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Application of Artificial Neural Networks in Adsorption Studies. A case study

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Abstract

The work focuses on the development of an artificial neural network (ANN) based model that can describe the adsorption of benzalkonium chloride from aqueous solutions onto commercially available kitchen paper. Various ANN architectures were tested in order to find the most suitable one in terms of overlapping between calculated and measured output data (coefficient of determination and mean absolute percentage error), as well as correctly interpolating outputs when using inputs form inside the experimental training range. The networks all had 4 inputs and 1 output, as well as a single hidden layer. Optimal ANN design was sought by varying both the number of neurons in the hidden layer and the type of transfer function towards it. The best find was employed in assessing the relative importance of input parameter values in the output, as well as the model's suitability for predictions outside the training range.

Keywords*: benzalkonium chloride, adsorption, modelling, artificial neural networks.*

1. Introduction

Due to the recent pandemic, attention has shifted to studying active ingredients in disinfectants. Due to antibacterial activity, hand sanitizers containing benzalkonium chloride (BAC) were recommended by the CDC and WHO, as an alternative to alcohol-based products [1–3].

The intensive use of BAC products is risky, for example its accumulation in different environments may cause environmental damage. High concentrations of BAC affect aquatic ecosystems due to endocrine disruption in fishes, while long-term consequences are still the subject of further research [4]. BAC also influences microorganism activity in soil, hence their nitrogen transformation capacity [5], while in plants it can induce nutrient deficiency [6]. Although levels of BAC concentrations are regulated, this chemical species still raises concerns due to the limited understanding of its long term effects [7].

Adsorption is commonly used for the removal of pollutants from aqueous solutions. Adsorbents such as natural clays [8, 9] and polyethylene microplastics [10] were reported. The current study employs household items (soft paper) as un-modified adsorbent material.

The complexity of the adsorption process and its dependence on several factors, such as: the type of adsorbent, temperature, mixing rate, mass ratio between adsorbed species and adsorbent, turns its modelling to a challenging task. An alternative to the traditional mathematical description of a process is the use of data-driven models, such as artificial neural networks (ANNs). Examples of their successful application in modelling adsorption have been reported for methylene blue [11], as well as sunset yellow [12]. In both cases ANN models gave accurate predictions in-between the experimental data points. Other studies used networks either for the design and optimization of a cyclic adsorption process [13], or for the determination of thermodynamic parameters in the adsorption of different ions [14].

The current study aims to model the adsorption of BAC on paper towels, thus removing it from aqueous solutions, by developing a suitable ANN. To the best of the authors' knowledge, this kind of modelling has not yet been applied either for

the BAC adsorption, or for the use of such a readily available adsorbent material. The benefits of such a network are: it could help the optimization of BAC removal by means of adsorption, be further used for forecasting, and lead to a better understanding of the underlying processes.

2. Materials and methods

2.1. Experimental database

Experimental data used to develop the ANN's were obtained during the laboratory scale adsorption of BAC on commercial paper towels. Absorbance of the aqueous BAC-paper mixtures were measured at 262 nm, resulting in values between 0.162 and 1.164. Experiments involved measurements at various temperatures (from 18 to 45 °C), initial BAC concentrations of the aqueous solution (from 0.25 to 1.00 g_{BAC}/L), and mass ratio values (from 25 to 100 $mg_{BAC}/g_{adsorbent}$).

2.2. Artificial neural networks

A feedforward artificial neural network architecture was taken into consideration for modelling this particular adsorption process. It is also known as multi-layer perceptron (MLP). Input data were provided by the experimental values of total liquid-solid contact time, temperature, initial BAC concentration and mass ratio, while the output of the model was set as the experimental absorbance value. In order to develop an accurate model, the optimal architecture for the MLP was sought by varying the number of neurons in the hidden layer, as well as the type of transfer function to the hidden layer. The first varied from 5 to 15. The latter was either a logarithmic sigmoid function (*logsig*), or a tangent sigmoid function (*tansig*). Transfer functions towards the output layer were always of linear (*purelin*) type.

The networks were trained using the Levenberg-Marquardt training algorithm. The database was divided as follows: 60% for the purpose of training, while 20% and 20% for validation and testing, respectively. All combinations of neuron numbers and transfer functions were developed, and the models were evaluated by two criteria: the value of the coefficient of determination (R^2) described by Eq. (1) and the value of the mean absolute percentage error (MAPE) shown in Eq. (2):

$$R^2 = 1 - \frac{\sum_{i=1}^{N}(y_i - x_i)^2}{\sum_{i=1}^{N}(y_i - \bar{y})^2} \quad (1)$$

$$MAPE = \frac{\sum_{i=1}^{N}\frac{|y_i - x_i|}{y_i}}{N} 100 \quad (2)$$

where N is the number of data points, y_i is the desired output at data point i, x_i is the ANN model output (prediction) at data point i, and $\bar{y}$ is the mean of the (y_i) values (y_i and x_i are non-scaled values).

Models exhibiting both R^2 close to 1 and MAPE less than 3 were considered accurate enough for further simulations and applications.

3. Results and discussion

3.1. ANN development

From the total of 297 data points 177 were utilized for training, 60 for validation, and 60 for testing. The training for each architecture was repeated 5 times in order to reduce the impact of random initialization of network weights. The values of the mentioned criteria on the testing dataset are presented in **Table 1** for the best network from the five repetitions and for each architecture, when using a logsig transfer function. **Table 2** contains the same information, but for networks employing a *tansig* transfer function.

Results considered best are highlighted in the tables. All models show good and somewhat comaparable R^2 values, while a logsig architecture (**Table 1**) with 9 neurons and a tansig one (**Table 2**) with 10 hidden neurons displayed the lowest MAPE values.

In order to decide on the best developed model which could be suitable for further simulations, their interpolation capability was tested. The model with a *logsig* transfer function is referred to as ANN 1, and the one with a *tansig* transfer function as ANN 2.

Table 1. *Evaluation criteria results for ANN models of logsig architectures*

Hidden neurons	*MAPE*	R^2
5	3.40	0.991
6	3.24	0.993
7	4.03	0.988
8	3.32	0.991
9	**2.82**	**0.994**
10	4.08	0.990
11	3.79	0.989
12	4.50	0.985
13	4.65	0.980
14	3.74	0.987
15	5.04	0.983

Table 2. *Evaluation criteria results for ANN models of tansig architectures*

Hidden neurons	*MAPE*	R^2
5	3.81	0.987
6	3.72	0.992
7	3.66	0.987
8	3.82	0.987
9	3.28	0.995
10	**3.00**	**0.990**
11	5.29	0.976
12	3.58	0.991
13	3.12	0.993
14	3.42	0.990
15	3.08	0.987

Figures 1a)–1c) illustrate the results of interpolation. The experimental data are represented as a scatter series, while the ANN-derived interpolated series are shown as scatter points connected by lines. The latter correspond to calculated output data obtained by averaging two experimental sets of input data. It is important to mention that only the parameters aimed for interpolation were varied.

It can be observed that ANN 2 shows better performance in case a), for temperature interpolation, as well as in case c), when both temperature and mass ratio interpolation was aimed for. In both cases ANN 1 underestimates the absorbance values, thus does not perform well. Hence, ANN 2 was chosen for further applications.

3.2. ANN model applications

A model corresponding to the arhitecture and interpolation capacity of ANN 2 was used to investigate the relative weight (importance) of input parameters in its output value, as well as for testing the forecasting ability of the model outside the range of training data.

3.2.1. Relative importance of input data

The relative importance (weight) of input variables was calculated by means of a method described by Gevrey et al [15]. This procedure uses the ANN model's connection weights for calculus. **Table 3.** contains the obtained results.

Results show that the total contact time between the liquid and the adsorbent is the most influential parameter for the investigated process, a finding that was expected. The second strongest

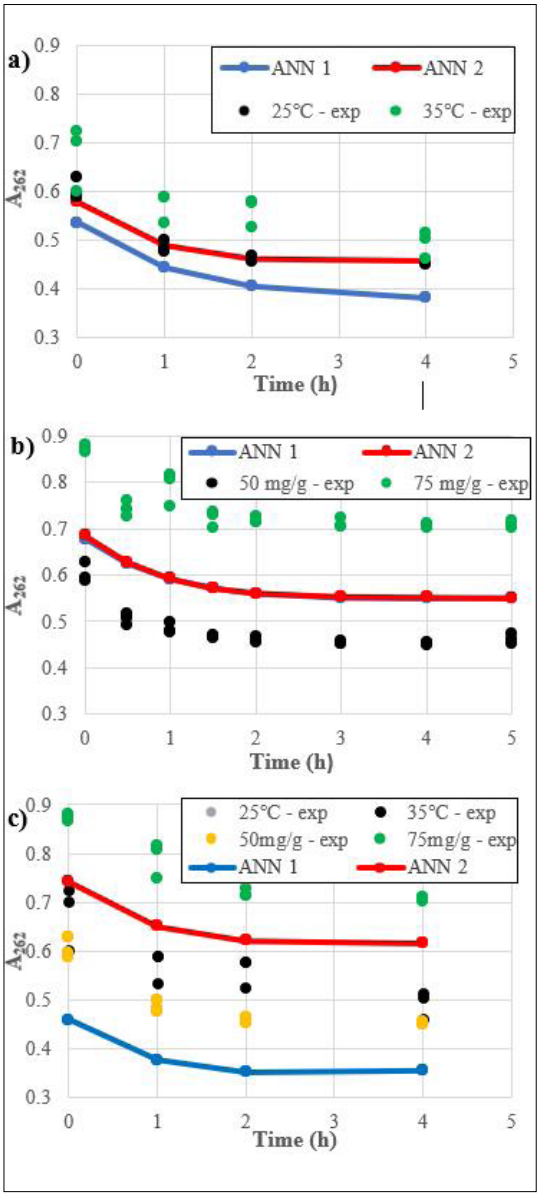

Figure 1. *Interpolation results of the two ANN models for: a) temperature interpolation; b) BAC/adsorbent mass ratio interpolation; c) both temperature and BAC/adsorbent mass ratio interpolation*

Table 3. *Relative importance of input parameters in the model's output value*

Model	Time (h)	Temperature (°C)	BAC initial concentration (g/L)	BAC/adsorbent mass ratio (mg/g)
ANN 2	34.0 %	15.7 %	22.9 %	27.4 %

variable influencing the output is the mass ratio of BAC and adsorbent. This leads to the understanding that changing the mass ratio is more influential on this adsorption process than changing the initial BAC concentration of the aqueous solution. Meanwhile, temperature proved to be the least influential.

3.2.2. Prediction capacity outside the range of training data

The ANN 2 model was used to predict output data when fed with inputs that exceeded the experimental range for one of the parameters (values are located outside the range of training data). The aim was to test whether the forecasting can be trusted, and the developed model is still suitable for a mass ratio of BAC and adsorbent reaching 120 $mg_{BAC}/g_{adsorbent}$. Simulated results were compared to experimental values for 100 $mg_{BAC}/g_{adsorbent}$ (see **Figure 2**). The results show good agreement with the experimental data in terms of the variation of the absorbance in time, however a new set of experiments would be needed to truly validate the simulated values. Since the simulated series is not above the experimental data, which is to be expected based on the trend also shown in **Figure 1b)** these kinds of forecasts ought to be handled with caution.

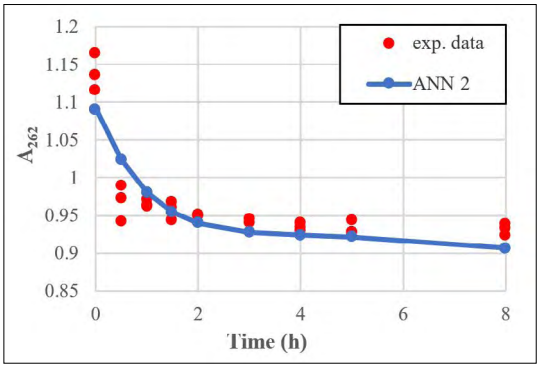

Figure 2. *Time series of predicted 120 $mg_{BAC}/g_{adsorbent}$ mass ratio (ANN 2) vs. experimental series (exp. data) for 100 $mg_{BAC}/g_{adsorbent}$ mass ratio*

4. Conclusions

Artificial neural network based models were developed to describe the adsorption of BAC on paper towels, resulting in accurate networks that exhibited MAPE values of 3 (or lower), together with R^2 values close to 1. The best architecture model was selected, not only based on the two performance criteria, but also taking into account the interpolation capability of it inside the range of training data. The selected model was further employed to determine the relative importance of input variables in the efficacy of an adsorption process. The latter is evaluated in agreement with the absorbance of the bulk phase absorbance of an aqueous BAC-paper mixture.

Other than time, the most important variable were found to be the mass ratio between BAC and the adsorbent, while temperature was the least influential parameter. Forecasting of absorbance using input data outside the training range was attempted for values exceeding just 20% of the upper limit, with fairly good overlap between the predicted and existing experimental outcomes.

Hence, the herby developed model seems to be suitable for further applications, such as: forecasting of unknown scenarios and/or optimization of the adsorption process in question, but only within the range of the training (experimental) data.

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