Neural Network Application in Fixed Bed Column Adsorption

M. M. Nourouzi, S. Keshani, and L. Chuah Abdullah

***Abstract*—Adsorption experiments were carried out in fixed bed column. Neural network (NN) was used to describe the fixed bed adsorption of POME pigment by resin. The general breakthrough models such as Thomas and Yoon–Nelson models resulted in poor fitness with experimental data (R^2 < 0.8). A wavelet neural network model (WNN) was developed to model the breakthrough curves in fixed bed column for multicomponent system and WNN model successfully described the adsorption process (R^2 = 1). At the initial stages, BDST model showed good agreement with the experimental data but diverged at higher C_b/C_0 ratio (> 0.11).**

***Index Terms*—Neural network, fixed bed column, adsorption, modeling.**

I. Introduction

The production of palm oil from the fruit *Elaeis guineensis* has grown into a major industry in Malaysia [1]. Malaysia is one of the world's largest palm oil producer with a total crude oil production of 17.56 million tonnes per year [2]. Palm oil mill effluent (POME) is the most significant pollutant from palm oil mills. Direct discharge of POME causes serious environmental pollution [3], [4]. POME is an oily wastewater containing 95–96% water, 0.6–0.7% oil and 4–5% total solids including 2–4% suspended solids [5]. Indeed, during the last decades major public complaints in respect to the water pollution have been directed at the palm oil industry [5].

The pigments present in POME are biologically stable and conventional biological degradation is insufficient to remove residual color and organic matter from wastewater. Thus, further treatment is therefore required to remove the color and enhance the quality of the conventionally treated POME. There are various methods developed for the removal of color from water and wastewater. Biological treatment is a conventional methods which is constrained to biodegradable compound [6]; coagulation-flocculation process is widely used for POME treatment [7]; but is limited for high-soluble compounds; photodegradation is a complicated chemical-photocatalytic process which is influenced by the transparency of the solution [8]; filtration is simple and low-cost method but, increasing the efficiency of filtration method is accompanied with the raise in cost [9]; low-cost adsorbents have increasingly received attention for decolorization of wastewater. However, the adsorption process is generally non-selective and is affected by the presence of other components of the wastewater [10]. The chelating ion-exchange can be used for selective sorption of color agent from solution. The ion-exchange is one of the most efficient methods to remove color due to their high affinity to the color compound, chemical stability, reusability and ability to control surface chemistry [11], [12].

Sorption of pigments can be described in the terms of adsorption to one of several unoccupied sites and exchange process in which a pigment displaces another ion. Ion-exchange is a reversible chemical reaction between an insoluble solid and a solution. During the reaction an ion from solution is interchanged by a similarly charged ion attached to a complex solid. The complex solids exist either naturally such as inorganic zeolite or synthetically produced such as organic resin. The synthetic organic resin is an insoluble polymer matrix usually in the form of small (1–2 mm diameter) beads. The material can trap temporarily one ion and release it to a regenerant solution [13].

Adsorption process can be described by breakthrough curve. A breakthrough curve represents concentration-time profile of the effluent and is necessary for the design of a column adsorption process. On the other hand, neural network (NN) has presented a potential to alternate logistic regression and classical statistical techniques with simulating human brain. NN has been successfully used for accounting, finance, health and medicine, marketing, engineering and manufacturing [14].

In this study a commercial anion resin (TULSION A-72 MP) was used to remove residual color in POME. Experiments were carried out in a column. Four kinetic models (Thomas, Yoon–Nelson, Wolborska) as well as NN model were used to predict the performance of the anion resin.

II. Materials and Methods

The continuous flow adsorption experiments were carried out in a glass column of the following dimensions Column diameter: 35 mm and column Height: 500 mm (as shown in Fig. 1).

The glass columns flow rate was controlled by using a rubber stopper. Plastic mesh (< 0.3 mm) was used to support the resin bed. Desired resin heights were mounted; the entrapped air was removed by fluidizing the column with deionized water. The POME was pumped downwards into the column with different flow rates of 250, 450 and 750 mL/h, using a peristaltic pump. POME color at the exit of the column was periodically measured at 440 nm by using the Hach DR 2500 spectrophotometer in the unit of

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mg (Pt/Co)/L. The experiments were carried out at temperature of 27 ±1 ℃.

Resin life is considered as one of the important parameter for industrial application. The cost of adsorption process can be reduced by achieving shorter process time and a longer resin life span. For regeneration, the resin bed was first washed downflow with 1 bed volume of distilled water within 15-20 min. Then, the column was regenerated with with the five bed volumes of the regenerant, 10% NaCl and 1% NaOH within 45 minutes. After this step, 20 bed volumes of distilled water were passed downflow through the bed within one hour. The resin life span was investigated by measuring the adsorption capacity after 30th regeneration. It was observed that the resin was 99% regenerable.

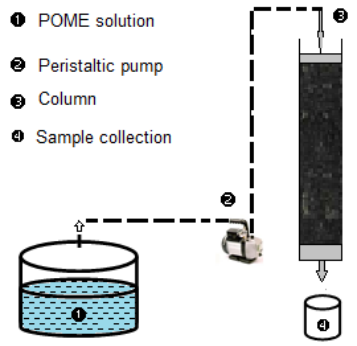

Fig. 1. Schematic diagram of the column adsorption.

Breakthrough curves are defined as a plot of relative concentration versus time. They are used to predict the fixed-bed adsorption process under certain operating conditions. The shapes of these curves depend on bed geometry, operating conditions, transport properties, heat effects and equilibrium adsorption isotherm(s) [3].

TABLE I: PREDICTING MODELS FOR BREAKTHROUGH CURVE

Model	Equation	
Thomas	$\ln\left(\frac{C_o}{C_t}-1\right)=\frac{k_{Th}q_oM}{V}-k_{Th}C_ot$	(1)
Yoon and Nelson	$\ln\left(\frac{C_t}{C_0-C_t}\right)=k_{YN}t-\tau k_{YN}$	(2)
Wolborska	$\ln\frac{C_t}{C_0}=\frac{\beta C_0 t}{N_0}-\frac{\beta Z}{U}$	(3)

The breakthrough time is the time the effluent concentration reaches to the influent concentration and exhaustion time is defined the time which the effluent concentration exceeds the standard limits for the target component. Several simple mathematical models have been developed to predict the breakthrough time. Some of these models are listed in Table I.

A general neural network (NN) structure consists of an input layer, one hidden layer and an output layer. Each layer has its corresponding units (neurons or nodes) and weighted connections. The connections can be feed-forward or feed-back. Feed-forward model does not have a connection back from the output to the input neurons. Each unit receives the sum of its weighted inputs and passes the result through a nonlinear activation function (transfer function). The activation function acts on the weighted sum of the unit's inputs.

NeuralPower v2.5, a commercial artificial intelligence software, was used in the NN studies. The input parameters used in training the best prediction model are listed in Table II. The maximum number of iterations was set to 1,000 (*i.e.* the default value).

Different numbers of nodes were used in order to determine the optimum number of hidden nodes (*i.e.* 4-10). Larger numbers of the hidden layer nodes create more flexibility for the network. On the other hand, NN is also sensitive to the number of nodes in its hidden layers. Too many neurons can contribute to overfitting. In additions, no enhancement was observed in performance of NN by increasing the number of hidden layers nodes.

To validate the developed model, the correlation coefficient R^2 was used as the error function. The R^2 measures the performance of the network according to the following equation:

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n}(y_i - \bar{y}_i)^2}$$

where y_i is the experimental y values, $\bar{y}_i$ is mean of y_i, $\hat{y}_i$ is predicted values and i is number of inputs.

The best model with regard to highest R^2 was selected.

TABLE II: TRAINING PARAMETERS USED IN NEURALPOWER V2.5

Parameter	
No. of hidden layers	1
No. of nodes in hidden layer	6
Learning Algorithm	QuickProp
Connection Type	Multilayer Normal feed Forward
Transfer Funtion	Morlet wavelet
Momentum factor	0.8
Learning rate	0.8
Maximum iterations	1000
MS error	0.01

III. RESULTS AND DISCUSSION

The breakthrough curves demonstrate effluent concentration as a function of time. Several models have been developed to predict the service time of packed column using the experimental data. The existing models such as Thomas, Adams–Bohart, Yoon–Nelson, and Wolborska models are well studied for a single adsorbate system but possess some limitations especially for the adsorption of multicomponent mixtures [15]. Since adsorption system practically contains more than one component, it would be useful if the application of the aforementioned models for multicomponent system to be studied [16].

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The model parameters obtained from corresponding

curve fitting and the values for model accuracy (R^2) and model precision (*COV*) are shown in Table III.

TABLE III: MODEL PARAMETERS OBTAINED BY NONLINEAR REGRESSION ANALYSIS FOR COLOR ADSORPTION ONTO ANION RESIN

Model	Model parameters		R^2	*COV* %
Thomas	k_{Th}	q_0		
	0.0000064	6.55	0.75	4.21
Yoon and Nelson	k_{YN}	τ		
	0.016	196.6	0.75	4.17
Wolborska	β	N_0		
	0.05	8400	0.72	5.57
WNN	-	-	1	0.0014

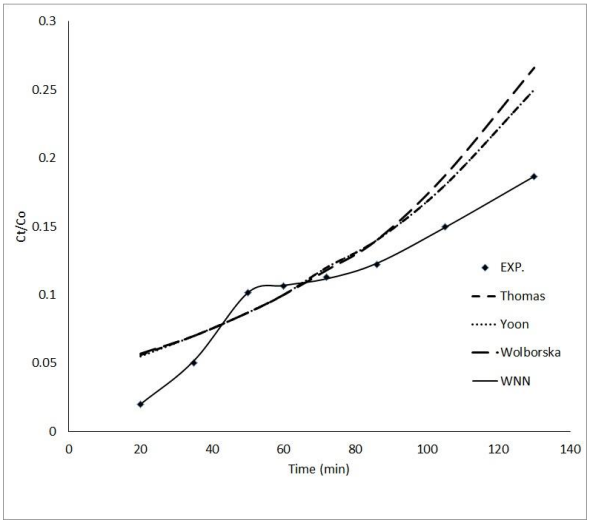

Fig. 2. Experimental and calculated breakthrough curves.

The breakthrough curves obtained for the color removal of POME are demonstrated in Fig. 2. From the statistical parameters and breakthrough curves, it was concluded that predicting models (Thomas, Yoon and Nelson and Wolborska) did not fit accurately the data from column experiments and a significant deviation between experimental and fitted data was observed ($R^2 < 0.80$). On the other hand, from *COV* values it was concluded that there was no significant difference between them (*COV* ≈ 2.5 %).

Typically, breakthrough curves should have followed characteristic S shape profile. The irregular shape of the breakthrough curve for color removal from POME was attributed to the different mass transfer behavior. The adsorption process was affected by the interaction of various pigments in POME and the shape of breakthrough curve was a consequence of multicomponent system with different physicochemical characteristics.

The Thomas model is based on the second order reaction kinetics and it is suitable for adsorption processes where the external and internal diffusions is not the limiting step. The Wolborska model describes the adsorption dynamics in which the adsorption rate is controlled by mass transfer for diffusion mechanisms. The chemical reaction kinetics is not usually limiting step in adsorption process, whereas interphase mass transfer resistance is expected to be more significant. This discrepancy may explain the lack of fit of the models for the multicomponent system. The Yoon–Nelson model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. This model is mathematically analogous to Thomas model and the same trend is to be observed when the mass transfer effect is significant [17].

NN is a valuable instrument in the design and optimization of adsorption processes. A properly trained NN links input and output parameters without the need for mechanistic models. NN does not require prior knowledge about the structure and relationships that exist between variables and this is useful in where the complexity of the mechanisms is high. One of the most important advantages of the NN model is that the developed model does not contain any model parameters. The NN modeling was used as a replacement for breakthrough models to predict the time dependency of the color removal by resin. The experimental and the predicted color removal are presented in Fig. 2. The results are obtained from column study at pH 3, flow rate 250 mL/h and bed height 30 cm. The value of R^2 = 1 shows excellent fitness of response models. On the other hand, the value of RSD for NN model is significantly smaller than those for breakthrough models (*COV* = 3.4E-06 %) demonstrating the higher accuracy of NN model.

NOMENCLATURE

Symbols	
COV	Coefficient of variation
C_0	Initial concentration (mg/L)
C_b	Breakthrough concentration (mg/L)
C_t	Concentration at time *t* (mg/L)
k_{Th}	Thomas rate constant (L/min mg)
k_{YN}	Yoon–Nelson rate constant (1/min)
i	Number of inputs
M	Mass of adsorbent (g)
q_{exp}	Total adsorption (mg/g)
q_0	Maximum solid phase concentration (mg/g)
R^2	Correlation coefficient
v	Flow rate (L/min)
Z	Height of the column bed (cm)
y_i	Experimental *y* values
$\bar{y}_i$	Mean of y_i
$\hat{y}_i$	Predicted values
β	Kinetic coefficient of the external mass transfer (1/min)
τ	Time for 50% breakthrough (min)

REFERENCES

[1] S. Z. Omain, A. B. A. Hamid, A. R. A. Rahim, and N. M. Salleh, "Supply chain management practices in Malaysia palm oil industry," presented at The 11th Asia pacific industrial engineering and management systems conference, Melaka, Malaysia, 7–10 December, 2010.

[2] M. K. Lam and K. T. Lee, "Renewable and sustainable bioenergies production from palm oil mill effluent (POME): Win--win strategies toward better environmental protection," *Biotechnol. Adv*, vol. 29, pp. 124—141, 2011.

[3] C. F. Robert and S. Menon, "Trade and Environment Dimensions in the Food and Food Processing Industries in Asia and the Pacific," Improving the Environmental Sustainability and the Export Competitiveness in the Food Sector: Case of the Malaysian palm oilindustry, Malaysia, 2007.

[4] P. E. Poh and M. F. Chong, "Development of anaerobic digestion methods for palm oil mill effluent (POME) treatment," *Bioresour. Technol*., vol. 100, pp. 1-9, 2009.

[5] A. R. Khalid and W. A. W. Mustafa, "External benefits of environmental regulation: Resource recovery and the utilisation of effluents," *Environ*, vol. 12, 1992, pp. 277-285.
[6] S. Mohan, N. Venkata, C. Rao, and P. N. Sarma, "Low-biodegradable composite chemical wastewater treatment by biofilm configured sequencing batch reactor (SBBR)," *J. Hazard. Mater*, vol. 144, no. 1, pp. 108-117, 2007.
[7] S. Bhatia and Z. A. L. Ahmad, "Pretreatment of palm oil mill effluent (POME) using Moringa oleifera seeds as natural coagulant," *J. Hazard. Mater*, vol. 145.1, pp. 120-126, 2007.
[8] M. Wu, Y. Jin, G. Zhao, M. Li, and D. Li, "Electrosorption-promoted photodegradation of opaque wastewater on a novel TiO2/carbon aerogel electrode," *Environ. Sci. technol*, vol. 44, pp. 1780-1785, 2010.
[9] M. H. Dore, R. G. Singh, G. Achari, and A. Khaleghi-Moghadam, "A. Cost scenarios for small drinking water treatment technologies," *Des. Water Treat*, vol. 5, pp. 3628-3638, 2013.
[10] E. Forgacs, T. Cserhati, G. Oros, "Removal of synthetic dyes from wastewaters: a review," *Environ. Int*, vol. 30, pp. 953-971, 2004.
[11] M. Chabani, A. Amrane, and A. Bensmaili, "Equilibrium sorption isotherms for nitrate on resin Amberlite IRA 400," *J. Hazard. Mater*, vol. 165, pp. 27-33, 2009.
[12] N. P. Cheremisinoff, *Handbook of water and wastewater treatment technologies*, Butterworth-Heinemann, 2002.
[13] M. Paliwal and U. A. Kumar, "Neural networks and statistical techniques: A review of applications," *Expert Syst. Appl*, vol. 36, pp. 2-17, 2009.
[14] I. Park and K. S. Knaebel, "Adsorption breakthrough behavior: Unusual effects and possible causes," *Am. Inst. Chem. Eng*, vol. 38, pp. 660-670, 1992.
[15] S. J. Kleinübing, E. Guibal, E. A. da Silva, and M. G. C. da Silva, "Copper and nickel competitive biosorption simulation from single and binary systems by Sargassumfilipendula," *Chem. Eng. J*, vol. 184, pp. 16-22, 2001.
[16] G. M. Walkera and L. R. Weatherleyb, "COD removal from textile industry effluent: pilot plant studies," *Chem. Eng J*, vol. 84, pp. 125–131, 2001.
[17] W. Zhang, L. Dong, H. Yan, H. Li, Z. Jiang, X. Kan, H. Yang, A. Li, and R. Cheng, "Removal of methylene blue from aqueous solutions by straw based adsorbent in a fixed-bed column," *Chem. Eng. J*, vol. 173, pp. 429-436, 2001.

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