Mathematical Model Describes Treatment of Waste Water Using Modified Activated Carbon

A.S. Ibrahim*, A.S. AL Buloshi, S.S. AL Zaabi and L.A. AL Yafai

Chemical Engineering Department, Dhofar University, Salalah, Sultanate of Oman

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Abstract: The proposed mathematical model covered in this paper includes the most important parameters associated with the rates of adsorption and desorption. Also, partial pressure is included since it is an important factor that affects rates of adsorption and desorption. The study focuses on the effects of the constant rates on adsorption of pollutant concentrations for benzene, nickel, cadmium, and copper using modified active carbon. When the rate constant of adsorption decreases, the pollutant concentration will also decrease, yielding high acceptable evidence of the logic of the proposed mathematical model. Also, the proposed model is compared with experimental data and other models to give good outcomes with high accuracy.

Keywords: Mathematical model, Waste water, Adsorption, Desorption, Activate carbon.

نموذج رياضي يصف معالجة مياه الصرف الصحي باستخدام الكربون النشط المعدل

أ.س. إبراهيم*، أ. س. البلوشي، س. س. الزعبي و ل. أ. اليافعي

الملخص: النموذج الرياضي المقترح في هذه المقالة يحتوي على أهم البارامترات المصاحبة لمعدلات الامتصاص والامتزاز. أيضاً الضغط الجزئي تم إدراجه حيث أنه عامل مهم يؤثر على هذه المعدلات. تركز هذه الدراسة على الآثار المترتبة لمعدلات ثابتة لامتصاص تركيزات الملوثات لكل من البنزين، النيكل، الكادميوم والنحاس باستخدام الكربون النشط المعدل. عندما ينخفض معدل ثابت الامتزاز، سوف يقل تركيز الملوثات مما يسفر عن القبول بالدليل للنموذج الرياضي المقترح. أيضاً تم مقارنة النموذج المقترح ببيانات عملية ونماذج أخري ليعطي مخرجات ذات دقة عالية.

الكلمات المفتاحية: النموذج الرياضي، مياه الصرف، الامتزاز، الامتصاص، الكربون النشط.

* Corresponding author's e-mail: ahmadsaadi47@yahoo.com

Nomenclature

Symbol	Definition (unit)
A	Waste water.
$K_{ad,1}^{+}$	Rate constant for adsorption of forward direction.
$C_{A.S}$	Concentration of pollution of adsorption for surf modified activated carbon.
C_A	Concentration of adsorption.
C_{Ai}	Initial concentration of adsorption.
C_V	V modified activated carbon concentration.
$K_{ad,1}^{-}$	Rate for constant adsorption of a reverse direction.
$K_{d,1}^{-}$	Rate for constant desorption of a reverse direction.
$K_{ad,1}^{+}$	Rate for constant desorption of a forward direction.
P_A	Partial pressure.
r_{ad}	Rate of adsorption.
r_d	Rate of desorption.
r_A	Rate of adsorption.
S	Modified activated carbonative carbon.
V_i	Volumetric flow rate.
V	Volume.
t	Time (s).
k_{fr}	Adsorption cap modified activated carbonity of the sorbent mg/g (l/mg)$^{1/n}$.
n	Freundlich's constants.
q_e	Amount of adsorbate adsorbed at equilibrium (mg/g).
q_{max}	Maximum monolayer adsorption cap modified activate carbonity of the adsorbent (mg/g).
C_e	Equilibrium concentration of adsorbate (mg/l).
K_{Ln}	Langmuir's adsorption constant related to free energy adsorption (l/mg).
C_{TM}	Temkin's constant related to the heat of sorption (J/mol).
C_{TMI}	Temkin's isotherm constant (l/g).
R	Gas constant (8.314 J/mol K).
T	Absolute temperature (K).
k_1	First-order rate constant (min^{-1}).
q_t	Amount of adsorbate adsorbed at any time (mg/g).

1. Introduction

Waste water is one of the biggest pollution problems in the world, and suggestions for its treatment have been drawn from experimental and theoretical works. In experimental work, a simplified method for ion exchange has been used to evaluate kinetic data. Many techniques have been explored using modified activated carbontivated carbon to remove carbon dioxide. One of the most important techniques that has been used is semi-batch remodified activated carbonator fixed inside modified activated carbontivated carbon to adsorb methane and carbon dioxide (Prasetyo and Dod 1998). Another technique used biomass of sargassum fluitant to make bio sorption for heavy metals and tannin gel has been used to adsorb chromium (Nakano *et al*. 2001). Some special materials have been used to remove cadmium and mercury ions from aqueous solutions using sorption on treated Pinus pinaster bark (Vazquez *et al.* 2002). Numerous experimental studies have used rice husk as an adsorbent for waste water treatment (Ajmal *et al.* 2003), and chitosan-cellulose hydrogel beads have been used to adsorb copper (Li and Bai 2005). Modified activated carbontivated carbon has been represented as one of the most effective modified activated carbontivated adsorption materials to be used to absorb carbon dioxide (Bog *et al.* 2006). Many researchers have used modified activated carbontivated carbon for waste water treatment (Afsaneh *et al.* 2008; Mohamed *et al.* 2008; Muhammad *et al.* 2008). A hybrid technique was used to produce a T-shirt model for waste water treatment.

Other exploratory works have explored waste water treatment options through a combination of experimental and theoretical work. The first adsorption mathematical model which was proposed in 1906 by Freundlich has been used in hetrogenous surf modified activated carbon adsorbent systems where the binding sites are not equivalent. A form of the Freundlich's model can be represented as follows:

$$q_e = k_{fr} {c_e}^{1/n} \tag{1}$$

$$lnq_e = lnk_{fr} + \frac{1}{n} lnc_e \tag{2}$$

The constants k_{fr} and n can be evaluated from the intercept and the slope of the linear plot of experimental data of ln q_e versus ln C_e.

A second important mathematical model for adsorption is Langmuir's isotherm model (Okieimen and Ogbeide 2009), which depends on an isothermal state when all the sites are homogenous compare to Freundlish's model, and all these sites are filled by molecules to be adsorbed. The linear form of the Langmuir isotherm can be represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{ln^k_{q_{max}}} + \frac{C_e}{q_{max}} \tag{3}$$

The values of the constants K_L and q_{max} can be evaluated from the intercept and the slope of the linear plot of experimental data of C_e/q_e versus C_e.

Temkin and Pyzhev (Lalhruaitluanga *et al*. 2010) studied extensively the heat of adsorption and the adsorbate-adsorbent intermodified activated carbonation on adsorption isotherms. Temkin and Pyzhev's mathematical model can be represented as follows:

$$q_e = C_{TM} \ln C_{TMI} + C_{TM} \ln C_e \tag{4}$$

The constants C_{TMI} and C_{TM} can be determined from the intercept and the slope of the linear plot of the experimental data of q_e versus ln C_e. The values of the constants C_{TMI} and C_{TM} are listed in Table 1.

The Lagergren mathematical model is represented as proportional to the first power of sorption cap modified activated carbonity of the adsorbent and can be expressed as follows (Khaled *et al*. 2009).

Table 1. Langmuir, Freundlich and Temkin models' constants and correlation coefficients for sorption of methylene blue (MB) into modified activated carbon.

Isotherm	Parameters	Values
Langmuir	Q_o (mg/g)	8.75
	K_{Ln} (l/mg)	0.23
Fruendlich	K_{Fr}	4.21
	n	4.13
Temkin	C_{TMI} (l/g)	11.3
	C_{TM}	1.5

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

Integrating Eq. (5) for the initial and end conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, and, after some rearrangement, a linear plot is obtained:

$$log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \quad (6)$$

values of k_1 and q_e were obtained from the slope and intercept, respectively. Table 2 lists Lagergren's mathematical model constants.

$$log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \quad (6)$$

Plots of log (q_e − q_t) versus t for the Lagergren mathematical model where the values of k_1 and q_e were obtained from the slope and intercept, respectively. Table 2 lists Lagergren's mathematical model constants.

2. Methodology

Deriving a mathematical model requires the provision of assumptions and a comparison with other models to create new ideas for a proposed model (Tables 3 and 4). Adsorption and desorption states represent active mechanisms for the system (Fig. 1) and can be derived as follows:

2.1. *Adsorption State*

This state depends on the properties of surface of adsorbent, partial pressure of fluid and rates constant of adsorption as seen in equations below:

$$A_1 + S \rightleftharpoons^{K^+_{ad,1}}_{K^-_{ad,1}} A_1 . S \quad (7)$$

$$r_{ad} = K^+_{ad,1} [\, P_A C_V - K^-_{ad,1} C_{A_1.S} \quad (8)$$

$$r_{ad} = K^+_{ad,1} [\, P_A C_V - \frac{C_{A_1.S}}{\frac{K^+_{ad,1}}{K^-_{ad,1}}} \quad (9)$$

substitute (9) in (8)

$$K^*_{ad} = {K^+_{ad,1}}\Big/{K^-_{ad,1}} \quad (10)$$

substitute (10) in (9)

Table 2. Correlation coefficients for adsorption of benzene on modified activated carbontivated carbon.

Initial concentration 10 g/l	$q_{e\,exp.}$ (mg/g)	Pseudo-first-order kinetic model		
		$q_{e\,cal.}$ (mg/g)	k_1 (1/min)	R^2
Benzene	4.14	2.3	0.003	0.915
Nickel	6.31	3.8	0.003	0.898
Copper	6.53	4.21	0.0037	0.927
Cadmium	7.31	5.47	0.0028	0.934

Table 3. The list of proposed mathematical model assumptions.

1. The fixed bed comprises liquid and solid phases.
2. No chemical remodified activate carbonation occurs inside a fixed bed.
3. Negligible radial temperature and concentration gradients exist in the fixed bed.
4. Adsorption occurs to adsorbent solid particles inside holes of modified activated carbon.
5. Desorption occurs to transfer solid particles from inside holes to the surf modified activated carbon of modified activated carbon.
6. Mass transfer occurs from surf modified activated carbon of modified activated carbon to the bulk flow.
7. The dynamics study is represented by the rates of adsorption and desorption at the surf modified activated carbon of modified activated carbon.
8. Heat transfer is considered in the new mathematical model.

Table 4. Differences between the proposed mathematical model and the other models.

No	Functions	New Mathematical model	Langmuir model	Freundlich isotherm model	Pseudo-first-order model
1	Phases	Liquid, gas and solid phase	Liquid phase	Liquid phase	Liquid phase
2	Mass transfer	Calculated without chemical remodified activate carbonation	Not calculated	Not calculated	Calculated without chemical remodified activate carbonation
3	Adsorption	Mass transfer from surf modified activate carbon to the entrails holes of modified activate carbon without chemical	Considered	Considered	Considered
4	Desorption	Mass transfer from entrails holes of MODIFIED ACTIVATE CARBON to the surface activate carbon without chemical	Not considered	Not considered	Not considered
5	Energy transfer	Considered	Not considered	Not considered	Not considered

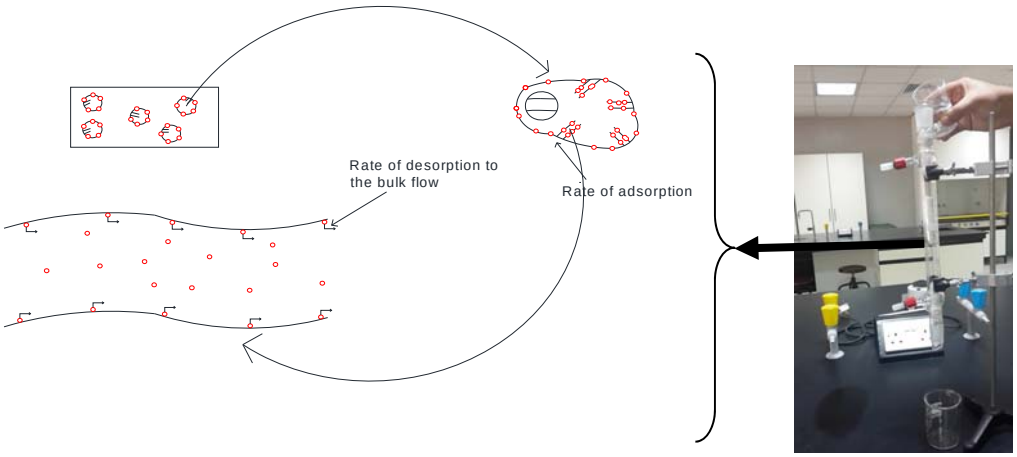

Figure 1. Steps of adsorption process.

2.2 Desorption State

This state depends on the same properties of adsorption but the molecules of adsorbent left to the bulk flow in opposite direction of adsorption's flowrate as seen in equations below:

$$r_{ad} = K^{+}_{ad,1} \left[P_{A_1} C_V - \frac{C_{A_1.S}}{K^{*}_{ad}} \right] \quad (11)$$

$$A_1.S \rightleftharpoons^{K^+_{S,1}}_{K^-_{S,1}} A_1 + S \quad (12)$$

$$r_d = K^+_{S,1} C_{A_1.S} - K^-_{S,1} P_{A_1} C_V \quad (13)$$

$$r_d = K^+_{S,1} \left[C_{A_1.S} \frac{P_{A_1} C_v}{\frac{K^+_{S,1}}{K^-_{S,1}}} \right] \quad (14)$$

$$K^*_S = \frac{K^+_{S,1}}{K^-_{S,1}} \quad (15)$$

Let

$$r_d = K^+_{S,1} \left[C_{A_1.S} - \frac{P_{A_1} C_V}{K^*_S} \right] \quad (16)$$

The mechanism of the rate of adsorption can be controlled in all states of the system. Thus, this is the most important assumption.

$rd = 0$. From equation (16)

$$\mathrm{C}_{A_1}.\mathrm{S} = \frac{P_{A_1} C_V}{K^*_S} \quad (17)$$

Substitute (17) in (11)

$$r_{ad} = K^+_{ad,1} \left[P_{A_1} C_V - \frac{P_{A_1} C_V}{K^*_S K^*_{ad}} \right] \quad (18)$$

$$C_T = C_{A.S} = \frac{P_{A_1} C_V}{K^*_S} \quad (19)$$

$$C_V = \frac{C_T K^*_S}{P_{A_1}} \quad (20)$$

Substitute (20) in (18)

$$r_{ad} = K^+_{ad,1} \left[C_T K^*_S - {C_T}/{K^*_{ad}} \right.$$

$$r_{ad} = K^+_{ad,1} C_T K^*_S - C_T K^-_{ad} \quad (21)$$

Representing the system as a continuous stirred-tank reactor (CSTR) process:

$$\frac{V_i}{V} \left[C_{Ai} - C_{A_1} \right] + r_A = \frac{dC_{A_1}}{dt} \quad (22)$$

The volumetric flow rate compared to the volume of the system is very limited, so

$$\frac{V_i}{V} = 0 \quad (23)$$

Equation (22) will be

$$r_a = \frac{dc}{dt} \quad (24)$$

The rate of remodified activate carbonation is represented as

$$r_a = -r_{ad} = \frac{dc_{A_1}}{dt} \quad (25)$$

Substitute equation (21) in (25)

$$-\left[K^+_{ad,1} C_T K^*_s - C_T K^-_{ad} \right] = \frac{dc_{A_1}}{dt} \quad (26)$$

Solve equation (26)

$$C_{A_1} = -\left[K^+_{ad,1} C_T K^*_s - C_T K^-_{ad} \right] \mathrm{t} + \text{constant} \quad (27)$$

Boundary conduction

At t=0 , $\mathrm{C}_{A_1} = \mathrm{C}_{\mathrm{Ai}}$, $constant = C_{Ai}$ (28)

Substitute in (21)

$$C_{A_1} = -\left[K^+_{ad,1} C_T K^*_s - C_T K^-_{ad} \right] \mathrm{t} + \mathrm{C}_{\mathrm{Ai}} \quad (29)$$

$$C_{A_1} = C_{Ai} - \mathrm{mt}$$

$$Where\ m = -C_T \left[K^+_{ad,1} K^*_s - K^-_{ad} \right]$$

3. Results and Discussion

The discussion that follows focuses on the experimental results associated with adsorbent benzene. The proposed mathematical model yielded good behavior for the experimental data from adsorbent benzene against the first order Lagergren model (Fig. 2).

Figure 3 shows results for adsorbent nickel using the proposed model and Lagergren model. Also, the proposed mathematical model was highly accurate, with results close to experimental data as compared to other models for copper and cadmium (Figs. 4 and 5, respectively).

Rates of adsorption and desorption have a big effect on pollutant concentrations. The rate of adsorption decreased the change of pollutant concentrations and also decreased the benzene, nickel, cadmium and copper (Figs. 6–9, respectively).

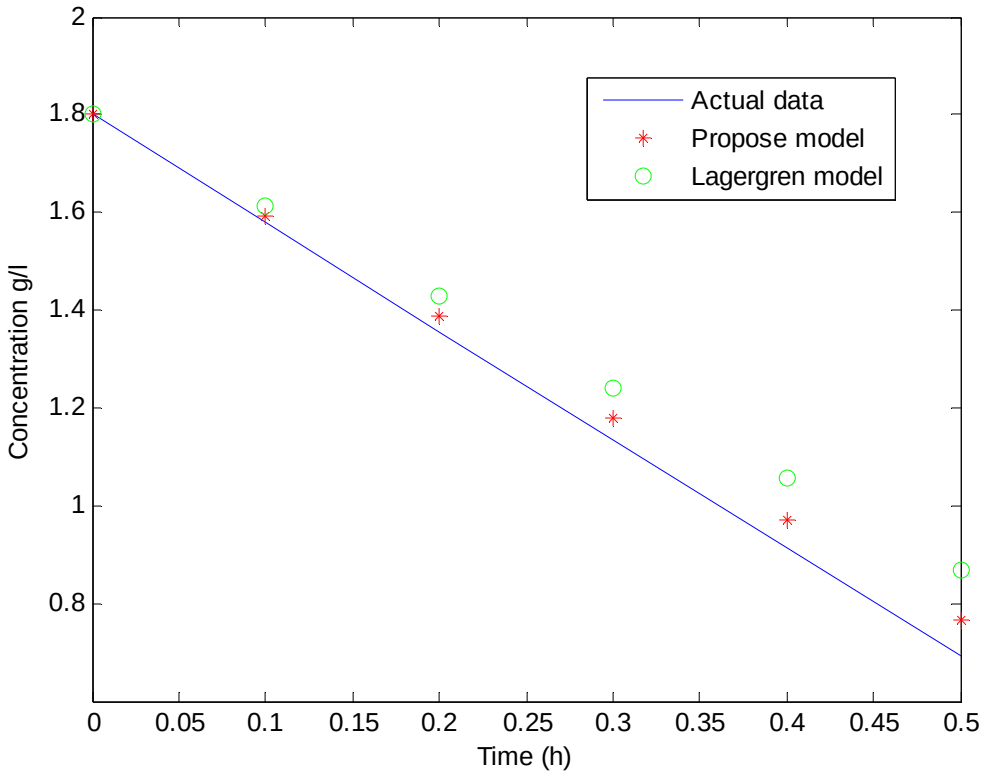

Figure 2. Comparison between proposed mathematical model and lagergren model for benzene.

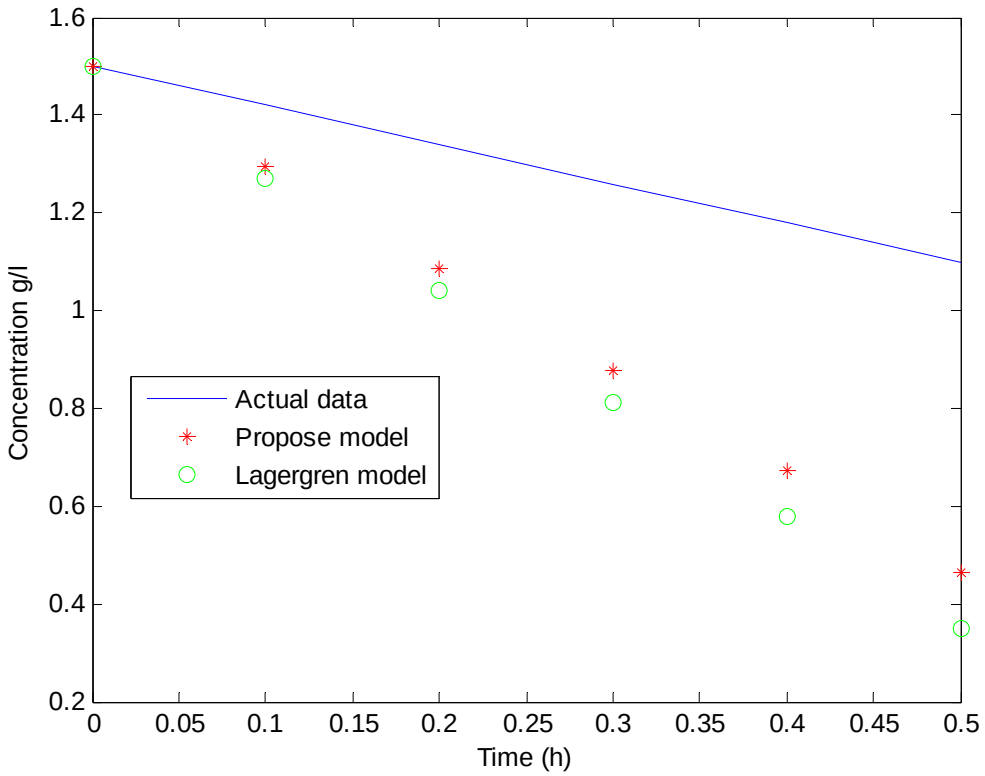

Figure 3. Comparison between proposed mathematical model and lagergren model for nickel.

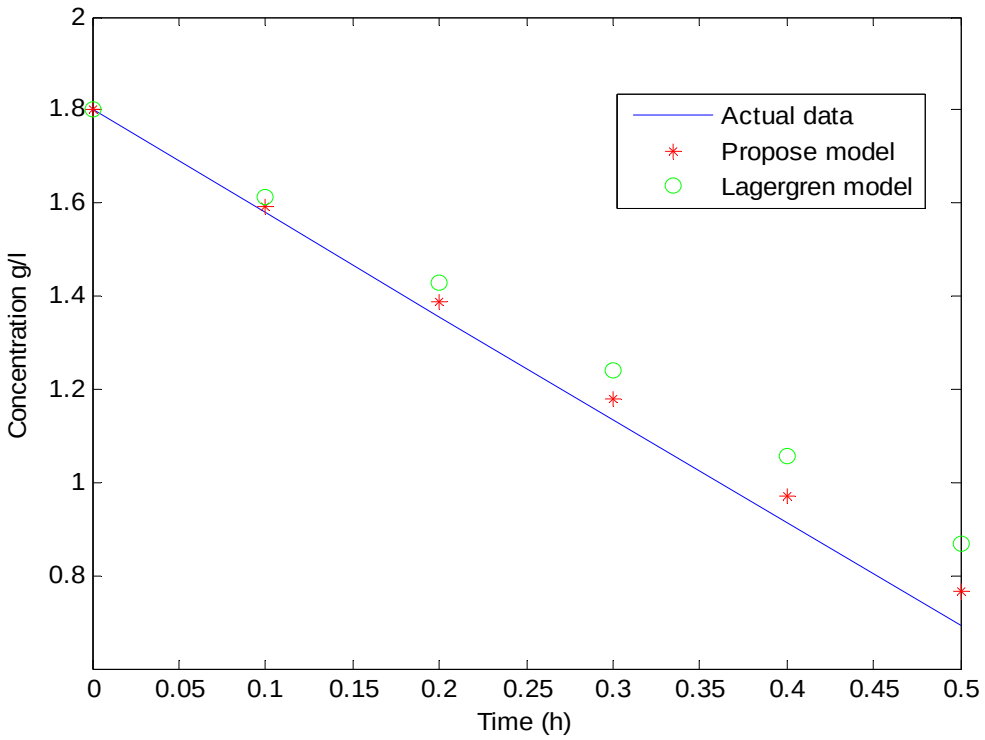

Figure 4. Comparison between proposed mathematical model and lagergren model for copper.

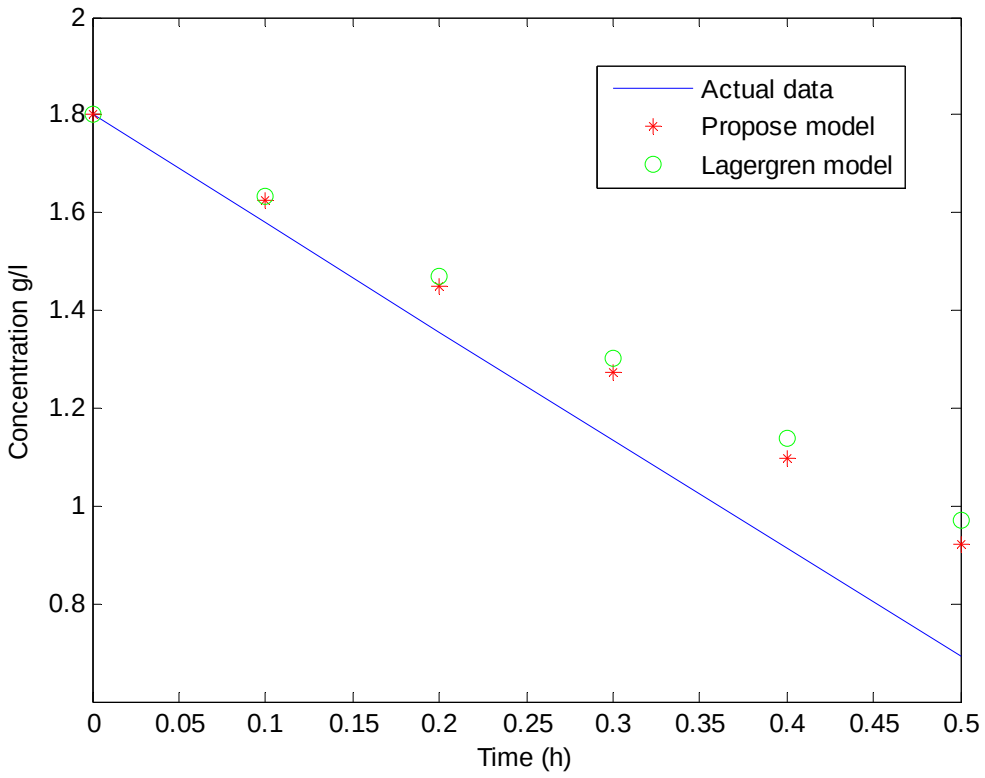

Figure 5. Comparison between proposed mathematical model and lagergren model for cadmium.

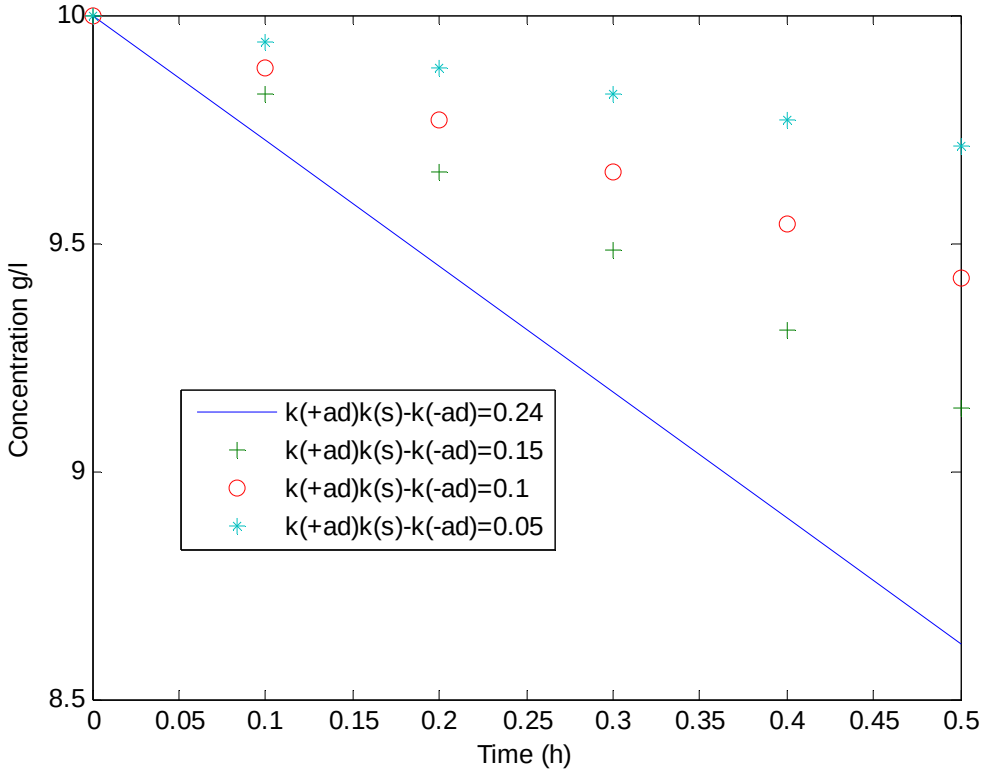

Figure 6. Effect of different rates of adsorption and desorption on pollutant concentration of benzene.

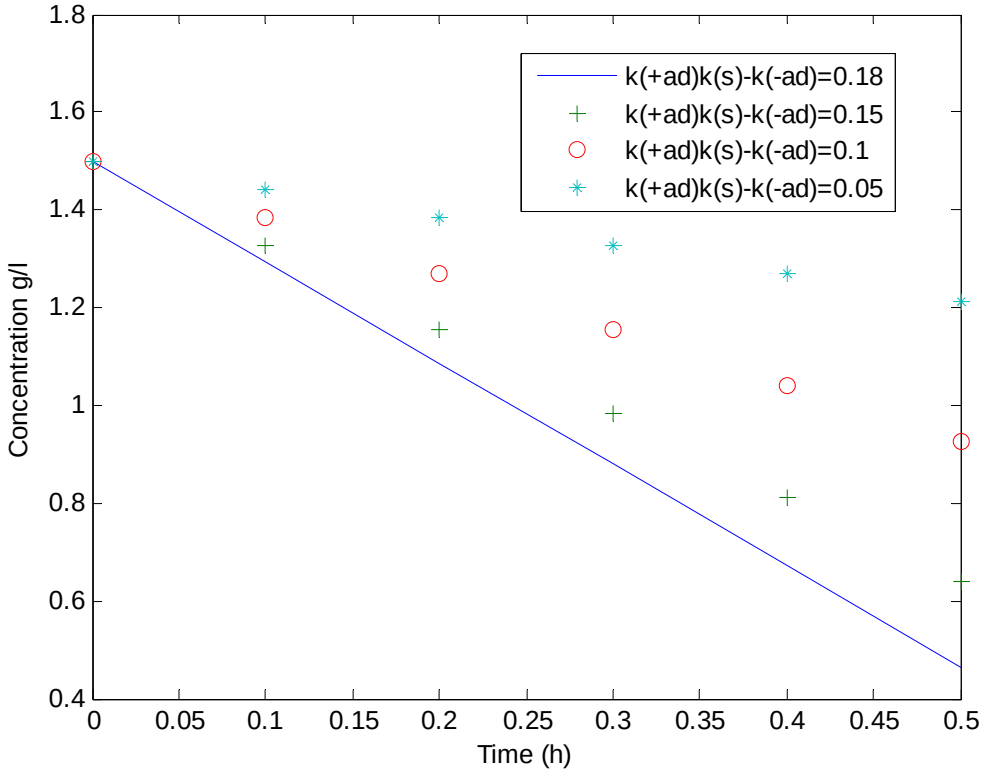

Figure 7. Effect of different rates of adsorption and desorption on pollutant concentration of nickel.

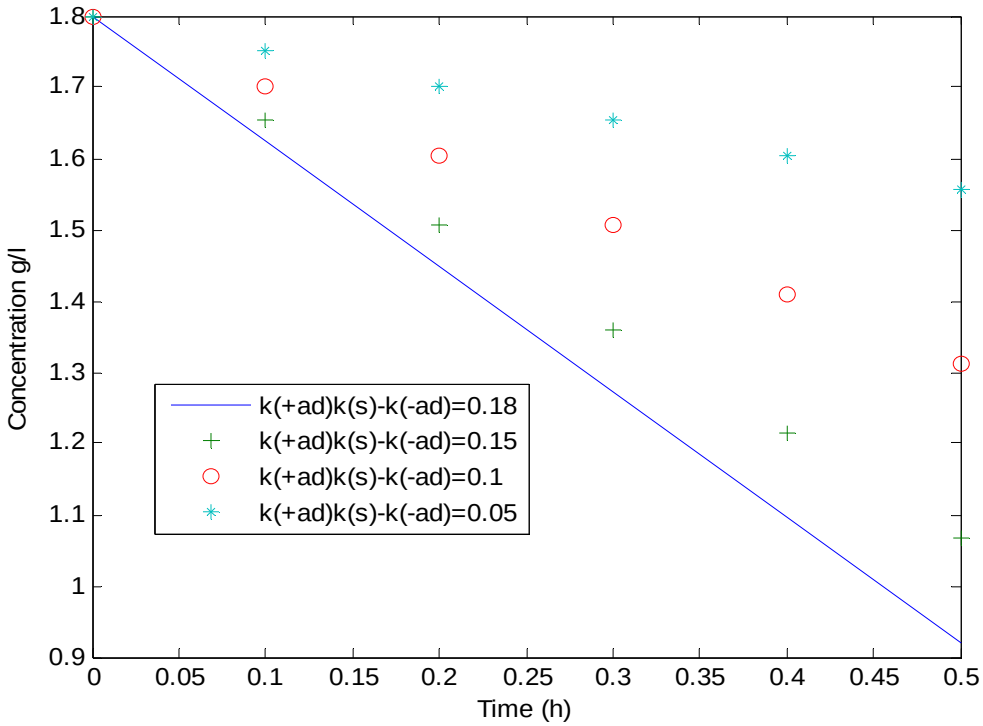

Figure 8. Effect of different rates of adsorption and desorption on pollutant concentration of cadmium.

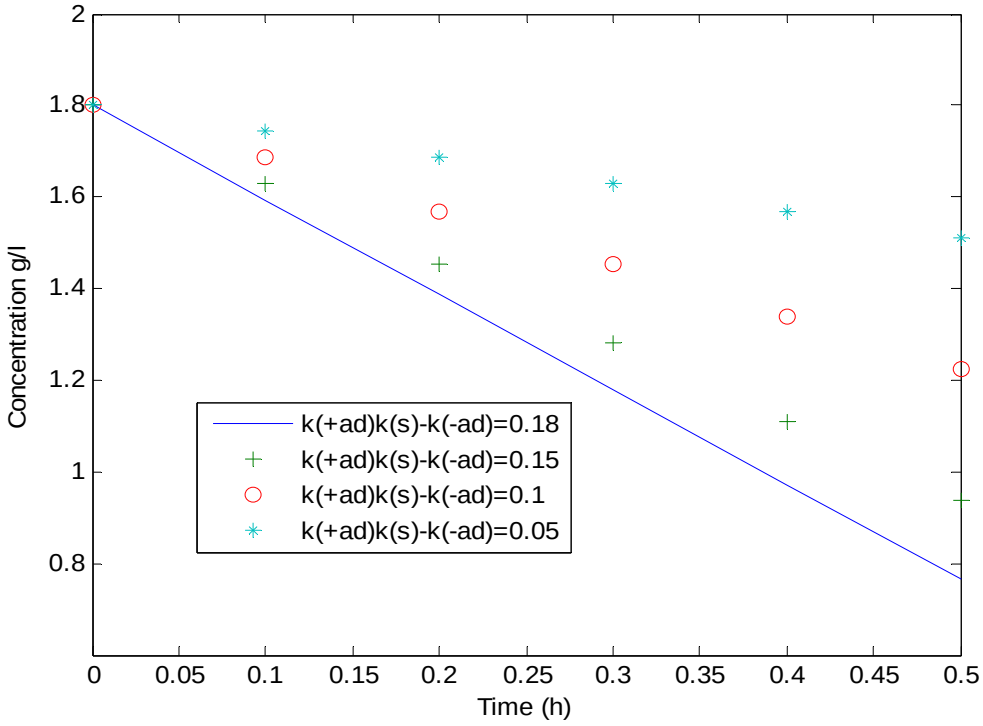

Figure 9. Effect of rates of adsorption and desorption on pollutant concentration of copper.

4. Conclusion

This proposed mathematical model has enough ability to evaluate dynamic adsorption and desorption for modified activate carbon to give clear view about mechanism of the system and very acceptable results due to inclusion of all

the rates types for adsorption and desorption compare to the other models.

References

Afsaneh S, Mohammad R, Hosein D, Amin G, Mohammad H (2008), Adsorption of carbon dioxide using impregnated modified activate carbontivated carbon promoted by Zinc. *International Journal of Greenhouse Gas Control* 3: 249-254.

Ajmal M, Rak R, Jamal A, Ahmad R (2003), Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater. *Bioresource Technology* 86: 147–149.

Bog G, Liping C, Kechang X (2006), Adsorption of carbon dioxide on modified activate carbontivated Carbon. *Journal of Natural Gas Chemistry* 15: 223-229.

Lin N. Bai R (2005), Copper absorption on chitosan-cellulose hydrogel beads: hydro-gel- beads: behaviors and mechanisms. *Separation And Purification Technology* 42: 237–247.

Lalhruaitluanga H, Jayaram K, Prasad M, Kumar K (2010), Lead (II) adsorption from aqueous solutions by raw and modified activate carbontivated charcoals of melocanna modified activate carboncifera roxburgh (bamboo)-A comparative study. *Journal of Hazardous Materials* 175: 311-318.

Khaled A, Nemr A, Sikaily A, Abdelwahab O (2009), Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon. *Desalination* 238: 210-232.

Mohamed K, Wan M, Chun Y, Donni A (2008), Adsorption cap modified activate carbonites of carbon dioxide, oxygen, nitrogen and methane on carbon molecular basket derived from polyethyleneimine impregnation on microporous palm shell modified activate carbontivated carbon. *Separation And Purification Technology* 62: 609–613.

Muhammad R, Raziya N, Muhammad A, Tariq M, Khalil R (2008), Pb (II) biosorption from hazardous aqueous streams using gossypium hirsutum (Cotton) waste biomass. *Journal of Hazardous Materials* 161: 88-94.

Nakano Y, Takeshita K, Tsutsumi T (2001), Adsorption mechanim of hevalent chromium by Redox within Condensed-Tannin Gel, *Water Research 35 :496-500.*

Okieimen C, Ogbeide S (2009), The Dependence On Temperature of Carbonization and chemical modified activate carbontivation on charmodified activate carbonteristics of granular modified activate carbontivated carbon charmodified activate carbonteristics. *Advanced Materials Research 62-64 : 398-403.*

Prasetyo I, Dod D (1998), Adsorption rate of methane and carbon dioxide on modified activate carbontivated carbon by the semibatch constant molar flow rate method. *Chemical Engineering Science* 53(19): 3459-3467.

Vazquez G, Gonzalez A, Freire S, Lopez, Antorrena G (2002), Removal of cadmium and mercury ions from aqueous solution by sorption on treated pinus pinaster bark: kinetics and isotherms. *Bioresource Technology* 822: 47-51.