Asian Journal of Chemistry Vol. 22, No. 1 (2010), 271-282

Adsorption Kinetic Modeling of Cyanide by Activated Carbon from Solution by Using of Kinetic Models and Adaptive Neuro-fuzzy Inference System

A. BEHNAMFARD* and M.M. SALARI RAD
Department of Mining and Metallurgical Engineering,
Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran
Fax: (98)(21)66405846; Tel: (98)9151603400
E-mail: behnamfard.ali@gmail.com

Adsorption kinetics of cyanide on coconut shell activated carbon were determined from batch tests. The kinetic data were fitted to pseudo-first-order and pseudo-second-order kinetic models and was found to follow closely the pseudo-second-order kinetic model. Remaining cyanide concentration in wastewater at several time after addition coconut shell activated carbon are modeled by adaptive neuro-fuzzy inference system (ANFIS) at different initial cyanide concentration. The results obtained in this work indicate that ANFIS is an effective method for prediction of remaining cyanide concentration in solution and have better accuracy and simplicity compared with results obtained from the applicable kinetic model.

Key Words: Coconut shell activated carbon, Cyanide, Kinetics, Adaptive neuro-fuzzy inference system.

INTRODUCTION

Cyanides can both occur naturally or be man-made and many are powerful and rapid-acting poisons[1]. Many of the cyanides in soil and solution come from industrial processes. The major sources of cyanides in water bodies are discharges from some metal mining processes[2,3], chemical synthesis (nylon, fibers, resins, herbicides)[4], plating industries (plating bath)[5] and publicly owned wastewater treatment facilities. Hydrogen cyanide, sodium cyanide and potassium cyanide are the forms of cyanide most likely to be in the environment as a result of industrial activities[6]. To protect the environment and water bodies, effluents containing cyanide from various industries must be treated before discharging into the environment. Hence, many countries and environmental protection agencies have imposed limiting standards for discharge of cyanide bearing wastewater to sewers. For instance the US Environmental Protection Agency (USEPA) set regulations for the amount of cyanide allowed in drinking water in which the maximum level allowed is 0.2 mg of cyanide per liter of water (0.2 ppm)[6].

Currently, wastewater containing cyanide is treated by chemical oxidation methods (alkaline chlorination, ozonization and wet-air oxidation)[7-9]. However, these methods are expensive and hazardous chemicals are used as the reagents (chlorine and sodium hypochlorite)[9]. This treatment produces toxic residues which implies the necessity of an additional level of detoxification[10]. The other treatment methods used such as reverse osmosis[11], biological oxidation/biodegradation[12,13], ozonation[14], acidification/volatilization and reneutralization[13,14], iron cyanide precipitation[14,15], catalytic oxidation[15-17], SO_2/air (INCO) process[18,19]. Each of the above processes has their own benefits and limitations.

Adsorbent-based processes using ion-exchange resins[20] and activated carbon[4,21-23] have been developed and tested over the past 50 years for the removal of free or metal-bound cyanide from solution. While these processes may be proven economic for specific cases, they are yet to find large-scale application directly to gold plant tailings. At high cyanide or metal tenors, rapid saturation of the adsorbent is likely to become an issue, resulting in high adsorbent turnovers and inventories. However, in cases where solid-liquid separation costs or operability are important, they may find application[18].

Knowledge of the adsorption kinetic constitutes the first step in investigation of the possibility of using an adsorbent for a particular separation task[24]. Pseudo first-order and second-order kinetic models extensively used to describe the rate of adsorption of inorganic and organic pollutants on various adsorbents[24-27]. In this work, kinetics of cyanide removal by activated carbons were examined using the pseudo first-order and second-order kinetic models.

One of the most important objectives of kinetic models is to determine the remaining concentration of cyanide in solution at various time after addition of activated carbon. In this investigation in order to show the applicability of adaptive neuro-fuzzy inference system (ANFIS) for prediction of remaining cyanide concentration in solution by activated carbon, a hybrid grid partitioning ANFIS was used.

Fuzzy logic reduces the possible difficulties in modeling and analysis of complex data and also, it is appropriate for incorporating the qualitative aspects of human experience within its mapping rules, which are to provide a way of catching information. Artificial neural networks (ANNs) have also been used to identify models of complex systems because of their high computational rates, robustness and ability to learn. For the same purpose neuro-fuzzy systems are fuzzy systems which use ANNs theory in order to determine their properties (fuzzy sets and fuzzy rules) by processing data samples. A specific approach in neuro-fuzzy is ANFIS that is one of the first integrated hybrid neuro-fuzzy models[28], but has shown promising applicability in modeling nonlinear functions and is faster in convergence when compared to the other neuro-fuzzy models[29].

In this study in addition to comparing the deviation of ANFIS output from the measured values, a comparison of them with the calculated values of remaining cyanide concentration obtained from applicable kinetic model is presented.

EXPERIMENTAL

Analytical grade sodium cyanide (NaCN), silver nitrate ($AgNO_3$), potassium iodide (KI) and sodium hydroxide (NaOH) were used.

In this study a size fraction of -2.36 +2 mm coconut shell activated carbon, produced through a steam activation process by Haycarb company, Srilanka, was employed. The activated carbon was of industrial grade and used in a carbon in pulp circuit at Mouteh gold processing plant in Iran. Prior to use, the activated carbon was dried with air. Following acid treatment of carbon with 1 % hydrochloric acid solution, the sample was thoroughly rinsed with distilled water prior to adding to cyanide aqueous solution with predetermined initial concentrations.

Adsorption experiments: For measurement of time-dependent uptake of cyanide by the activated carbon, 1.5 g portion of prepared activated carbon was poured in 2.5 L glass bottles containing 500 mL cyanide aqueous solution with known concentration and pH of 10. The solutions were bottle rolled at a constant rotation of 100 rpm for 72 h.

Sampling was performed by removing 5 mL aliquots which were then analyzed for cyanide by titrating against standard silver nitrate solution (0.001 M) in the presence of potassium iodide (10 g/L in distilled water) as indicator.

Batch kinetic studies: The aqueous samples were taken at preset time intervals and the concentrations of cyanide were measured. The amount of adsorption at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of cyanide at zero time (initial con.) and t, respectively. V is the volume of the solution (L) and W is the mass of dry carbon used (g).

The kinetic data were then fitted using both pseudo-first and second-order models.

Pseudo-first-order kinetic model: The rate constant of adsorption is determined from the pseudo-first-order equation given by Langergren and Svenska[30] as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e and q_t are the amounts of cyanide adsorbed (mg/g) at equilibrium and at time t (h), respectively and k_1 is the adsorption rate constant (h^{-1}).

Pseudo-second-order kinetic model: The pseudo-second-order equation[31] based on equilibrium adsorption is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 (g/mg h) is the rate constant of second-order adsorption.

Adaptive neuro-fuzzy inference system (ANFIS): The ANFIS is a multilayer feed-forward network consisting of nodes and directional links, which combines

the learning capabilities of a neural network and reasoning capabilities of fuzzy logic[32,33]. This hybrid structure of the network can extend the prediction capabilities of ANFIS beyond artificial neural network (ANN) and fuzzy logic techniques when they are used alone. Analyzing the mapping relation between the input and output data, ANFIS can establish the optimal distribution of membership functions using either a back-propagation gradient descent algorithm alone or in combination with a least-squares method.

Adaptive neuro-fuzzy inference system uses the fuzzy if-then rules involving premise and consequent parts of Sugeno-type fuzzy inference system[28]. To describe this system, it is simply assumed that the inference system has two inputs x and y and one output f. A typical rule set with two fuzzy if-then rules for a first-order Sugeno fuzzy model can be expressed as:

1. If x is A_1 and y is B_1, then $f_1 = p_1x + q_1y + r_1$
2. If x is A_2 and y is B_2, then $f_2 = p_2x + q_2y + r_2$

where p_1, p_2, q_1, q_2, r_1 and r_2 are linear parameters in the consequent part and A_1, A_2, B_1 and B_2 are nonlinear parameters.

The corresponding equivalent ANFIS architecture for two input first-order Sugeno fuzzy model with two rules is shown in Fig. 1. The architecture of the ANFIS system consists of five layers, namely, the fuzzy layer, product layer, normalized layer, de-fuzzy layer and total output layer. The node functions in the same layer are of the same function family as described in the following[28] (Fig.1).

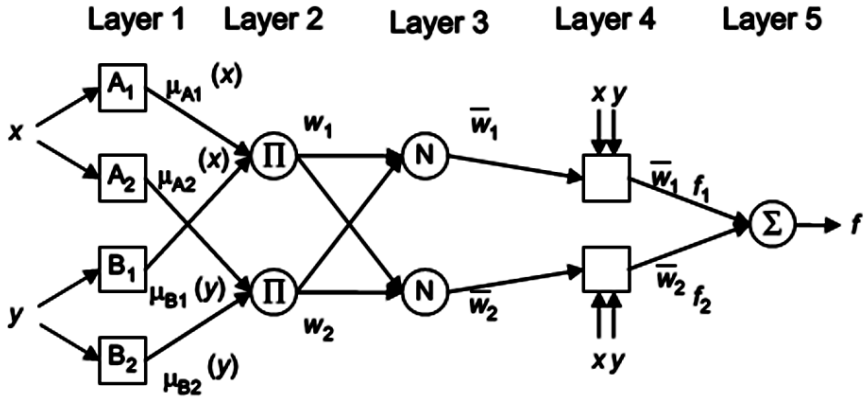

Fig. 1. An ANFIS network structure for a simple FIS

Layer 1: The first layer is called fuzzy layer. The adjustable nodes in this layer are represented by square nodes and marked by A_1, A_2, B_1 and B_2 with x and y outputs. A_1, A_2, B_1 and B_2 are the linguistic labels (small, large, *etc.*) used in the fuzzy theory for dividing the membership functions. The node function in this layer that determines the membership relation between the input and output functions can be given by:

$$O_{1,i} = \mu_{Ai}(x),\ i = 1,2$$
$$O_{1,j} = \mu_{Bi}(y),\ j = 1,2 \quad (4)$$

where $O_{1,i}$ and $O_{1,j}$ denote the output functions and μ_{Ai} and μ_{Bj} denote the appropriate membership functions.

Layer 2: This is the product layer and every node is a fixed node marked by a circle node and labeled by Π. The outputs w_1 and w_2 are the weight functions of the next layer. The output of this layer, $O_{2,i}$, is the product of the input signals and given by:

$$O_{2,i} = w_i = \mu_{Ai}(x)\,\mu_{Bi},(y),\ i = 1,2 \quad (5)$$

The output signal of each node, wi, represents the firing strength of a rule.

Layer 3: This is the normalized layer and every node in this layer is a fixed node, marked by a circle node and labeled by N. The nodes normalize the firing strength by calculating the ratio of firing strength for this node to the sum of all the firing strengths, *i.e.*

$$O_{3,i} = \overline{w} = \frac{w_i}{w_1 + w_2}, \qquad i = 1,2 \quad (6)$$

Layer 4: This is the de-fuzzy layer having adaptive nodes and marked by square nodes. The node function in this layer is given by a non-fuzzy equation:

$$O_{4,i} = \overline{w}_i f_i = \overline{w}_i (p_i x + q_i y + r_i), \quad i = 1,2 \quad (7)$$

where $\overline{w}_i$ is the normalized firing strength output from the previous layer and p_i, q_i and r_i are the parameters set of this node. These parameters are linear and referred as consequent parameters of this node.

Layer 5: This is the last layer that simply computes the overall system output as the summation of all incoming signals.

Every node in this layer is a fixed node, marked by circle node and labeled by S. The node function is given by:

$$O_{5,i} = \sum_i \overline{w}_i f_i = \frac{\sum_i \overline{w}_i f}{\sum_i \overline{w}_i}, \qquad i = 1,2 \quad (8)$$

It is noted that the system output is the weighted sum of the results of the rules. The number of fuzzy sets is determined by the number of nodes in layer 1. On the other hand, the dimension of layer 4 determines the number of fuzzy rules employed in the architecture that shows the complexity and flexibility of the ANFIS architecture. When compared to the neural networks, fuzzy rules can be considered as the equivalent of the neurons.

An ANFIS network can be trained based on supervised learning to reach from a particular input to a specific target output. In the forward pass of the hybrid algorithm of the ANFIS, the node outputs go forward until layer 4 and consequent linear parameters, (p_i, q_i, r_i), are identified by the least-squares method using training

data[28]. In the backward pass, the error signals propagate backwards and the premise nonlinear parameters, (a_i, b_i, c_i), are updated by gradient descent.

Development of ANFIS models: Adaptive neuro-fuzzy inference system (ANFIS) is powerful model in solving complex problems[35]. Since ANFIS has the potential of solving nonlinear problem and can easily achieve the input-output mapping, it is perfect to be used for solving the predicting problem. In this work, the ANFIS model on the basis of grid partitioning algorithm with two inputs (time t, initial cyanide concentration) and one output (remaining cyanide concentration) was designed for prediction remaining cyanide concentration at various time after addition activated carbon. In the grid partitioning method, the domain of each antecedent variable is partitioned into equidistant and identically shaped membership functions. The total number of fuzzy rules (Stotal) increase exponentially with input dimension, *i.e.*, Stotal = Mn where n is the input dimension and M is the number of partitioned fuzzy subsets for each input variable. It is clear that for this type of partition the number of fuzzy rules will increase exponentially with the number of input dimension, so the number of rules will be tremendous when the number of input dimension is large and a lot of computations are needed. The Gaussian membership function defined in eqn. 9 used in the ANFIS model:

$$f(x;\sigma,c) = \exp\left(-\frac{(x-c)^2}{2\sigma^2}\right) \tag{9}$$

where c and σ are parameters of the membership function, governing the Gaussian functions accordingly.

Hybrid learning rule is used to train the model according to input/output data pairs. A hybrid algorithm can be divided to forward pass and a backward pass. The forward pass of the learning algorithm stop at nodes at layer 4 and the consequent parameters are identified by least squares method. In the backward pass, the error signals propagate backward and the premise parameters are undated by gradient descent. It has been proven that this hybrid algorithm is highly efficient in training the ANFIS[28].

The applicability of the kinetic model to describe the adsorption process was validated by the normalized standard deviation(NSD %) and average relative deviation (ARD %) which are defined as:

$$ARD\% = \frac{\sum_{i=1}^{N}\left|\frac{(y_i^{exp} - y_i^{cal}}{y_i^{exp}}\right|}{N} \times 100 \tag{10}$$

$$NSD\% = \sqrt{\frac{\sum_{i=1}^{N}\left|\frac{(y_i^{exp} - y_i^{cal}}{y_i^{exp}}\right|^2}{N-1}} \times 100 \tag{11}$$

where y_i^{exp} and y_i^{p} are target and network output for the ith output and N is the total number of events considered.

All ANFIS calculations were carried out using Matlab7 mathematical software with fuzzy logic toolboxes for windows running on a personal computer.

RESULTS AND DISCUSSION

Values of k_1 for the pseudo-first-order kinetic model were obtained from the slopes of the linear plots of ln ($q_e - q_t$) *versus* t (figure not shown). The correlation coefficient values obtained were relatively small and the experimental q_e values did not agree with the calculated values obtained from the linear plots, as shown in Table-1. This shows that the adsorption of cyanide onto the activated carbon did not follow the pseudo-first-order equation.

TABLE-1
PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETIC MODEL PARAMETERS FOR DIFFERENT INITIAL CYANIDE CONCENTRATIONS AT 30 ºC

Initial cyanide concentration (ppm)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		$q_{e,cal}$ (mg/g)	k_1 (h)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/g h)	R^2
102	17.33	14.67	0.135	0.988	18.52	0.019	0.997
202	23.33	20.57	0.119	0.958	25.64	0.010	0.995
306	26.67	23.34	0.112	0.991	29.41	0.008	0.997
396	30.00	26.05	0.101	0.987	33.33	0.006	0.997
532	33.33	29.87	0.106	0.971	37.04	0.005	0.997

If the pseudo-second-order kinetic model is applicable, the plot of t/q_t *versus* t should show a linear relationship. q_e and k_2 can then be determined from the slope and the intercept of the plot. This procedure is more likely to predict the behaviour over the whole range of adsorption. The linear plot of t/q_t *versus* t, as shown in Fig. 2, shows a good agreement between the experimental and the calculated q_e values (Table-1). Besides, the correlation coefficients for the second-order kinetic model were greater than 0.99 for all cyanide concentrations, indicating the applicability of the second-order kinetic model to describe the adsorption process of cyanide on the activated carbon which is in agreement with the results of other researchers[23].

In this work a hybrid grid partitioning ANFIS by Gaussian membership function was used in order to prediction of remaining cyanide concentration in solution. The original data needing for establish ANFIS models obtained from present adsorption experiments. This data set was randomly divided into two category, training set and testing set.

In this study, we set as an aim to measure the predictive ability of ANFIS models by comparison with applicable kinetic model (pseudo second order kinetic model) for remaining cyanide concentration. Therefore in Table-2, the predicted remaining

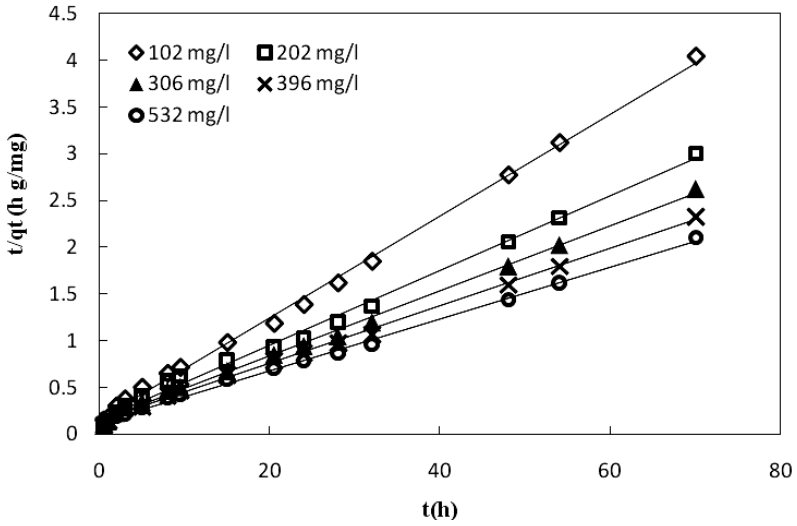

Fig. 2. Pseudo-second-order kinetics for adsorption of cyanide on to granular activated carbon at 25 ºC

TABLE-2
AVERAGE RELATIVE DEVIATION (ARD %) AND NORMALIZED STANDARD DEVIATION (NSD %) FOR PSEUDO SECOND ORDER KINETIC MODEL AND ANFIS

Initial cyanide concentration (ppm)	Pseudo-second-order kinetic model		ANFIS	
	ARD (%)	NSD (%)	ARD (%)	NSD (%)
102	4.38	5.12	2.058	2.50
202	3.28	5.07	1.027	1.29
306	1.60	3.19	0.32	0.36
396	1.05	2.67	0.46	0.23
532	0.93	2.18	0.17	0.22

cyanide concentrations in solution by ANFIS are compared with those predicted by using pseudo second order kinetic model. As the results presented in this table indicates ANFIS is more accurate for predicting of remaining cyanide concentration in solution, with a good degree of accuracy. Also, the advantage of the ANFIS compared to applicable kinetic model is estimation speed, simplicity, error free and capacity to learn from examples.

In Figs. 3-7 the prediction of remaining cyanide concentration in solution by the artificial neural network model was plotted against the experimental values for the training and testing set. As shown in these figures, difference between experimental data and calculated data is very low and it is showing that ANFIS are powerful tools for predicting of remaining cyanide concentration in solution. Furthermore, Figs. 3-7 shows calculated remaining cyanide concentration against the experimental values that has been resulted from pseudo second order kinetic model. As being shown, the predicted results by ANFIS model compared with pseudo second order kinetic model is closer to experimental values.

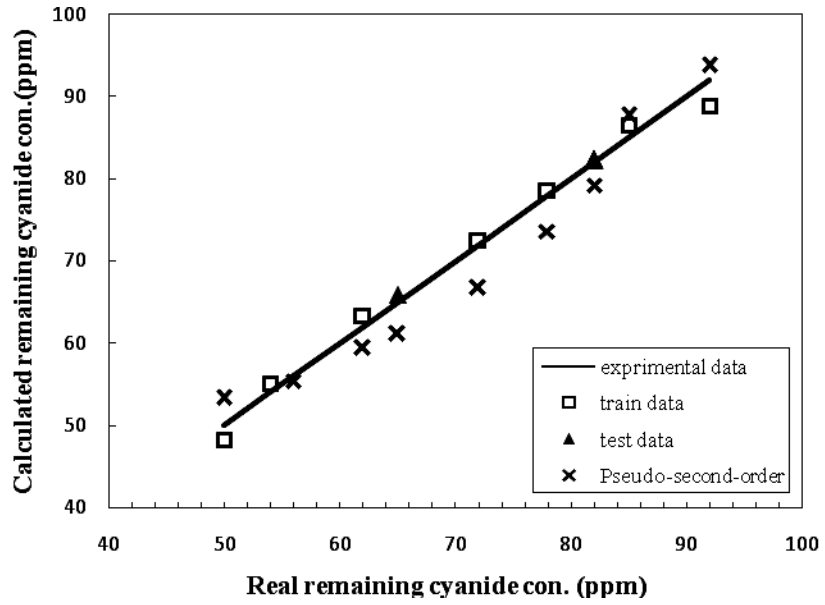

Fig. 3. Calculated remaining cyanide concentration in solution *versus* experimental remaining cyanide concentration at 102 mg/L initial cyanide concentration

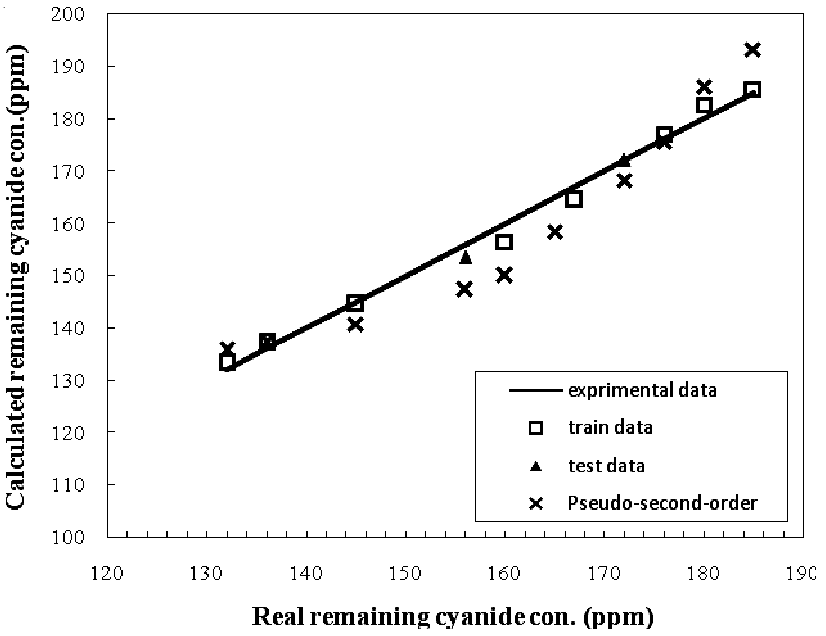

Fig. 4. Calculated remaining cyanide concentration in solution *versus* experimental remaining cyanide concentration at 202 mg/L initial cyanide concentration

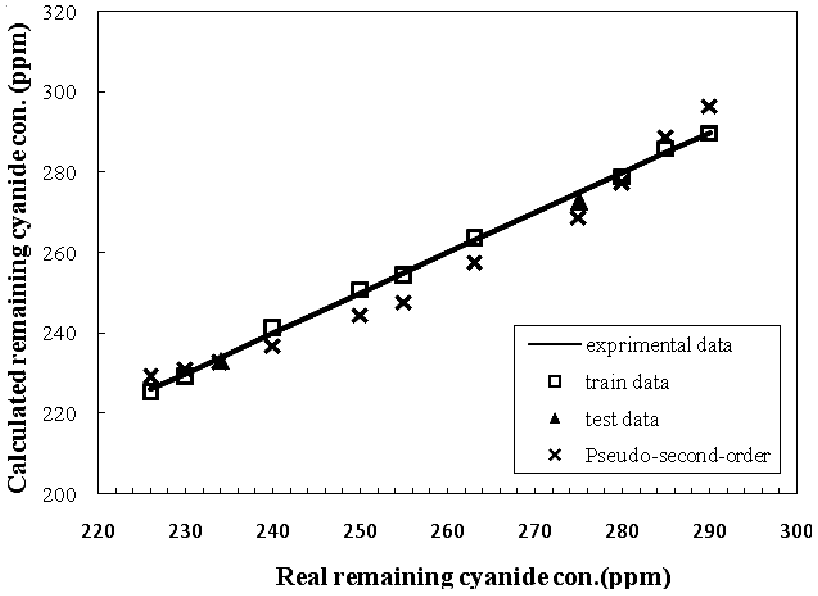

Fig. 5. Calculated remaining cyanide concentration in solution *versus* experimental remaining cyanide concentration at 306 mg/L initial cyanide concentration

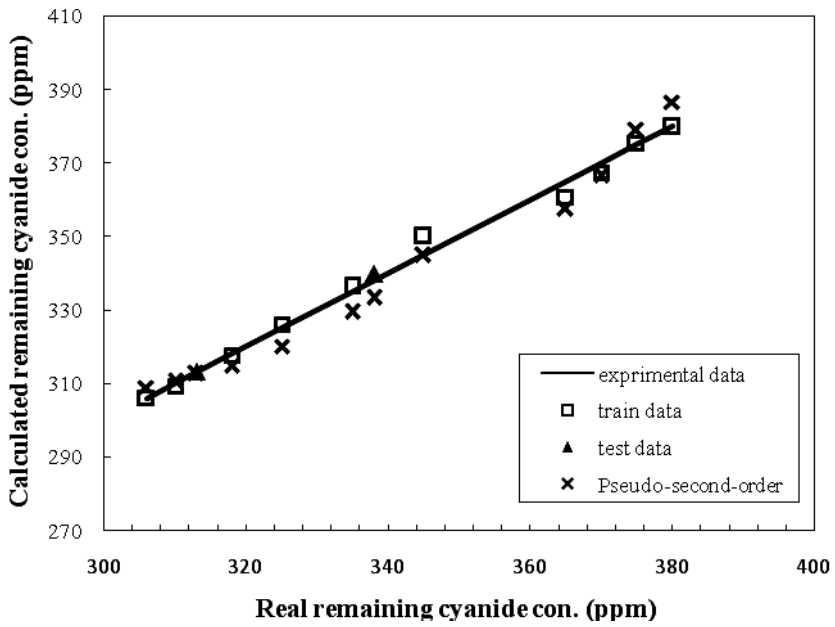

Fig. 6. Calculated remaining cyanide concentration in solution *versus* experimental remaining cyanide concentration at 396 mg/L initial cyanide concentration

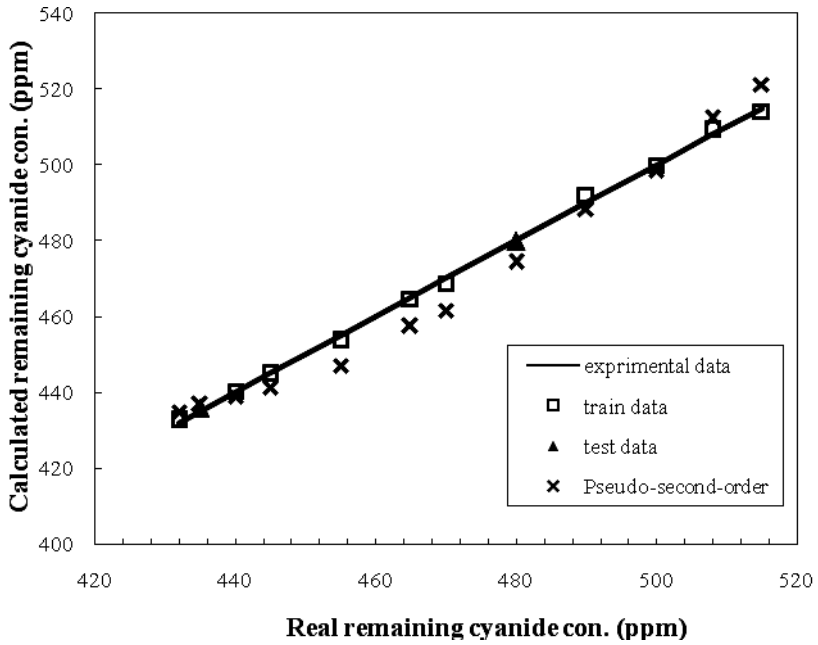

Fig. 7. Calculated remaining cyanide concentration in solution *versus* experimental remaining cyanide concentration at 532 mg/L initial cyanide concentration

Conclusion

The present investigation showed that the adsorption kinetics of cyanide from solution by coconut shell activated carbon follow closely the pseudo-second-order kinetic model.

ANFIS is capable to predicting the remaining cyanide concentration, with a high degree of accuracy. Comparing result of ANFIS with the results obtained by applicable kinetic model indicate that this model is more accurate than pseudo-second-order kinetic model. The advantage of the ANFIS compared to classical methods is estimation speed, simplicity and error free.

REFERENCES

1. Agency for Toxic Substances and Disease Registry (ASTDR), Toxicological Profile for Cyanide, Atlanta, Georgia, USA (1995).
2. Mineral Policy Center, Cyanide Uncertainities: Observations on the Chemistry, Toxicity and Analysis of Cyanide in Mining-Related Waters, Issue Paper No. 1 (1998).
3. J.W. Patterson, Industrial Wastewater Treatment Technology, Butterworth, Boston, USA (1985).
4. N. Adhoum and L. Monser, *Chem. Eng. Processing*, **41**, 17 (2002).
5. J.K. Easton and J. Water, *Pollut. Control Fed.*, **39**, 1621 (1967).
6. Agency for Toxic Substances and Disease Registry Division of Toxicology and Environmental Medicine, Cyanide: Public Health Statement, Atlanta, USA.
7. J.R. Parga, S.S. Shukla and F.R. Carrillo-Pedroza, *Waste Manage.*, **23**, 183 (2003).

8. S.A.K. Palmer, M.A. Breton, T.J. Nunno, D.M. Sullivan and N.F. Suprenant, Metal/Cyanide Containing Wastes: Treatment Technologies, Noyes Data, Park Ridge, NJ (1988).
9. A. Watanabe, K. Yano, K. Ikebukuro and I. Karube, *Microbiology*, **144**, 1677 (1998).
10. M.G. Campos, P. Pereira, J.C. Roseiro, *Enzyme Microb. Technol.*, **38**, 848 (2006).
11. J.D. Desai, C. Ramakrishna, P.S. Patel and S.K. Awasthi, *Chem. Eng. World*, **33**, 115 (1998).
12. R.R. Dash, A. Gaur and C. Balomajumder, *J. Hazard. Mater.*, **163**, 1 (2009).
13. F. Gurbuz, H. Ciftci and A. Akcil, *J. Hazard. Mater.*, **162**, 74 (2009).
14. N.L. Nemerow, Liquid Waste of Industry: Theory, Practices and Treatment, Addison-Wesley Publishing Co. (1971).
15. C.A. Young and T.S. Jordan, Proceedings of the 10th Annual Conference on Hazardous Waste Res., pp. 104-129 (1995).
16. K. Chiang, R. Amal and T. Tran, *Adv. Environ. Res.*, **6**, 471 (2002).
17. K. Chiang, R. Amal and T. Tran, *J. Mol. Catal. A-Chem.*, **193**, 285 (2003).
18. M. Adams and V. Lloyd, *Miner. Eng.*, **21**, 501 (2008).
19. E.A. Devuyst, B.R. Conard, R. Vergunst and B. Tandi, *J. Met.*, **41**, 43 (1989).
20. E. Goldblatt, *Ind. Eng. Chem.*, **51**, 241 (1959).
21. M.D. Adams, *Miner. Eng.*, **7**, 1165 (1994).
22. R.R. Dash, C. Balomajumder and A. Kumar, *Chem. Eng. J.*, (in press).
23. H. Deveci, E.Y. Yazici, I. Alp and T. Uslu, *Int. J. Miner. Process.*, **79**, 198 (2006).
24. K. Lin, J. Pan, Y. Chen, R. Cheng and X. Xu, *J. Hazard. Mater.*, **161**, 231 (2009).
25. B.K. Nandi, A. Goswami and M.K. Purkait, *J. Hazard. Mater.*, **161**, 387 (2009).
26. B. Ji, F. Shao, G. Hu, S. Zheng, Q. Zhang and Z. Xu, *J. Hazard. Mater.*, **161**, 81 (2009).
27. A. Olgun and N. Atar, *J. Hazard. Mater.*, **161**, 148 (2009).
28. J. Jang, *IEEE Trans. Systems Man Cybernetics*, **23**, 665 (1993).
29. M.A. Akcayol, *Adv. Eng. Software*, **35**, 129 (2004).
30. S. Langergren and B.K. Svenska, *Veternskapsakad Handlingar*, **24**, 1 (1989).
31. Y.S. Ho and G. McKay, *Chem. Eng. J.*, **70**, 115 (1998).
32. E.H. Mamdani and S. Assilian, *Int. J. Man-Machine Studies*, **7**, 1 (1975).
33. M. Sugeno, Industrial Applications of Fuzzy Control, Elsevier, Amsterdam (1985).

(*Received*: 29 December 2008; *Accepted*: 5 September 2009) AJC-7832