio of shungite to the rice husk and sorption time factors proved to be the first two ranked candidates. They were further considered in the study.

The design and training the ANN model were conducted in successive steps, iterated for randomly chosen ANN parameters. These parameters were the number of hidden layers, the neurons in the hidden layers, the transfer function for the neurons in the hidden layers and the training algorithms. The best trained ANNs were subsequently used for testing the sorption capacity prediction.

2.1. Preparation of Oil-Contaminated Soil Samples

The objects of the study were the shungite samples from the Koksu deposit with a dispersion of 1 mm. The samples of shungite mixed with the rice husk were subjected to a carbonization process. The ratio of shungite (Sh) to rice husk (RH) was 1:1.7; 1:4; 6:1. The carbonization process was carried out at a temperature of 600 °C in an inert argon atmosphere for 1 h [34].

For the preparation of the samples of the oil-contaminated soils, the crude oil from the Karazhanbas field was selected. The oil was characterized by high density (931.6 kg/m^3 at 20 °C), viscosity (7.5 mm^2/s at 50 °C) and coking (7.0%) properties. The high values of the viscosity-density indicators were predetermined by the high resin content (24.5%) of the oil and the low content of the light hydrocarbons (3.8%). A distinctive feature of the oil was a high content of sulfur compounds (2.1%) and the content of asphaltenes was 5.7%.

To test the developed sorbents, the samples of the oil-contaminated soils were prepared. For the preparation of the 10% oil-contaminated soil, 5.0 g of oil was added to 50.0 g of soil. Then, 2.0 g of the sorbent samples was introduced into the soil samples. At different time intervals (from 5 to 60 days), the sorption capacities of the sorbents were determined. For the preparation of the 15% oil-contaminated soil, 7.5 g of oil was added to 50.0 g of soil. Then 5.0 g of the sorbent sample was introduced into the prepared soil samples.

The sorption capacity of the sorbents was calculated by the ratio of the mass of oil absorbed by the sorbent to the mass of the initial sorbent, according to the Equation (1) [35]:

$$A = \frac{m_{oil}}{m_{sorbent}}, \tag{1}$$

where A—the sorption capacity (g/g), m_{oil}—the mass of the absorbed oil by the sorbent (g) and $m_{sorbent}$—the mass of the initial sorbent (g).

The masses of the samples were determined using a laboratory electronic balance VIBRA AJH-620 CE (Shinko Denshi Co., Ltd, Tokyo, Japan). The mass of the initial sorbent was the mass of the initial shungite, the mass of the carbonized mixture of shungite and rice husks at various ratios and the mass of the carbonized rice husks without the addition of shungite. The mass of these sorbents after the sorption of oil after a certain period of time provided the mass of the sorbent with the absorbed oil.

2.2. Modeling Using Artificial Neural Networks

Implemented on computer systems, Artificial Neural Network models are built using sets of measured data. The ANN is based on the simplified representation of the natural neural cell and comprises an ensemble of simple computing entities, called artificial neurons. The artificial neuron receives the input signals and processes them by computing the output signal in a similar way its natural twin does. However, the computation is typically based on simple algebraic mathematical relationships and functions. The weights, the bias signal and the computing function (also called the activation or transfer function), are the main elements of the artificial neuron that makes it versatile in reproducing any relationship between its inputs and outputs. The simplified representation of the artificial neuron and its computing methodology is presented in Figure 1.

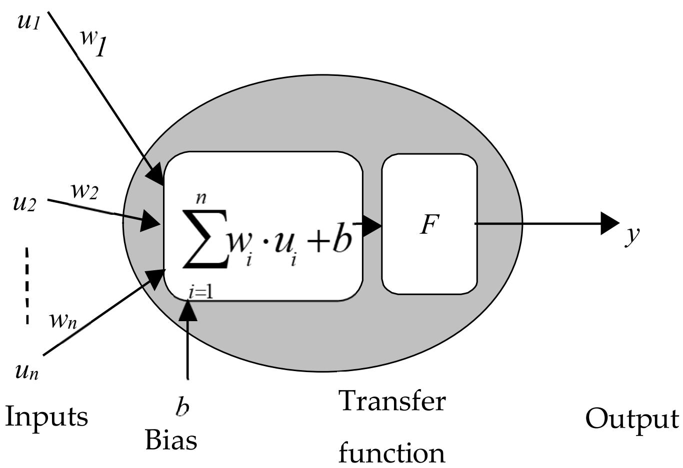


Figure 1. Typical structure of the artificial neuron.

The neurons of the ANN are organized in layers, arranged in a successive order for processing data that starts from the input layer and ends with the output layer. The intermediate layers are called hidden layers. The typical topology of a multilayer ANN is presented in Figure 2.

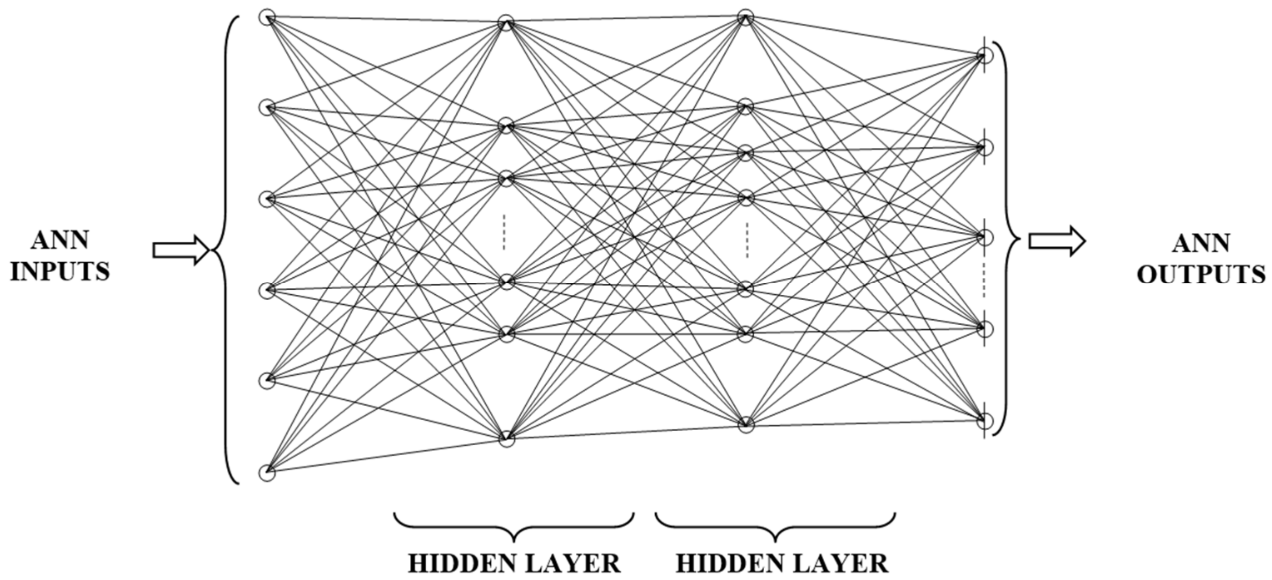


Figure 2. Typical structure of a multilayer ANN.

The process of finding the appropriate values for the weights, bias and form of the transfer function, in order to obtain the desired output values for the given input values, is called training. The ANN training is usually an iterative process, performed until the ANN computed outputs for the given inputs are sufficiently close to the desired output values. The total set of input-desired output pairs of data is commonly split in three parts. One is used for the actual training, one for the testing and one for preventing the ANN to become overtrained and be susceptible to losing its generalization capability. This latter step is frequently called the validation set and is used during the training step to avoid overtraining by stopping the training process early when overfitting appears.

The development of ANN black box models is highly appreciated in applications where the detailed controlling rules of the involved phenomena are not known [36] and the first principle modeling is not possible due to the inherent complexity of the system [37]. Additionally, the ANN trained models require reduced computational resources, such as computing time and hardware capacity, making them appropriate for online optimization and advanced model-based control [38].

2.3. Sorption Modeling with ANNs

As the sorption of oil using a carbonized mixture of shungite with rice husk as a sorbent is a very complex process. The first principle modeling of sorption is very difficult, but the modeling based on ANNs becomes a feasible modeling alternative.

The present study investigated this latter modeling approach and presents the methodology for building the ANN models and their prediction performance. The ANN models are aimed to describe the sorption of oil from the soil using the mixture of carbonized sorbents of shungite and rice husk. The ANN models are trained to make predictions on the sorption of oil at different time intervals and for different values of the shungite to rice husk ratio in the carbonized mixture.

The basic structure of the ANN models is presented in Figure 3.

Two ANN models were designed and trained to predict the sorption capacity on the carbonized shungite and rice husk sorbent mixture with different ratios, i.e., of the 10% and 15% oil-contaminated soil.

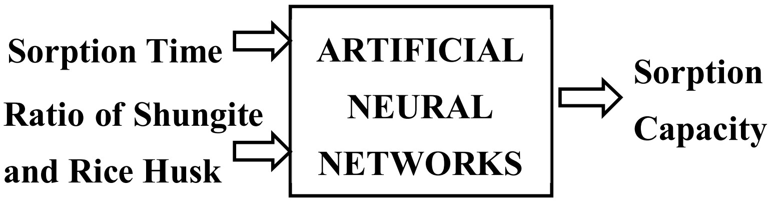


Figure 3. Structure of the ANN model for sorption capacity prediction.

Each of the two designed ANNs were trained with experimental measured data consisting of the values of the sorption capacity determined for 12 intervals of time (multiples of 5 days and ranging from Day 5 to Day 60) and for five mixture values (shungite, shungite and rice husk at ratio of 1:1.7, shungite and rice husk at ratio of 1:4, shungite and rice husk at ratio of 6:1 and the carbonized rice husk alone).

For each ANN model, the total set of the 60 pairs of available input-desired output data was split into the training, validation and testing data subsets, according to the proportions of 70% (42 data pairs), 15% (nine data pairs) and 15% (nine data pairs). The validation subset of the input-desired output data was used for preventing the ANNs to overfit, by stopping the training performed early on the training data subset. The testing subset of the data was used for assessing the capability of the trained ANN to make predictions for new inputs not yet seen at the previous training and validation steps.

The data used for the training, validation and testing were first scaled into the interval $[-1; 1]$ to provide the necessary computation accuracy. The data constituting the training, validation and testing data sets were randomly selected from the total data set, according to the previously mentioned proportions.

The type of the ANN used for the modeling was the feed-forward network with one hidden layer and backpropagation algorithm was utilized for the training. It was designed using a minimal ANN architecture, with a reduced number of hidden layers and complexity for the following reasons. First, the development of the reduced structure for the ANN topology was apriori targeted, considering that keeping the ANN model as simple as possible typically needed a simpler and more reliable training procedure. Second, the computation resources and running time needed for both the training and prediction steps were less demanding by the minimally structured ANN models when compared to more complex AI models, such as the support vector regression [39], evolutionary computing [40], machine learning [41] or neuro-fuzzy [42] approaches. Additionally, the latter reason was directly related to the significant increase in the computation time when the developed ANN models were to be used in the real time optimization and control tasks, such as the specific equipment design, online operation optimization or adaptive automatic control of the sorption process and plant. The software implementation was performed using the Deep Learning Toolbox of Matlab. Several training algorithms, transfer functions, number of layers and neurons in each layer were investigated for identifying the ANN with the best results. The correlation coefficient R (the linear regression between outputs and targets) and the weighted sum of the absolute values of the relative errors were used for assessing the ANN modeling performance during the training step.

3. Results and Discussion

3.1. Experimental Results

Table 1 shows the results of the sorption by the sorbents of oil from the samples of the oil-contaminated soils. The results of the oil sorption from the soils with 10% oil contamination were revealed to be superior when compared to the sorption of oil with 15% oil contamination. As expected, the sorbents with the maximum values of the sorption capacity were obtained after 60 days of investigation. In the case of using the shungite alone, the sorption capacity turned out to be low and amounted to only 0.25–0.38 g/g for the 10% oil contamination and to 0.13–0.67 g/g for the 15% oil contamination.

Table 1. Results of the sorption of oil from soil samples with oil contamination of 10% and 15% by sorbents based on shungite rocks.

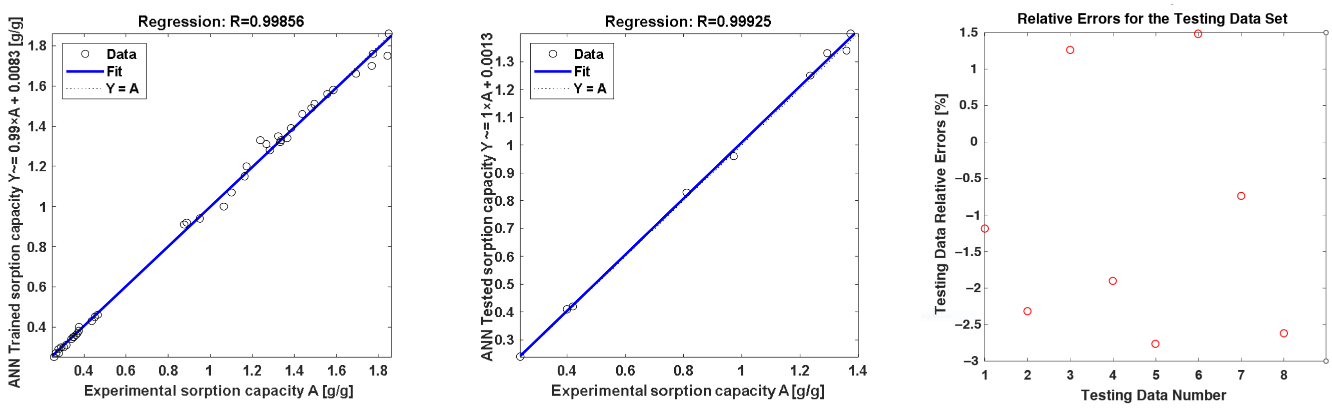
Time	Shungite		Sh:RH = 6:1		Sh:RH = 1:1.7		Sh:RH = 1:4		Rice Husk	
Days	10%	15%	10%	15%	10%	15%	10%	15%	10%	15%
	Sorption Capacity [g/g]									
5	0.25	0.13	0.48	0.40	0.83	0.36	0.91	0.31	0.12	0.13
10	0.27	0.42	1.25	0.41	0.92	0.40	0.94	0.42	0.24	0.15
15	0.29	0.55	1.28	0.45	0.96	0.40	1.00	0.50	0.27	0.19
20	0.30	0.63	1.32	0.47	1.00	0.41	1.07	0.62	0.31	0.23
25	0.30	0.63	1.39	0.52	1.15	0.43	1.20	0.62	0.35	0.25
30	0.31	0.64	1.46	0.57	1.31	0.44	1.33	0.62	0.40	0.26
35	0.32	0.64	1.51	0.60	1.40	0.5	1.33	0.64	0.41	0.27
40	0.34	0.65	1.56	0.63	1.49	0.55	1.33	0.66	0.42	0.28
45	0.35	0.65	1.61	0.66	1.58	0.61	1.34	0.68	0.43	0.29
50	0.36	0.66	1.66	0.68	1.67	0.65	1.34	0.70	0.45	0.30
55	0.37	0.66	1.70	0.71	1.76	0.69	1.34	0.71	0.46	0.31
60	0.38	0.67	1.75	0.73	1.86	0.74	1.35	0.73	0.47	0.33

The carbonization of shungite with the rice husk led to an improvement in the sorption capacity. The carbonization product of a mixture of shungite and rice husk in a ratio of 1:1.7 showed a maximum sorption capacity equal to 1.86 g/g for the 10% oil contamination and after 60 days. For comparison, the product of the rice husk carbonization was also tested but without the addition of shungite. Its sorption activity was lower than that of the carbonization products with the addition of shungite and the maximum sorption capacity was of 0.47 g/g after 60 days of testing with an oil contamination of 10%.

The sorption results presented in Table 1 demonstrate the superiority of the oil sorption capacity when the mixture of the carbonization of shungite with the rice husk is used. This improvement is observed irrespective of the 10% or 15% oil contamination, the origin of the oil source and whether the sorption mixture results are compared to the cases when the shungite or rice husk sorbents were used alone. It is also worthy to notice the existence of an optimal sorption capacity in the interval of the investigated values of the carbonization of the shungite and rice husk ratio.

3.2. ANN Training and Testing Results for Modeling Oil Sorption

The first ANN was trained to model the sorption capacity of the 10% contaminated soil (Table 1). The results presented in Figure 4a show the regression plots for the training data and Figure 4b shows the testing data subsets. The relative errors for the testing data subset are presented in Figure 4c.



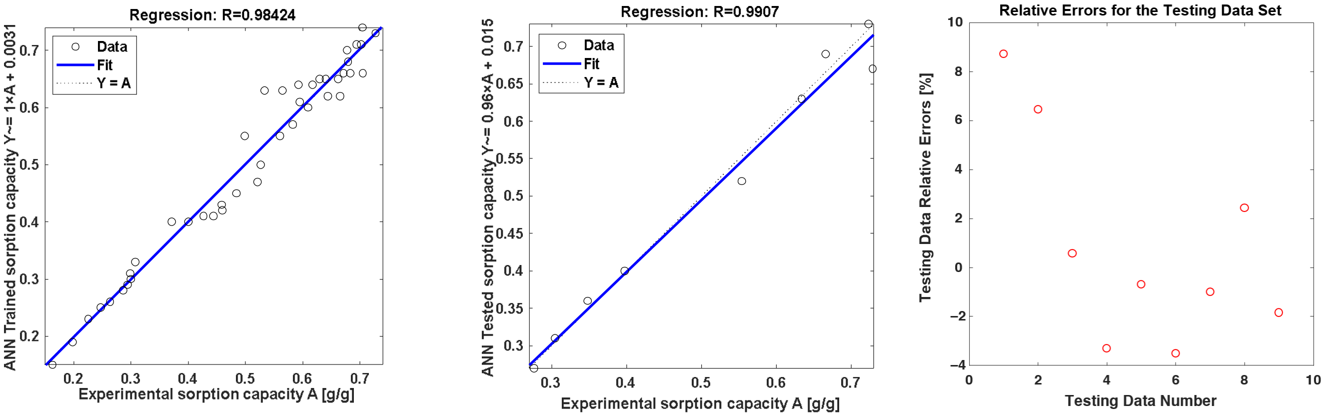
(a) (b) (c)

Figure 4. Regression (**a**,**b**) and relative errors (**c**) between ANN simulated data and target data for the training (**a**) and testing data (**b**) subsets, case of ANN sorption model for the 10% contaminated soil.

The trained ANN model has a good prediction aptitude, as it shows the relative errors less than 2.8% for the testing subset of the data and a mean absolute percentage error of 1.60%.

The second ANN model was trained to model the sorption capacity of the 15% contaminated soil.

The results presented in Figure 5a reveal the regression plots for the training data and Figure 5b shows the testing data subsets. The relative errors for the testing data subset are presented in Figure 5c.



(**a**) (**b**) (**c**)

Figure 5. Regression (**a**,**b**) and relative error (**c**) between ANN simulated data and target data for the training (**a**) and testing (**b**) subsets, case of ANN sorption model for the 15% contaminated soil.

The prediction results of the ANN model for the testing subset presented larger relative errors, but their mean absolute percentage error of 3.16% could be considered as very good.

The architecture of the feed-forward backpropagation ANN trained models consisted of a topology with one hidden layer with four neurons where either the log-sigmoid logsig or the hyperbolic tangent sigmoid tansig transfer function was used in the hidden layer and the purelin transfer function in the output layer. The Levenberg–Marquardt backpropagation training algorithm trainlm provided the best training results. The prevention of the ANN overfitting was achieved by the stopping the methodology that used a maximum number of six validation checks early before the training was stopped.

As the results show in Figures 4 and 5, the training of the ANN models was successful, and the simulation results of the trained ANN were also good when the trained ANN was used for predicting the sorption capacity with the new and previously unknown inputs of the testing data subset. The ANN good prediction performance was sustained by the high values of the correlation coefficient R and the reduced mean absolute percentage error. The latter ANN performance index quantifies, for the testing data subset, the relative errors between the ANN predicted values of the sorption capacity and the experimental measured ones. These very favorable values of the assessment indices for the ANN performance obtained during the testing were shown for a minimal ANN topology and for the appropriate selection of both the neural layers transfer functions and training algorithm. They were found as result of the systematic search intended to discover the ANN with the most promising prediction aptitude.

According to the best knowledge of the authors, there are no results reported in literature for the ANN modeling of the oil sorption capacity on the carbonized rice husk and shungite mixture. However, the performance of the two trained ANN models, evaluated by the coefficients of determination of R^2 = 0.998 and R^2 = 0.981, was compared to the ANN sorption modeling results recently reported in literature. The performance of ANN adsorption models was stated by the coefficients of determination of R^2 = 0.8 and R^2 = 0.944, for the oil on amphiphilic MoS_2/cellulose acetate sponge [43] and for benzene on soils [44]. Another rich set of results on ANN-based modeling adsorption from the aqueous phase of dyes, metals, organic compounds, nutrients, pharmaceuticals, drugs, pesticides or personal care products on different adsorbents—such as activated carbon, metal oxides, biomaterials, natural or synthetized materials and zeolites—were reported and they showed coefficients of determination that range from $R^2 = 0.902$ to $R^2 = 0.999$ [33]. These results demonstrate that the ANNs designed, trained and tested for modeling the oil sorption using the carbonized mixture of shungite have very good performance, as they are situated closely the upper limit of the literature reported assessments.

3.3. Results of ANN Sorption Prediction for Oil-Contaminated Soil

The good quality results obtained by the trained and tested ANNs for the sorption capacity computation proposed the ANN model for making new predictions. The potential of the trained ANNs to act as universal function approximators was valorized by using the network models to provide new information on the oil sorption mixture capacity at different time intervals and for different shungite and rice husk mixture ratios. Other ANN model predictions were made for new inputs that were not available from the experimental results. A set of these new sorption prediction results are presented in the following.

As first illustration of the prediction capability, the first designed and trained ANN was used to predict the sorption capacity at new time intervals for the 10% oil-contaminated soil and for a mixture of shungite and rice husk at a ratio of 1:1.7. The new time intervals were chosen at: 7.5 d, 12.5 d, 17.5 d, 22.5 d, 27.5 d, 32.5 d, 37.5 d, 42.5 d, 47.5 d, 52.5 d and 57.5 d, starting from the initiation of the sorption process. The results of the predictions are presented in Figure 6 where the experimentally measured values are shown with blue dots and the ANN predicted values with line-connected red dots.

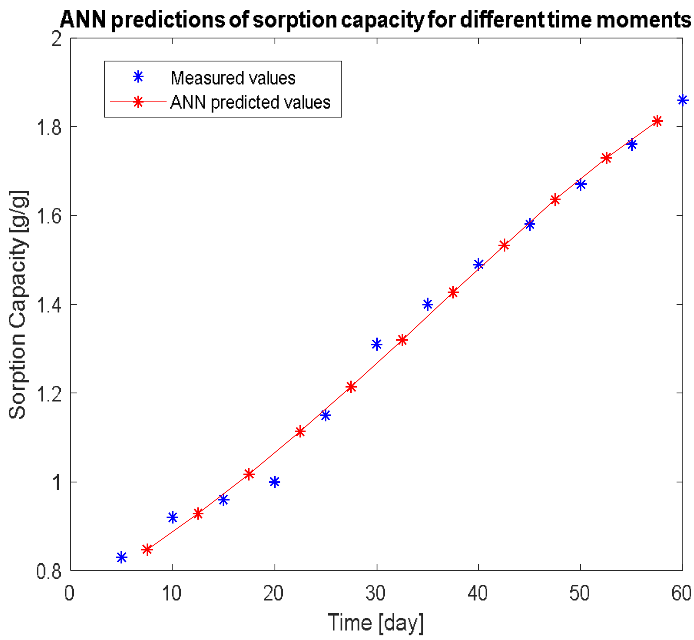


Figure 6. ANN predictions of the sorption capacity at different time intervals for shungite and rice husk at a ratio 1:1.7 and for the 10% oil-contaminated soil.

The predicted values demonstrate the interpolation power of the ANN trained model and its utility for computing the sorption capacity for any time intervals between 0 d and 60 d.

The same ANN was used to predict the sorption capacity of the 10% oil-contaminated soil, but for the mixture of shungite and rice husk new ratio value of 1:3. This shungite and rice husk ratio of 1:3 was situated between the 1:1.7 and 1:4 experimental ratios. For the latter values of the ratios, the sorption capacity was experimentally determined. The results of the predictions are presented in Figure 7 where the measured values are shown with blue dots for the ratio 1:1.7, with green dots for the ratio 1:4 and for the ANN predicted values with line-connected red dots.

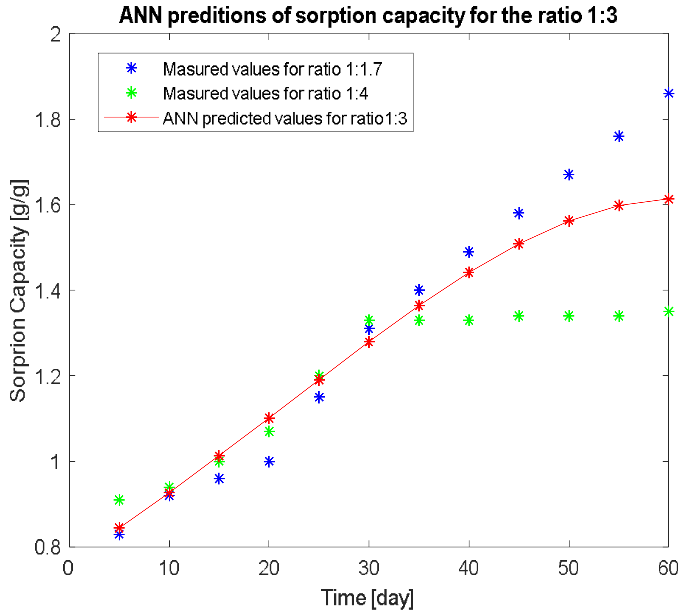


Figure 7. ANN predictions of the sorption capacity for the shungite and rice husk new ratio of 1:3, case of the 10% oil-contaminated soil.

Again, the ANN predicted values revealed realistic and valuable sorption capacity estimates that appropriately complied with the experimental measurements.

As a second evidence of the prediction capability, the secondly designed and trained ANN was used to predict the sorption capacity of the 15% oil-contaminated soil for a mixture of shungite and rice husk at a ratio of 6:1, but at different time instances. The new considered time intervals were: 7.5 d, 12.5 d, 17.5 d, 22.5 d, 27.5 d, 32.5 d, 37.5 d, 42.5 d, 47.5 d, 52.5 d and 57.5 d. The results of the predictions are presented in Figure 8 where the measured values are shown with blue dots and ANN predicted values with line-connected red dots.

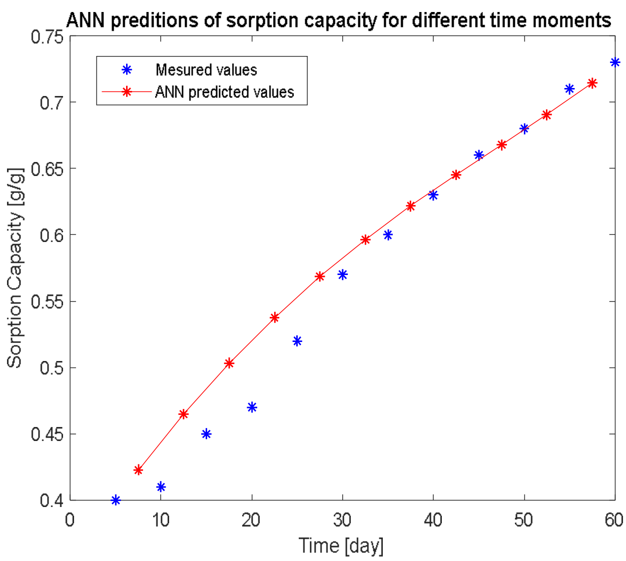


Figure 8. ANN predictions of the sorption capacity at different time intervals for shungite and rice husk at a ratio of 6:1 and for the 15% oil-contaminated soil.

It may be considered that the sorption predictions of the ANN generalize the measured values for performing reliable sorption evaluations. The differences from the first time period between the predictions and the experimental data of the 15% oil-contaminated soil are attributed to the more complex phenomenological oil adsorption mechanisms at a high oil content and the induced ANN training.

This second trained ANN was also used to predict the sorption capacity of the 15% oil-contaminated soil for the mixture of shungite and rice husk at a new ratio of 1:1. The shungite and rice husk new ratio of 1:1 was situated between the 6:1 and 1:1.7 ratios. For the latter values of the ratios, the sorption capacity was determined by the experiments. The results of the predictions are presented in Figure 9 where the measured values are shown with blue dots for the ratio 6:1, with green dots for the ratio 1:1.7 and for the ANN predicted values with line-connected red dots.

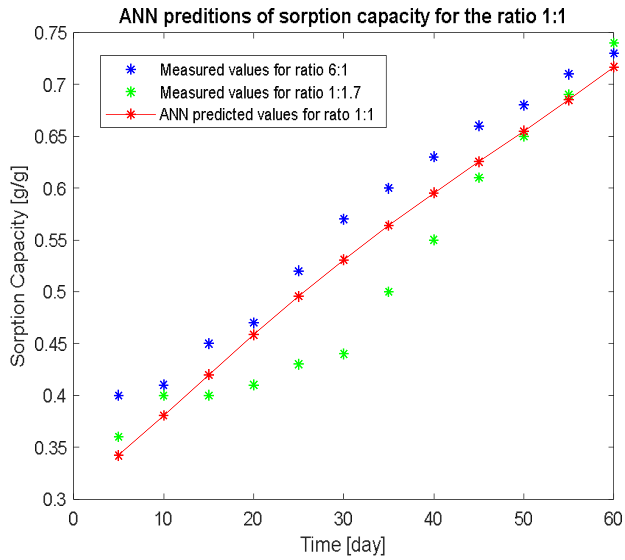


Figure 9. ANN predictions of the sorption capacity at a new shungite and rice husk ratio of 1:1 for the 15% oil-contaminated soil.

The prediction results again confirmed the aptitude of the trained ANN to make an appropriate interpolation between the measured values of the sorption capacity and to appropriately perform a filtering of the measurements due their intrinsic generalization power and valorize these abilities when the predicted values are computed.

4. Conclusions

Based on a set of experimentally determined data, aimed to investigate the oil sorption capacity of the contaminated soil by the mixture consisting of the carbonized rice husk and shungite from the Koksu deposit, the paper proposed, developed and assessed the performance of an ANN set of sorption models. Their goal was to describe the complex dependence of the sorption capacity on time and on a carbonized rice husk to shungite ratio, for the 10% and 15% oil-contaminated soil from the Karazhanbas source.

Subsequent to the data preprocessing procedure, the ANN architecture design, training, validation and testing methodology, followed by the prediction performance assessment, were carried out and the results of the best trained ANN models were revealed. The best trained model had a feed-forward backpropagation structure with a topology with one hidden layer. The log-sigmoid or the hyperbolic tangent sigmoid transfer function was used in the hidden layer and the linear transfer function in the output layer. The Levenberg–Marquardt backpropagation training algorithm provided the best training results. ANN overfitting was achieved by the early stopping methodology.

The prediction capability of the developed ANN models was very good, and it was evaluated in two steps. The first step assessed the sorption capacity for the testing set of data not previously seen during the training and validation steps. The prediction results demonstrated high correlation coefficient values and the mean absolute percentage error ranging from 1.60% to 3.16% when the predictions were compared to the experimentally determined values.

In the second evaluation step, the sorption capacity prediction potential of the ANN models was proven by making predictions on the sorption capacity at different time intervals and for different shungite and rice husk ratio values. They were compared with the neighboring values of the experimentally determined sorption capacities. The results of this second testing procedure demonstrated the interpolation power of the ANN trained models and their utility for computing the sorption capacity at any time during the investigated time interval and for new values of the shungite and rice husk mixture ratios.

The ANN developed model may be further used for planning new experiments, finding the most favorable conditions for obtaining the desired or maximized sorption capacity and for the design of dedicated laboratory, pilot or scale-up specific equipment.

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