Southeast-Asian J. of Sciences: Vol. 2, No 1 (2013) pp. 1-10

MODELING FOR METALS CONTAMINATED WASTEWATER BY ALGEA ADSORPTION

P. Chankitkan*, B. Pimpunchat*†, K. Chamsri*, W. Triampo‡, S. Amornsamankul**

***Indust. Math. Research Unit and Department of Mathematics*
King Mongkut's Institute of Technology Ladkrabang
Bangkok 10520, Thailand
Center of Excellence in Math., Bangkok 10400, Thailand
chankitkan_p@hotmail.com; knbusaya@kmitl.ac.th; kckannan@kmitl.ac.th

‡ Department of Physics, Faculty of Science
Mahidol University, Bangkok 10400, Thailand
Inst. for Innovative Learning, Mahidol Univ., Nakorn Prathom 73170, Thailand
C. of Excellence in Math., Bangkok 10400, Thailand
email: scwtr@mahidol.ac.th

***Dept. of Mathematics, Faculty of Science*
Mahidol University, Bangkok 10400, Thailand
Center of Excellence in Math., Bangkok 10400, Thailand
email: somkid.amo@mahidol.ac.th

Abstract

We studied the ability of adsorption of algae in wastewater polluted by alloys. A mathematical model is developed to describe the biosorption of metals by algae in the contaminated water. The analytic solution is obtained by using Similarity method. The result provides understanding the advection and diffusion of the metals in the contaminated water at various times and positions. It was found that the concentration of metals in the contaminated water consisting of the algae decreases over time and asymptotically reaches the equilibrium state. Moreover, the analytic results were validated by comparing with experimental data. This work is expected to greatly benefit an environmental science particularly concerning the wastewater treatment.

Key words: Biosorption, Wastewater, Advection, Diffusion, Similarity method, Equilibrium state.
*† Corresponding author

1 Introduction

Nowadays wastewater is one of the most problems of environment stem from community, agriculture and industrial effluents which are different amount of the byproduct of industrialization.With the industrial increase nowadays the problem of wastewater has become even more severe especially when lacking of good wastewater management. Industrial wastewaters differ in their impurities and here metals contaminated wastewater is considered for treatment aspect using microalgae. Normally, wastewater treatment can be as simple as chemical addition or as complex as the combination of multiple unit processes for a complete water treatment system. Here the process of adsorption is focused. The microalgae is used as an adsorption agent, thus the process is so called biosorption. Because aerobic treatment reservoir in our system has abundant the algae and the aquatic plant, they then act as wastewater cleaning metal alloys agent in the contaminated water. The mathematical model is developed to describe the biosorption of metals by algae in the contaminated water and the analytic solution is obtained for having insight into the problem[1-3].

In (2005)[4] Kumar and co-workers studied about adsorption of malachite green onto *Phithophora sp.* with the initial malachite green of (20-100 mg/l). They found that algae posses some capacity to uptake 64.4 mg/g at higher dye concentration of 100 mg/l and approach the equilibrium state around at 50 minutes. Recently,[5] Sukhuum and Inthorn have studied about removal of Cr^{+3} by *Rivularia sp.* and *Stigonema minutum.* They considered the initial concentration of Cr^{+3} 500 mg/l and found that Rivularia sp. and Stigonema minutum had the highest Cr^{+3} adsorption at 38.27 and 43.59 mg/g then reach equilibrium state at 120 minutes.

In this study the ability of adsorption of algae in wastewater polluted by alloys was investigated and mathematically analyzed particularly on concentration of metals in contaminated water by using mathematical model at any time and various distance.

2 Model formalism

By using the conservation of mass, the amount of metals remaining in after the contaminated water is given by the initial amount of the alloy in the wastewater minus and the amount adsorbed on the algae.

$$C = C_0 - C_t \tag{1}$$

where C is the concentration of metals in the remaining in the contaminated water (mg/l), C_0 is the initial concentration of metals in the contaminated water (mg/l), and C_t is the concentration adsorbed on the algae at any time(mg/l). The remaining concentration of metals in the contaminated water is obtained from the following mass balance

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} + f(t) \tag{2}$$

where D_x is a diffusion coefficient, v is the velocity in the x direction , t is time of adsorption. To find the function $f(t)$, we begin with by pseudo first order model.

$$\frac{dq}{dt} = k_1(q_{al} - q) \tag{3}$$

where q_{al} and q are the amount of adsorbed metals on algae at equilibrium and at any time (mg/g), respectively , k_1 is the rate constant first order biosorption.

Integrating Equation (3);

$$\int_0^{q_t} \frac{dq}{q_{al} - q} = \int_0^t k_1 dt$$

$$q_t = q_{al} + e^{-k_1 t}(q_0 - q_{al}) \tag{4}$$

Then formula ability adsorp of algae

$$q_0 = \frac{M_0}{M_s},\ q_t = \frac{M_t}{M_s},\ q_{al} = \frac{M_{al}}{M_s} \tag{5}$$

where q_t is the amounts of adsorbed metals on algae at any time (mg/g), M_s is the mass of algae (g), M_0, M_t and M_{al} is the mass of adsorbed metals on algae at initial time, any time and equilibrium state(mg), respectively.

Solving (4) and (5), we obtain;

$$M_t = M_{al} + e^{-k_1 t}(M_0 - M_{al}) \tag{6}$$

Let M is the remaining mass of metals in the contaminated water (mg). From conservation of mass we have:

$$M = M_{total} - M_t \tag{7}$$

where M_{total} is total mass of metal (mg).

Substituting (6) into conservation of mass (7), we obtain;

$$M = M_{total} - (M_{al} + e^{-k_1 t}(M_0 - M_{al})) \tag{8}$$

Let V be a constant volume (l). Dividing Equation (8) by V, we have:

$$C = e^{-k_1 t} C_{al} + (C_0 - C_{al}) \tag{9}$$

Differentiating (9) with respect to t, equation (9) can be rewritten as:

$$f(t) = -k_1(C - (C_0 - C_{al})) \tag{10}$$

Substituting (10) into (2) yields:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - k_1(C - (C_0 - C_{al}))$$

Let $C^* = C - C_0 + C_{al}$:

$$\frac{\partial C^*}{\partial t} = D_x \frac{\partial^2 C^*}{\partial x^2} - v\frac{\partial C^*}{\partial x} - k_1 C^* \tag{11}$$

The initial condition is

$$C^*(x,0) = C_0 \tag{12}$$

and the boundary conditions are

$$C^*(0,t) = C_1, \ \frac{\partial C^*}{\partial x}(L,t) = 0, \ 0 \le x \le L \tag{13}$$

where C_1 is a constant. The equation (11) is the mathematical model for this problem. We derive the similarity solution of equation (11) using the group theory method of similarity analysis.

3 Similarity Analysis by Invariance Groups

3.1 The Analysis of invariance

There are several thechniques for solving partial differential equation by using similarity methods such as Free Parameter Method, Separation of Variables Method, Group Theory Method and Dimensional Analysis Method. Among these methods, we consider to apply the group theory method of similarity methods for solving the equation (11).

To solve Equation (11) using the one parameter group of transformation

$$\begin{aligned} T &= a^n t \Rightarrow t = a^{-n} T \\ X &= a^m x \Rightarrow x = a^{-m} X \\ C &= a^p C^* \Rightarrow C^* = a^{-p} C \end{aligned} \tag{14}$$

where T, X, and C are functions of t, x, and C^*, respectively, $'a'$ is an variable and m,n, p are the parameters.

Employing Equation (14) into Equation (11), we have:

$$\frac{\partial C^*}{\partial t} - D_x\frac{\partial^2 C^*}{\partial X^2} + v\frac{\partial C^*}{\partial X} + k_1 C^* = a^{-p+n}\frac{\partial C}{\partial T} - D_x a^{-p+2m}\frac{\partial^2 C}{\partial X^2} + v a^{-p+m}\frac{\partial C}{\partial X} + k_1 a^{-p} C \tag{15}$$

Equating the powers of $'a'$, becomes;

$$-p + n = -p + 2m = -p + m = -p$$

Let

$$\begin{aligned} -p+2m &= -p+m \Rightarrow m=0 \\ -p+n &= -p+m \Rightarrow m=0,\ n=0 \end{aligned}$$

Employing these values in Equation (15) , becomes ;

$$\frac{\partial C^*}{\partial t} - D_x \frac{\partial^2 C^*}{\partial X^2} + v \frac{\partial C^*}{\partial X} + k_1 C^* \ = \ a^{-p} \left(\frac{\partial C}{\partial T} - D_x \frac{\partial^2 C}{\partial X^2} + v \frac{\partial C}{\partial X} + k_1 C \right)$$

If $p \equiv 0$then the equation will reduce into the constant conformally invariant.

3.2 Similarity Solution

Let

$$\eta \ = \ xt^s \tag{16}$$

To reduce equation (21) to the constant conformaly invariant;

$$\eta = xt^s = \left(a^{-m}X\right)\left(a^{-n}T\right)^s = a^{-m-ns} \cdot XT^s \left(only\ if - m - ns = 0,\ s = \frac{-m}{n} \right)$$

Hence

$$\eta = xt^{\left(-\frac{m}{n}\right)}$$

Again consider the another function g which is the function of also the dependent variable C^* as well as the independent variable t

Let

$$g \ = \ C^* t^r \tag{17}$$

To reduce into constant conformaly invariant;

$$g \ = \ \left(a^{-p}C\right)\left(a^{-n}T\right)^r \ = \ a^{-p-nr} C T^r \quad \left(only\ if - p - nr = 0,\ r = \frac{-p}{n} \right)$$

Then

$$g \ = \ C^* t^{\left(-\frac{p}{n}\right)}$$

Choose: $g \ = \ C^* t^{\left(-\frac{p}{n}\right)} \ = \ F(\eta)$

Now, we have to define the value of $F(\eta)$:

$$\begin{aligned} \frac{\partial C^*}{\partial t} &= t^{\left(\frac{p-n}{n}\right)} \left(\frac{pF(\eta) - m\eta F'(\eta)}{n} \right) \\ \frac{\partial C^*}{\partial x} &= t^{\left(\frac{p-m}{n}\right)} F'(\eta) \\ \frac{\partial^2 C^*}{\partial x^2} &= t^{\left(\frac{p-2m}{n}\right)} F''(\eta) \end{aligned} \tag{18}$$

Substituting (18) into (11) , can be written:

$$t^{\left(\frac{p-n}{n}\right)}\left(\frac{pF-m\eta F^{'}}{n}\right)-D_{x}t^{\frac{p-2m}{n}}F^{''}+vt^{\frac{p-m}{n}}F^{'}+k_{1}t^{\frac{p}{n}}F \tag{19}$$

From: $-p+n=-p+2m=-p+m=-p$

Thus: $-\left(\frac{p-n}{n}\right)=-\left(\frac{p-2m}{n}\right) \;=\; -\left(\frac{p-m}{n}\right) \;=\; -\frac{p}{n}$

We consider:

1) If $\frac{p-n}{n}=0$, then $\frac{p}{n}=1$ & $\frac{p-2m}{n}=0$ then $\frac{p}{n}=\frac{2m}{n}\Rightarrow\frac{m}{n}=\frac{1}{2}$

2) If $\frac{p-n}{n}=0$, then $\frac{p}{n}=1$ & $\frac{p-m}{n}=0$ the $\frac{p}{n}=\frac{m}{n}\Rightarrow\frac{m}{n}=1$

We choose case 2). Then the equation (19) becomes:

$$D_{x}F^{''}(\eta)+(\eta-v)F^{'}(\eta)+(1+k_{1})F(\eta) \;=\; 0 \tag{20}$$

The initial condition is

$$F(\eta(x,0)) \;=\; 0 \tag{21}$$

and the boundary conditions are

$$F(\eta(0,t))=(C_{1}-C_{0}+C_{al})\,t^{\left(-\frac{p}{n}\right)},t\geq 0,\frac{\partial F(\eta(L,t))}{\partial\eta}=0\;,\forall x,t \tag{22}$$

From equation (20) assuming that: $F^{(\eta)}=e^{a\eta}$

We get: $e^{a\eta}\left(D_{x}a^{2}+(\eta-v)\,a-(1+k_{1})\right) \;=\; 0 \quad ,e^{a\eta}\neq 0$

General solution is form: $F(\eta)=c_{1}F_{1}(\eta)+c_{2}F_{2}(\eta)$

Thus;

$$F(\eta) \;=\; c_{1}e^{\left(-\frac{(\eta-v)}{2D_{x}}+\frac{1}{2}\sqrt{\left(\frac{\eta-v}{D_{x}}\right)^{2}+\frac{4(1+k_{1})}{D_{x}}}\right)\eta}+c_{2}e^{\left(-\frac{(\eta-v)}{2D_{x}}-\frac{1}{2}\sqrt{\left(\frac{\eta-v}{D_{x}}\right)^{2}+\frac{4(1+k_{1})}{D_{x}}}\right)\eta}$$

Substituting the boundary conditions to find the arbitrary constants, we have;

$$F(\eta) \;=\; (C_{1}-C_{0}+C_{al})\,t^{\left(-\frac{p}{n}\right)}e^{\left(-\frac{(\eta-v)}{2D_{x}}-\frac{1}{2}\sqrt{\left(\frac{\eta-v}{D_{x}}\right)^{2}+\frac{4(1+k_{1})}{D_{x}}}\right)\eta}$$

or

$$C(x,t) \;=\; (C_{1}-C_{0}+C_{al})\,e^{\left(-\frac{\left(xt^{\left(-\frac{m}{n}\right)}-v\right)}{2D_{x}}-\frac{1}{2}\sqrt{\left(\frac{xt^{\left(-\frac{m}{n}\right)}-v}{D_{x}}\right)^{2}+\frac{4(1+k_{1})}{D_{x}}}\right)xt^{\left(-\frac{m}{n}\right)}} \tag{23}$$

4 Results and Discussion

In this research, We use experimental data of the adsorption of malachite green onto *Phithophora sp.*[4]. We shows the comparing analytical results with experimental data also with the average analytical result.

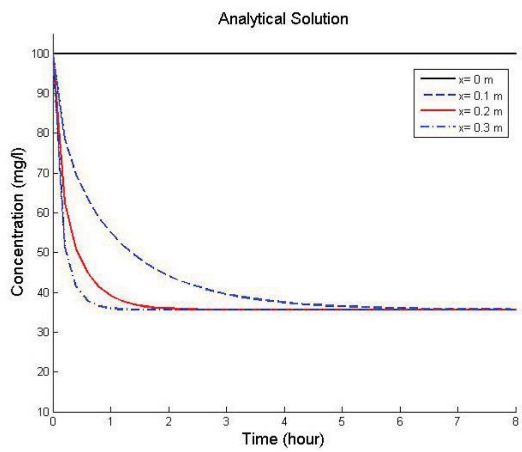

Figure 1: Shows the remainder of concentration of dye in water with analytic solution after adsorption by *Phithophora sp.* The result shows any position decrease and asymptotically reaches the equilibrium state at 35.7 mg/l

In research [9] studied adsorption of chromium (VI) from electroplating factory by chitosan resin. We use experiment data for comparing analytical result and average analytical result as shown in Figure 1-4.

5 Conclusion

The proposed results of concentration of metals contaminated in water with algae showed that the concentrations of contaminated water in mathematical model decrease to equilibrium state in every case. The results from two related papers, chromium adsorption with chitosan resin and dye adsorption by Phithophora sp. had been compared with our results. There has been satisfactory agreement between the theoretical mathematical model and experimental data.

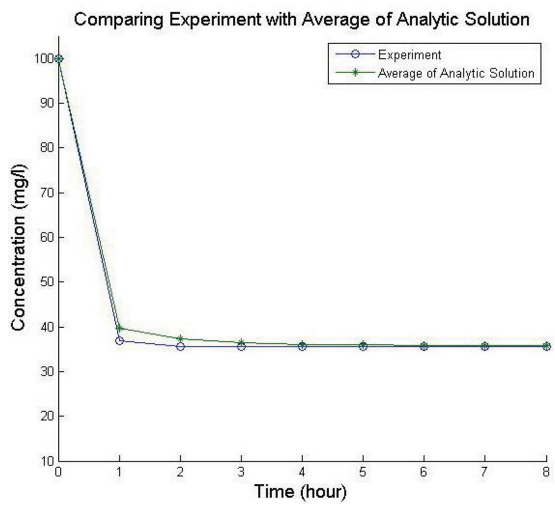

Figure 2: Comparing experiment with average analytic solution found that experimental result conform to average analytic solution and asymptotically reaches the equilibrium state 35.7 mg/l at 50 minutes.

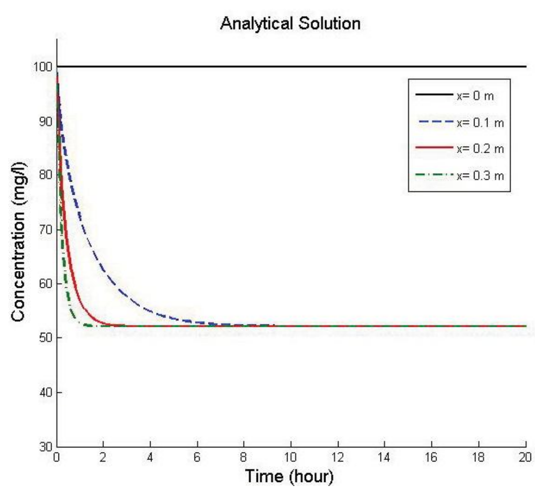

Figure 3: Shows the remainder of concentration of chromium (VI) in water with analytic solution after adsorption by chitosan resin. The result shows any position decrease and asymptotically reaches the equilibrium state at 52.2 mg/l

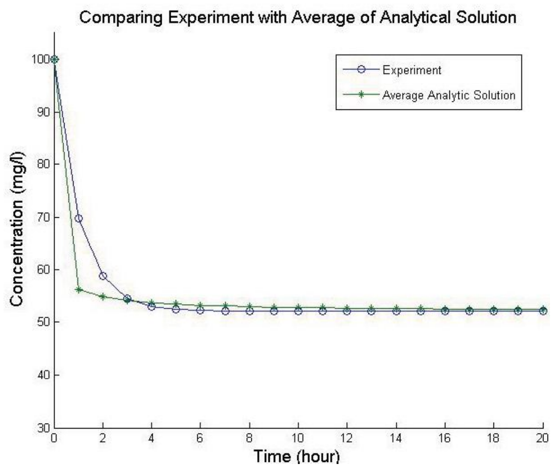

Figure 4: Comparing experiment with average analytic solution found that experimental result conform to average analytic solution and asymptotically reaches the equilibrium state 52.2 mg/l at 6 hour.

6 Acknowledgments

This work is partially supported by Centre of Excellence in Mathematics, The Commission on Higher Education, Thailand.

References

[1] *Equilibrium biosorption performance*,[online]27 February 2012 Time 14.22 pm.,From http://biosorption.mcgill.ca/publication/book/6.1-4w (103-16).pdf.

[2] Pradthana P,*Adsorption process*,[online] 27 February 2012 Time 13.05 pm., From http://pradthana.wordpress.com/2008/04/13/adsorption-process/.

[3] SA.Gujarat,*Similarity Solution of the Telegraph Equation to Oceanic Diffusion*, Int. J, of Appl. Math and Mech, 8(14) (2012), 88–104.

[4] K. Vansanth Kumar, S.Sivanesan and V. Rammamurthi,*Adsorption of malachite green onto Pithophora sp. a fresh water algae: Equilibrium and kinetic modeling*, Elsevier Ltd., 40 (2005), 2865–2872.

[5] C.Sukhuum , D. Inthorn,*Removal of Cr+3 by Rivularia sp. and Stigonema minutum*, The 11th Khon Kean University 2010 Graduate Research Conference.

[6] D.Sarkar and D.K. Chattoraj, *Action Parameters for Kinetics of Protien Adsorption* , Silica - WaterInterface, J. Colloid Interface Sci.157, 219–226.

[7] Zawani Z, Luqman Chuah A, Thomas S. Y. Choong,*Equilibium, Kinetics and Thermodynamic Studies : Adsorption of Removal Black 5 on the Palm Kernel Shell Activated Carbon*,(PKS - AC), European Journal of Scientific Research ISSN 1450 - 216X, vol.37 N0.1(2009), 63–71.

[8] C.F. Chan Man Fong, D De Kee,P.N. Kaloni,*Advance Mathematics for Engineering and Science*,Apr 2003., pp.523.

[9] K.Piyamongkol, J.Tanwat, P.Pomongkolkul,C.Kongsompak,*Kinetic Adsorption of Chromium (VI) from Electroplating Factory onto Chitosan Resin*, The Journal of KMUTNB, 18 (1), Jan - Apr (2008).