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Modelling the solid–liquid adsorption processes using artificial neural networks trained by pseudo second order kinetics

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ABSTRACT

A three-layer feed forward neural network was constructed and tested to analyze the second order kinetics of solid–liquid adsorption process. The pseudo second order kinetics of auramine O onto activated carbon was used to train the artificial neural network (ANN) to model the sorption system for various operating conditions. The operating variables studied are the contact time, initial dye concentration, agitation speed, temperature, initial solution pH and activated carbon mass. The studied operating variables were used as the input to the constructed neural network to predict the dye uptake by pseudo second order kinetics at any time as the output or the target. The dye uptake predicted by ANN trained by pseudo second order kinetics was found to be precise in representing the experimental kinetics of auramine O uptake by activated carbon. The constructed network was also found to be precise in predicting the sorption kinetics of auramine O by activated carbon for the new input data which are kept unaware of the trained neural network showing its applicability to determine the dye uptake rate for any operating conditions under interest. The ANN was also trained using pseudo second order kinetics of sorption of divalent metal ions onto peat particles and also using the second order kinetics of cadmium ions onto tree fern particles. The ANN and pseudo second order kinetics compliment each other to model the studied sorption systems for a wide range of operating conditions.

1. Introduction

Activated carbon adsorption processes are proved to be effective for the removal of various pollutants from aqueous solutions. Activated carbon prepared from various precursors has been reported as useful for the removal of various pollutants from the aqueous solutions [1,2]. Adsorption kinetics gives important information about the rapidity of the sorption process. Information of adsorption kinetics is required for selecting the optimum operating conditions for the full-scale batch process [3]. The kinetics of adsorption processes are usually modelled using the semi empirical expressions and mechanism based models [4–9]. Although these kinetic models have the advantage of representing the kinetics of the adsorption process, they have the usual limitation of their applicability for a particular experimental condition. Several empirical expressions have been reported for many solid–liquid sorption systems by correlating the determined kinetic constants and the operating variable of interest [10–12]. Although these kinetic models can be useful in simulating the adsorption kinetics, generation of any expression correlating the operating variables involved is not possible as the sorption process is highly influenced by operating parameters such as pH, initial dye concentration, adsorbent mass, agitation speed and temperature. It would be interesting and useful to utilize these theoretically sound models to simulate the kinetics of solid/liquid sorption systems to validate a wide range of operating conditions. However the attempt to make any theoretical kinetics valid for any operating conditions would be a complicated process as the theoretical models are sensitive to various operating variables such as initial dye concentration, adsorbent dosage, pH, agitation speed and solution temperature. In this research the aim was to make these theoretical kinetic models applicable to predict the sorption kinetics for all experimental conditions.

Currently artificial neural networks (ANN) are found to be excellent options for solving these types of complex issues. In chemical engineering, ANN was also found to be successfully applied to predict the adsorption equilibrium of solid–liquid systems [14], activity coefficients of aromatic organic compounds [13], kinetics of catalytic hydrogenation reaction [15] and solubility of proteins [16]. ANN was previously used to simulate the equilibrium and kinetics of the biosorption process [17]. In this research the aim was to train the ANN using theoretical sorption kinetics in order to simulate the experimental kinetics. The pseudo second order kinetics of

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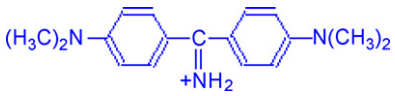

Fig. 1. Structure of auramine O.

auramine O sorption onto activated carbon under different experimental conditions was used to train the ANN. Pseudo second order kinetics was used as a model kinetic expression to train the ANN. Pseudo second order kinetic expression was found to be successful in representing the kinetics of several sorption systems. A review on the pseudo second order kinetics for different sorption systems was made recently by Ho [18]. In general the sorption system following a pseudo second order kinetics can be represented as [18]

$$\frac{dA_t}{dt} = k(A_0 - A_t)^2 \quad (1)$$

where A_0 and A_t represent the number of active sites occupied on the adsorbent at time, $t = 0$ and at any time t. If q and q_e represent the amount of solute adsorbed onto unit mass of adsorbent at any time and at equilibrium, the kinetic rate equation according to a pseudo second order kinetics can be given by

$$\frac{dq}{dt} = k(q_e - q)^2 \quad (2)$$

where k is the kinetic rate constant. With respect to the initial conditions, the boundary conditions for Eq. (2) are given by

$$q = 0;\ t = 0 \quad \text{and} \quad q = q;\ t = t \quad (3)$$

Integrating Eq. (2) with respect to the boundary conditions as in Eq. (2), the pseudo second order kinetic expression after linearization can be obtained

$$\frac{t}{q} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (4)$$

Eq. (4) can be used to determine the kinetic constant and the equilibrium uptake from the kinetics from the plot of t/q versus t.

In this study, the kinetic constants were obtained using Eq. (2) and were used to train and test the performance of ANN in predicting the experimental kinetics. The operating variables include the initial dye concentration, adsorbent dosage, initial solution pH, system temperature and contact time. The idea of using theoretical kinetics to train the ANN was extended to the literature data on the sorption of cadmium ions by tree fern [19] and on the sorption of divalent metal ions (Cu, Ni and Pb) by sphagnum moss peat [20].

2. Experimental

The dye auramine O, used in this study, was obtained from Central Drug House, Mumbai. Synthetic stock dye solutions were prepared by dissolving 1 g of dye powder in 1 L of distilled water. All working solutions of desired initial concentration were prepared from the stock solution by subsequent dilution. The structure of the dye auramine O is shown in Fig. 1. The powdered activated carbon used in this study was obtained from E-Merck Limited, Mumbai, India. The laboratory grade activated carbon obtained was directly used as adsorbent without any pretreatment.

Sorption kinetics experiments were carried out using mechanically agitated overhead laboratory stirrers at different initial dye concentrations or different operating conditions. The effect of dye concentration on the adsorption rate was estimated by agitating 1.5 L of dye solution of known initial dye concentration with 0.3 g of activated carbon in 2 L beakers at room temperature (32 °C) at desired solution pH. Unless specified all the experiments were carried out at a solution pH of 8 and at a constant agitation speed of 800 rpm. 2.5 mL of samples were pipetted out using 10 mL syringe filter at different time intervals. The collected samples were then centrifuged and the concentration in the supernatant solution was analyzed for the solute concentration. The concentration of auramine O was measured using UV spectrophotometer (Deep vision 301E) at a maximum absorption wavelength of 430 nm. Unless specified, all the kinetic experiments were carried out for a pre-designed fixed operating line of 1.5 L/0.3 g. The range of operating conditions studied in this study that are used to train and test the neural network are given in Table 1.

3. Characterization of adsorbent

Some of the specifications of the activated carbon used in this study as supplied by the manufacturer are given by: substances soluble in water ≤1%, substances soluble in HCl ≤3%, Cl ≤0.2% and SO_4^{2-} ≤0.2%; heavy metals as lead (Pb) ≤0.005% and iron (Fe) ≤0.1%; and incomplete carbonization: passes test, methylene blue adsorption ≤180 mg/g, loss on drying ≤10% and residue on ignition ≤5%. The surface morphology of the carbon particles was characterized by SEM analysis and is explained elsewhere [21]. The BET surface area for the commercial activated carbon used in this study was determined by nitrogen adsorption using t-method and was found to be 1000.1 m^2/g. The detailed physical characteristics including the pore size distribution of the commercial activated carbon used in this study are given elsewhere [21].

4. Construction of ANN

ANN consists of an input layer and an output layer connected by several nodes. In this study a feed forward or back propagation network with multiple layers was constructed. In this study a Levenberg–Marquardt's optimization was used to train the ANN. The feed forward ANN adjusts the transfer function that is associated with the inputs and outputs. Multiple layer networks can perform almost any linear or non-linear computation and can approximate any function reasonably well [22]. In this study, initially, a network with two hidden layers was constructed, trained and tested to represent the kinetics of activated carbon adsorption process.

The detailed structure of the network and the training strategy of the constructed neural network are shown in Figs. 2 and 3 respectively. Fig. 2 shows the feed forward network with one hidden layer. P_1 is the input vector to the hidden layer whereas W_1 and b_1 represents the weight and bias of the hidden layer. The information from the hidden layer is transferred to the output layer as shown in Fig. 3. The term P_2 represents the output vector and can be determined from the weight W_2 and bias b_2 of the output layer. A *tansig* function and a *purelin* function were used as the propagation functions in the hidden layer and in the output layers respectively. The training strategy of the network is shown in Fig. 3. The input vectors and the corresponding output vectors are used to train the network until it approximates the propagation function. The proposed network with a sigmoid hidden layer and a linear output layer was found

Table 1
Range of operating variables used to train the network

Operating variable	Range
Initial dye concentration (mg/L)	85, 100, 140, 170, 180, 200
Adsorbent mass (g/1.5 L)	0.3, 0.6, 1.2, 1.8
Initial solution pH	3, 4, 5, 6, 7, 8
Agitation speed (rpm)	800, 700, 600, 500, 400
Irradiation time (min)	0, 1, 2, 3, 4, 5, 10, 20, 25, 30, 45, 50, 60, 90, 120
Temperature (K)	305, 313, 323, 333

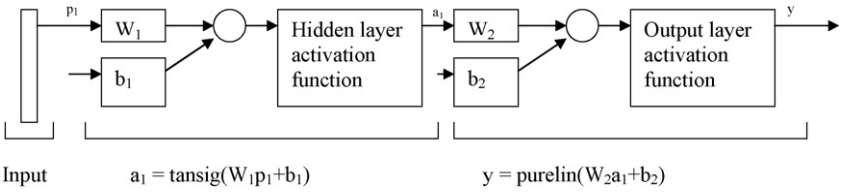

Fig. 2. Structure of the constructed two-layer network and the flow of information within the network.

to be capable of approximating the adsorption kinetics. The bias and the weights were obtained from the training process, which is based on the pseudo second order kinetics. The operating variables initial dye concentration, adsorbent dosage, initial solution pH, system temperature and contact time were used as input vectors whereas the dye uptake in mg/g was defined as the output vector.

5. Neural network modelling

The neural network toolbox Version 4 of MATLAB, Mathworks Inc. was used for simulation. The pseudo second order kinetics was used as a target and the experimental conditions were preprocessed so that the mean and standard deviation is 0 and 1. The experimental conditions and the corresponding pseudo second order kinetics were set as the input and the target vectors. The neural network was trained in a batch mode. Training the neural networks by Levenberg–Marquardt's algorithm is sensitive to the number of neurons in the hidden layer. The more the number of neurons, the better is the performance of the neural network in fitting the data. However too many neurons in the hidden layer may result in the over fitting. During the training process, several trials were made by increasing the number of neurons in the hidden layers gradually while optimising the transfer function for the given input and output conditions. In order to avoid the problems due to overfitting, a Bayesian regularization in combination with Levenberg–Marquardt's training method was used. The Bayesian regularization works best when the networks input and outputs are scaled within the range of −1 to +1. After many trials, the neural network with seven hidden layers was found to be excellent in representing the pseudo second order kinetics irrespective of the operating variables studied. The training is automatically stopped when the convergence is reached and the network is set ready for the prediction. The convergence is reached when the sum of the squared errors and the weights and biases reach some constant values. As the target and input vectors are normalized before training, the neural networks predict the output with mean and standard deviation of zero and one. Thus the predicted values were converted back to the original target values. The details of the completely trained neural network used to model the auramine O uptake by activated carbon is given in Table 2. Fig. 4 shows the plot of q predicted by ANN and the q predicted by pseudo second order kinetics during the training process. From Fig. 4, it can be observed that the newly constructed ANN was found to be successful in representing the pseudo second order kinetics for the range of operating variables used during the training process. Fig. 4 also shows the plot $q_{,\text{experimental}}$ versus $q_{,\text{pseudo second order kinetics}}$ for the range of operating conditions studied. Further from Fig. 4, it can be observed that the ANN predicted kinetics deviates from the experimental data for some conditions. This is due to the poor representation of the experimental data with the pseudo second order kinetics corresponding to these conditions. Fig. 5 shows the plot of error difference between the experimental data and the pseudo second order kinetics. Fig. 5 also shows the error difference between the experimental data and the ANN predicted kinetics and the error difference between the pseudo second order kinetics and ANN predicted kinetics. From Fig. 5, it can be observed that the deviation of ANN predicted kinetics and the kinetics by pseudo second order with the experimental kinetics was more or less the same. Thus the pseudo second order kinetics if representing the experimental data well, will compliment the ANN to represent the kinetics

Table 2
Details of the trained neural network used to predict the dye uptake kinetics of solid/liquid adsorption process

Type	Value/comment
Layer 1	6 neurons
Layer 2	7 neurons
Layer 3	1 neuron
Number of data used for training	272
Function in hidden layer	Tansigmoid
Function of output layer	Linear

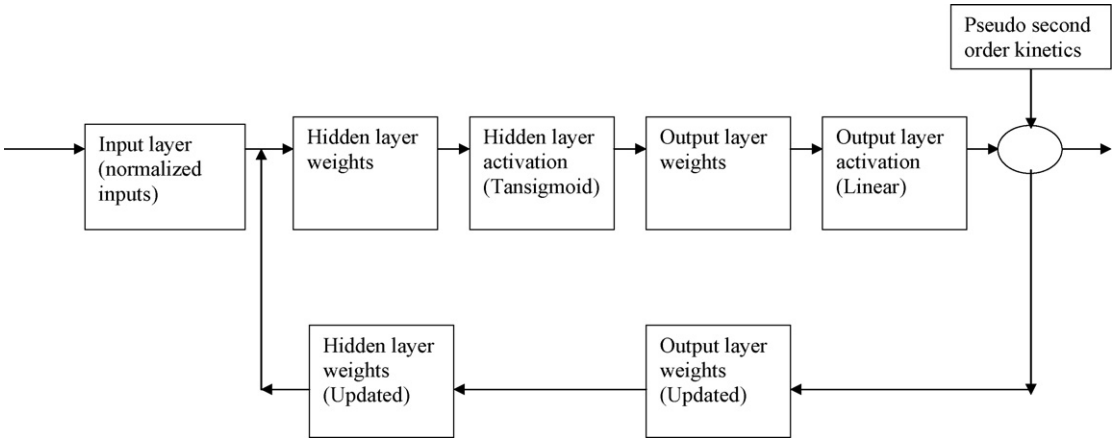

Fig. 3. Training strategy of the constructed feed forward artificial neural network.

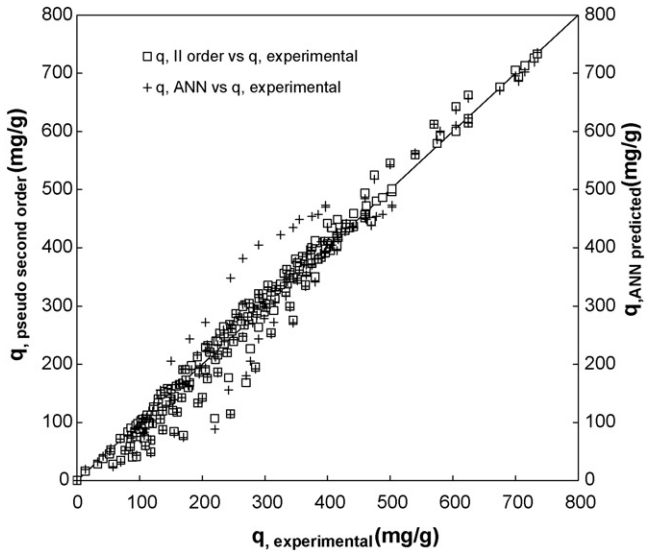

Fig. 4. Parity plot between pseudo second order kinetics and the amount of dye adsorbed, q, predicted by artificial neural networks during the training process.

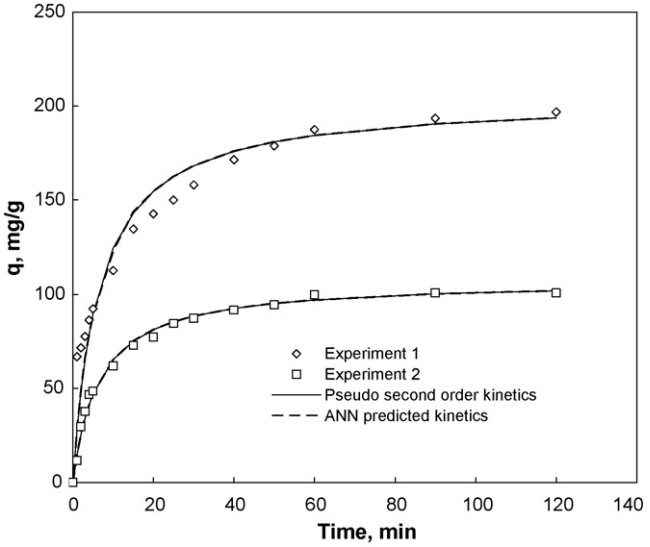

Fig. 6. Experimental data and predicted kinetics using ANN trained by pseudo second order kinetics during the testing process. (Experiment 1: C_0, 200 g/L; agitation speed, 800 rpm; activated carbon mass, 1 g; volume of solution, 1.5 L; initial pH, 8; temperature, 305 K. Experiment 2: C_0, 200 g/L; agitation speed, 800 rpm; activated carbon mass, 2 g; volume of solution, 1.5 L; initial pH, 8; temperature, 305 K.)

of adsorption system as the whole for the range of operating conditions studied. If the pseudo second order kinetics is accurate to represent the experimental kinetics, then ANN could be a very useful tool in modelling the adsorption systems for a range of operating conditions.

From design point of view it would be helpful to use ANN to predict the kinetics of adsorption process for any given new input conditions. Thus it is important to check how well the constructed network was helpful in determining the sorption kinetics of auramine O onto activated carbon using the ANN trained with pseudo second order kinetics for new inputs. To test the performance of the trained network, new inputs, which are not used while training, were fed to the neural network and the corresponding dye uptake rate was determined from the neural network. In addition the trained network was tested with new inputs which are out of the range of operating conditions used to train the ANN during the training process. Fig. 6 shows the experimental data of q versus time for different operating conditions. Fig. 6 also the kinetics predicted by ANN and pseudo second order expression for the sorption of auramine O onto activated carbon. From Fig. 6, it can be observed that the ANN trained by pseudo second order kinetics was found to be excellent in predicting the experimental kinetics of auramine O by activated carbon. From Fig. 6, it can be further observed that the successfulness of ANN in predicting the kinetics of auramine O onto activated carbon depends on the best fit of pseudo second order kinetics in the experimental data. From Fig. 6, it can be also observed that the newly constructed neural network was good in predicting the adsorption kinetics of auramine O by activated carbon even for new experimental conditions. The coefficient of determination between the experimental data and pseudo second order kinetics and the coefficient of determination and the mean square error difference between experimental data and ANN predicted kinetics for the range of new experimental conditions used to test the trained ANN was given in Table 3. From MSE and r^2 (Table 3) it can be observed that the ANN was good enough in predicting the experimental kinetics of auramine O by activated carbon and the error difference between experimental data with ANN predicted kinetics and pseudo second order kinetics was exactly the

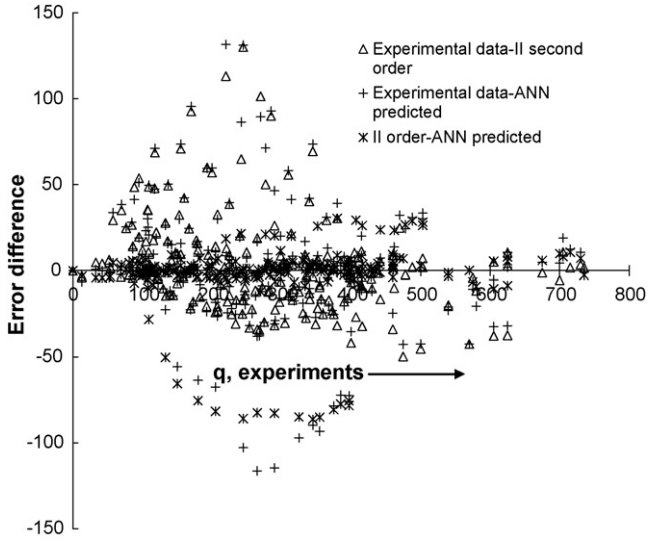

Fig. 5. Plot of error difference between experimental data with pseudo second order kinetics and ANN predicted kinetics.

Table 3
Coefficient of determination r^2 between experimental data and predicted kinetics using ANN and pseudo second order expression

Operating conditions	Coefficient of determination, r^2	
	$q_{experimental}$ vs $q_{second\ order\ kinetics}$	$q_{experimental}$ vs q_{ANN}
C_0: 200 mg/L Agitation speed: 800 rpm Activated carbon mass: 1 g Volume of solution: 1.5 L Initial pH: 8 Temperature: 305 K	0.99 (185.88[a])	0.99 (183.49[a])
C_0: 200 mg/L Agitation speed: 800 rpm Activated carbon mass: 2 g Volume of solution: 1.5 L Initial pH: 8 Temperature: 305 K	0.99 (7.329[a])	0.99 (7.233[a])

[a] Mean squared error (MSE).

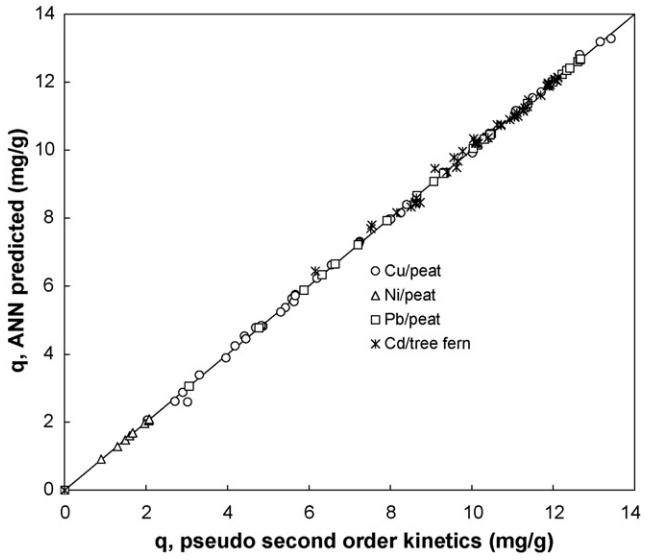

Fig. 7. Parity plot between pseudo second order kinetics and the q, predicted by artificial neural networks for the sorption of divalent metal ions, Cu, Ni and Pb, onto peat particles and cadmium ions onto tree fern particles.

same. Thus the pseudo second order kinetics will complement ANN very well if the experimental data follows a pseudo second order kinetics at all the operating conditions studied. The r^2 value of 0.99 between the ANN predicted kinetics and experimental data suggest that the newly constructed ANN, which is trained using pseudo second order kinetics, was precise in predicting the adsorption kinetics of auramine O by activated carbon for the new experimental conditions. Another advantage of the newly constructed neural network model is its accuracy to predict the adsorption kinetics rate for any initial concentration, temperature, agitation speed, pH and contact time within the ranges studied and also for the new experimental conditions outside the studied range.

The ANN was further used to model the pseudo second order kinetics of sorption of divalent metal ions onto peat particles and for the sorption of cadmium ions onto tree fern particles based on the information from the literature [19,20]. The ANN was trained using the pseudo second order kinetic constants reported in the literatures for the sorption of divalent metal ions, Cu, Ni and Pb, onto peat particles and for cadmium ions onto tree fern. The ANN with 5 neurons (contact time, initial dye concentration, adsorbent mass, agitation speed and particle diameter) in the input layer 3 neurons in the hidden layer was used to train the ANN to model the kinetics of uptake of cadmium ions by tree fern particles. The ANN was constructed with two input neurons representing the contact time and initial dye concentration to model the kinetic uptake of Cu, Ni and Pb onto peat particles. The ANN with five, six and ten neurons in the hidden layer was found to be successful in simulating the pseudo second order kinetics of Cu, Ni and Pb onto peat particles respectively.

Fig. 7 shows the plot of pseudo second order kinetics versus q, predicted by ANN for Cu, Ni and Pb onto peat particles and also the plot of pseudo second order kinetics versus q, predicted by ANN for Cd ions onto tree fern particles for the range of operating variables reported in the literature [19,20]. From Fig. 7, it can be observed that the ANN was successful in modelling the pseudo second order kinetics of sorption of divalent metal ions onto peat particles and cadmium ions onto tree fern particles. Fig. 7 also show that the ANN and pseudo second order kinetics complement each other in modelling the solid/liquid adsorption system as a whole which is valid for the range of operating variables studied.

6. Conclusions

This study showed ANN as a powerful tool in modelling the kinetics of solid/liquid sorption systems for a wide range of operating conditions. The experimental data of auramine O onto activated carbon was used to analyze the performance of ANN trained using the pseudo second order kinetics in modelling the sorption kinetics. The ANN trained by pseudo second order kinetics was found to be excellent in representing the kinetics of auramine O uptake by activated carbon particles. The ANN can train by itself and can be useful in predicting the kinetics of sorption process even for the new experimental conditions within the ranges used to train the ANN. However this study is limited to find the applicability of ANN technique in modelling the adsorption process as a whole using the theoretical second order kinetics. A 6–7–1 neural network was found to be successful to model the adsorption kinetics of the studied system for the range of operating conditions studied. The MSE difference between the experimental data and the experimental data and the MSE between the pseudo second order kinetics and the experimental data vary only by <2%. The ANN trained with pseudo second order kinetics was successful to simulate the dye uptake process for the range of operating conditions studied. The pseudo second order kinetics for the sorption of divalent metal ions onto peat particles and cadmium onto tree fern was used to train the ANN and was found to be successful in modelling the sorption system as a whole for a wide range of operating conditions. The pseudo second order kinetics and ANN complement each other to model the solid/liquid sorption system as a whole for a wide range of operating conditions.

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