LATTICE GAS AUTOMATA SIMULATION OF ADSORPTION PROCESS OF POLYMER IN POROUS MEDIA

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Abstract   Lattice gas automata (LGA) model is developed to simulate polymer adsorption process by adding some collision rules. The simulation result of the model is matched with batch experiment and compared with accepted isothermal adsorption equations. They show that the model is viable to perform simulation of the polymer adsorption process. The LGA model is then applied for simulating continuous polymer solution flow through porous media. Some parameters such as concentration, surface area and porosity are varied to examine their effects. The concentration and porosity parameters are found to affect adsorption rate at the transient period whereas the surface area affects the maximum number of adsorbed polymer molecules. Meanwhile, the polymer adsorption in porous media may decrease its permeability and fluid velocity.

چکیده   مدل LGA برای شبیه سازی فرایند جذب سطحی پلیمر از طریق قـوانین برخـورد توسـعه داده شـده است. نتیجه شبیه سازی با داده های آزمایش غیر پیوسته وفـق داده شـده و بـا معـادلات شـناخته شـده جـذب سطحی تک دما مقایسه شده است. مدل ساخته شده قادر به شبیه سازی فرایند جذب سطحی پلیمر بوده اسـت. مدل LGA سپس برای شبیه سازی جریان پیوسته محلول پلیمر در محیط متخلخل بکار برده شده اسـت. برخی پارامترها مانند غلظت، مساحت سطح و تخلخل تغییر داده شد تا میزان تاثیر آنها معین شـود. غلظـت و تخلخـل در دوره گذرا بر سرعت جذب سطحی تاثیر می گذارد. مساحت سطح بر حداکثر تعداد مولکولهای پلیمر جذب شـده تاثیر می گذارد. در حالی که جذب سطحی پلیمـر در محـیط متخلخـل نفـوذ پـذیری و سـرعت سـیال را محتملا" کاهش می دهد.

1. INTRODUCTION

In polymer flooding, polymer is used to viscosify the displacing fluid, which increases the sweep efficiency of the process. The interaction between polymer molecules and solid may cause adsorption. The adsorption of polymer plays an important role for the success of a polymer flooding in oil reservoir. Adsorption at solid surface of porous media is largely the result of binding forces between the molecules of the polymer and the molecules of solid [1].

The occurrence of polymer adsorption in porous

media may alter some properties of rock and fluid. Physically, the precipitation of polymer on solid surface may constrict the pore channel. This causes the ability of the porous media to let the fluid flow through the pore channel reduces. This measure is well known as permeability.

Some researchers have developed simulators of polymer flow in porous media using macro-scale approach [2-5]. The macro-scale approach does not usually consider the behavior of polymer particles. The discussions about polymer adsorption are only limited in macroscopic phenomena such as the volume of adsorbed polymer, while in reality adsorption can occur
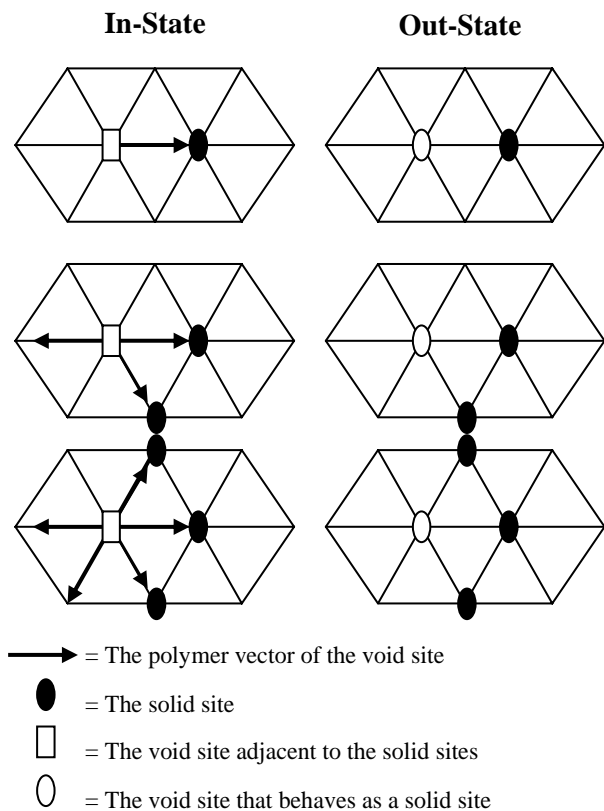
In-State   **Out-State**

➜ = The polymer vector of the void site

⬤ = The solid site

▢ = The void site adjacent to the solid sites

◯ = The void site that behaves as a solid site

Figure 1. Collision rules for polymer adsorption process.

monolayer or multilayer. Modeling microscopic phenomena such as polymer adsorption process should be investigated using micro-scale approach.

Various methods of meso-scale approach have been also applied to simulate the formation, the dynamics, and the interaction of polymers using lattice polymer automata [6] and lattice molecular automaton [7]. In this paper, meso-scale approach i.e. FHP-III of LGA model [8] is used to simulate the monolayer polymer adsorption in porous media. In order to correlate between meso-scale and micro-scale, the simulation result of the LGA model is matched with batch experiment. Here, the correlation between LGA particle and molecule number of real polymer is determined. The simulation result is also compared with Langmuir and Freundlich adsorption equations to know

the agreement among them.

The model is then used to simulate adsorption process in continuous fluid flow in porous media. Some related factors to the adsorption such as polymer concentration, surface area of solid material, and porosity of porous media are examined to estimate their effects. The impacts of polymer adsorption to the fluid and rock properties i.e. velocity of fluid and permeability of porous media are predicted.

2. MODELING OF POLYMER ADSORPTION

The arrangement of adsorbed polymer molecules on solid surface can be classified into two types. The monolayer adsorbed polymer molecules form only one molecular layer on solid surfaces where all adsorbed molecules are in contact with the surface. The multilayer adsorbed polymer particles can form more than one molecular layer [9]. The experimental curve of isothermal adsorption on sand grains conforms to monolayer polymer adsorption [10]. Referring to the experiment, the process of monolayer polymer adsorption is modeled.

In order to simulate the phenomenon of polymer adsorption in LGA model, new collision rules should be introduced. We define that a void site, that is a neighbor of solid sites, will behave as a solid site if the net vector of its polymer particles tends to the solid sites. Polymer particles that contained in the site will become stationary particles and adhere to the surface. The polymer particles give place as fluid particles and counted as adsorbed polymer particles. As a consequence the total particles number of polymer in solution will reduce.

The collision rules allow particles of polymer near the solid surface to be bound. The bounding process may continue until the entire surface was covered with the adsorbed polymer particles. The collision rules are intended for monolayer polymer adsorption process. In this model, the adsorption processes of the polymer particles for LGA are shown in Figure 1.
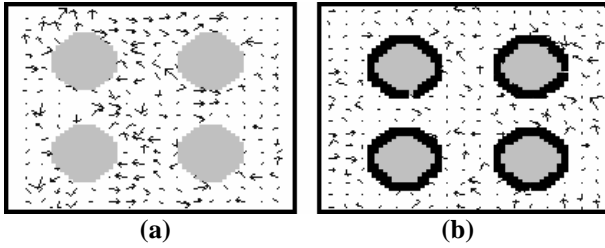
Figure 2. The modeling of batch system. Initial condition of the system (a). Adsorption process has taken place (b). Gray regions represent solid material. Direction and length of each arrow represent direction and speed of local flow. Black layers represent adsorbed particles. White region represents pore space.

Figure 3. The modeling of continuous system. Initial condition of the system (a). Adsorption process has taken place (b).

The combinations of polymer, porous media, and solvent factors determine the level of polymer adsorption. Since the combinations of the factors are rarely uniform in entire porous media, the binding process of polymer particles may not the same in every part of solid surface of porous media. To satisfy the condition we use the probability factor of polymer adsorption occurrence. This factor is connected to the collision rules. The probability factor (P_{pa}) is defined by the following equation:

$$P_{pa} = f(C) \qquad (1)$$

where C is concentration of polymer in solution (ppm).

2.1. Simulation Models   The adsorption process in Batch and continuous systems may be simulated. To perform the simulation, previously the systems should be modeled into LGA.

A. Batch System The simulation of adsorption in batch system can be conducted using the following way:
1. The lattice of LGA model is arranged to represent sand grains in a pack as depicted in Figure 2A. In the figure, the surface length of solid particles should correspond to the surface area of sand grains. Closed borders express the pack.
2. Moving fluid particles are placed on the white region to represent the motions of polymer solution among the sand grains in shaken pack.
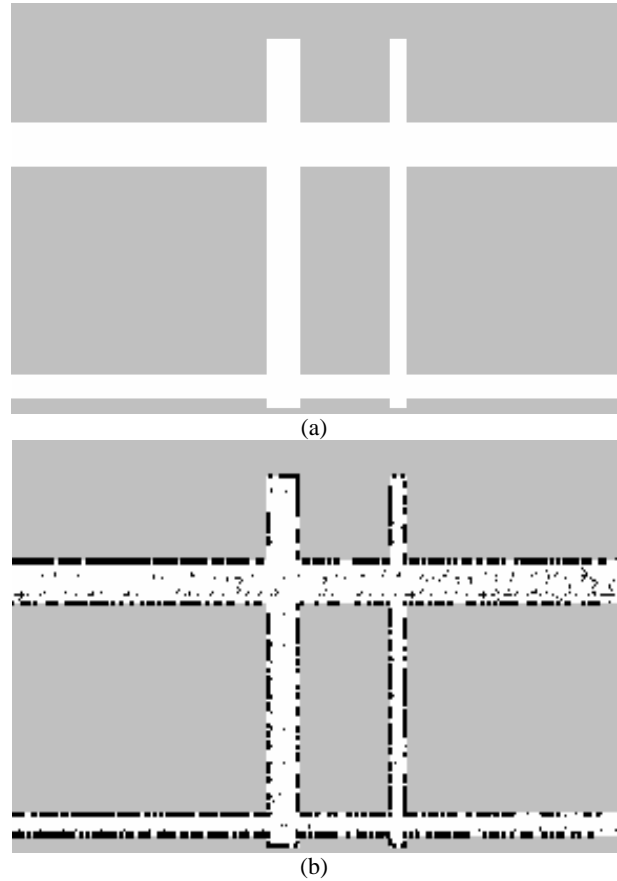
3. The collision rules (Figure 1) are applied to activate the adsorption process.
The distribution of the adsorbed polymer molecules on sand surface may be represented by the adsorbed LGA particles (black layers) as given in Figure 2B.

B. Continuous System   Meanwhile, the simulation of adsorption of continuous polymer flow in porous media can be conducted as follows:
1. An LGA porous medium is built to describe the real porous rock as depicted in Figure 3A. The physical properties of the medium such as porosity and permeability should be adjusted.
2. Moving fluid particles are introduced at the left side of the medium. The particles will flow along the pore space.
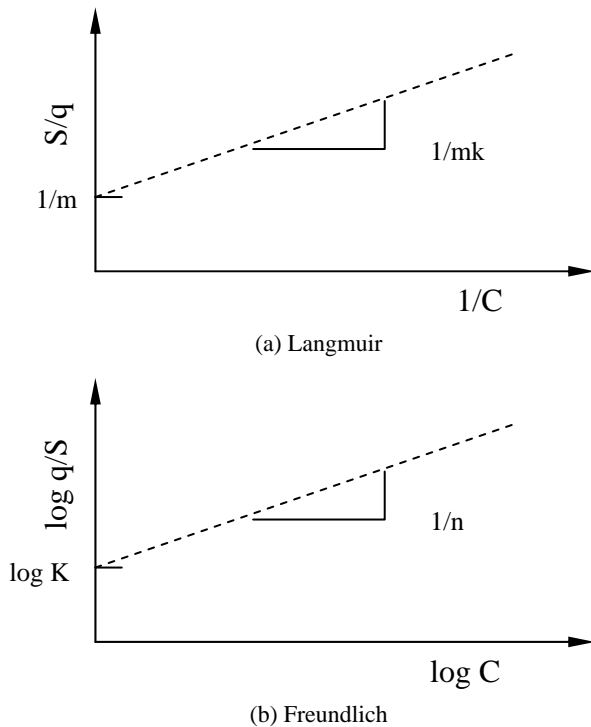3. The collision rules (Figure 1) are applied to

(a) Langmuir

(b) Freundlich

Figure 4. Graphical evaluation of isothermal constants.

activate the adsorption process.

The adsorbed particles (black line segments) on the solid surface are shown in Figure 3B.

2.2. Langmuir And Freundlich Equations

The measurement of the amount adsorbed on adsorbent versus equilibrium concentration at a particular constant temperature results in an adsorption isotherm. Adsorption isotherm is useful for characterizing adsorbents with respect to different adsorbates [1,11]. Many isotherm equations describe models of adsorption [12]. Two adsorption isotherm equations that used to describe the adsorbed polymer on sand are Langmuir, Freundlich [1,13,14]:

The form of the Langmuir model to estimate the number of adsorbed molecules on surface may expressed by

$$\frac{q}{S} = \frac{mKC}{1+KC} \qquad (2)$$

which can be arranged to a straight line form

$$\frac{S}{q} = \frac{1}{m} + \frac{1}{mKC} \qquad (3)$$

where q is number of molecules adsorbed on solid when equilibrium concentration is C; S is surface area; C is concentration of particles in solution at equilibrium; m and K are Langmuir isotherm constant; 1/m is slope of the line; 1/mk is intercept of the line. Langmuir isotherm equation is used for the case of monolayer adsorption [15].

The Freundlich isotherm model is defined by

$$\frac{q}{S} = KC^{1/n} \qquad (4)$$

which can be expressed into a straight line form

$$\log\frac{q}{S} = \log K + \frac{1}{n}\log C \qquad (5)$$

where K and n are Freundlich isotherm constants; log k is intercept of the line; 1/n is the slope of the line. The constants K and n are obtained by plotting C and q on log-log plot. If the coefficient n is equal to or approach to 1, then the Freundlich isotherm equation becomes a linear relationship and may be used for monolayer adsorption [16]. The advantage of Freundlich equation is in cases where the actual identity of the adsorbate is not known [17]. Whereas, the disadvantages of using the Freundlich equation are that it is only useful for limited concentration ranges and it has no predictive ability with regard to adsorption isotherms for similar adsorbates. A new Freundlich plot must be produced for each adsorbate-adsorbent combination [11]. Equations (3) and (5) can be expressed in form of graphic as shown in Figure 4.

3. EXPERIMENT AND SIMULATIONS

A. Experiment and Simulation of Polymer Adsorption in Batch System The validation of adsorption process using LGA simulator is verified with batch experiment [10]. The brief of
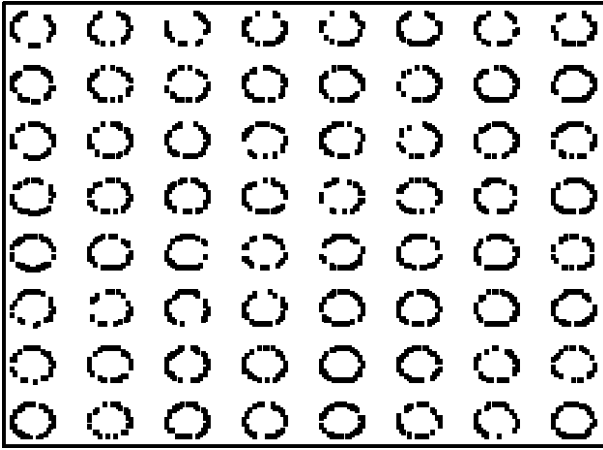
Figure 5. Simulation of polymer adsorption for the batch experiment after 5000 seconds. Concentration of polymer is 200 ppm.
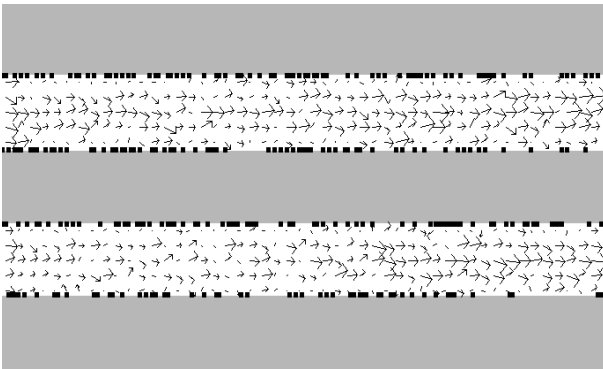

Figure 6. Polymer adsorption in the porous medium 1 after 5000 seconds. Concentration of polymer is 2000 ppm.
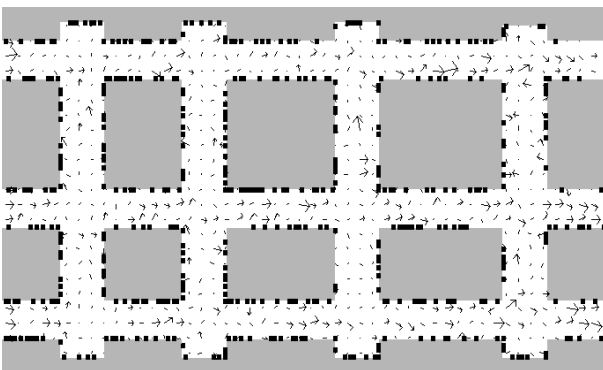

Figure 7. Polymer adsorption in the porous medium 2 after 5000 seconds. Concentration of polymer is 2000 ppm.

whole experiment is as follows:

Sand Selection and Treatment   Sand was sieved and cleaned. The particle diameter distribution was ranged from about 150 to 500 μm.

The Polymer Solution   The polymer used in the experiment was xanthan with molecular weight being equal to 5.106 g/mole. Polymer concentrations of 200, 500, 1000, 1500, and 2000 ppm were prepared.

The procedure of batch experiment was as follows:
1. Each polymer solution of 200 ml with a certain concentration was placed in 250 ml Erlenmeyer flasks each containing 20 gr of sand particle.
2. The flasks then placed in a constant temperature shaker bath at certain temperature (27°C) and shaking rate of 80 strokes per minute for 3 hours to reach the equilibrium condition.
3. Testing samples (10 ml) were be taken from each flask at each 15 minutes for 3 hours to be analyzed using the spectrophotometer.

Polymer adsorption in batch experiment is simulated to validate the LGA model. A representative sand pack is arranged as depicted in Figure 5. Since the porosity of a pile of sand grains is not considered, the surface length parameter becomes important to be matched. Equation B.3 may be used to estimate the surface length of the sand grains. The surface length of sand grains that have mass of 20 g, average diameter of 325 μm, and density of 2.65 g/cm^3 is about 37.327 cm.

The simulator was run for 10800 time steps (3 hours). The simulations were conducted 5 times for polymer concentrations of 200, 500, 1000, 1500, and 2000 ppm, respectively.

B.   Simulation of Polymer Adsorption in Continuous System   The LGA model is then used to simulate polymer flow in porous media. We arranged four porous media of size 2 cm and 1 cm as shown in Figures 6 to 9 to examine the effect of porosity and surface length to polymer adsorption. The regular shapes of pore space were established to avoid the effect of irregularity. The data of porosity and surface length of the four porous media are listed in Table 1. Simulations
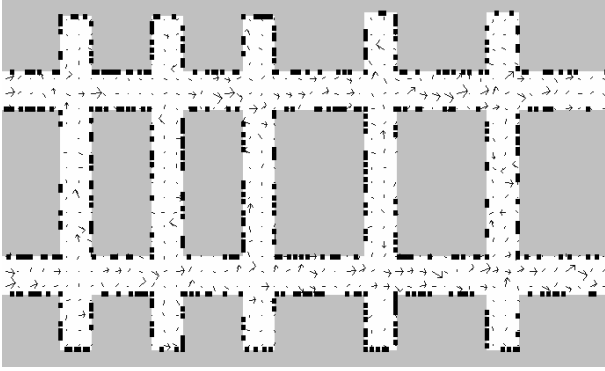
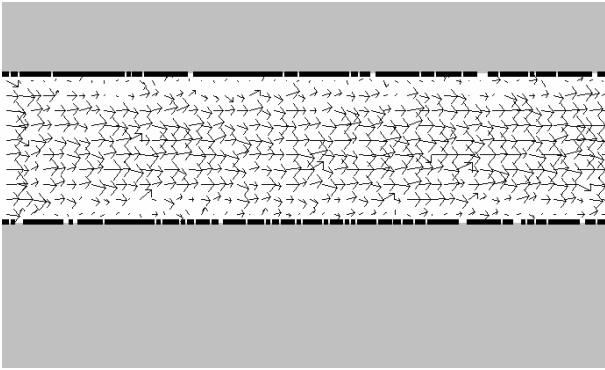**Figure 8**. Polymer adsorption in the porous medium 3 after 5000 seconds. Concentration of polymer is 2000 ppm.

Figure 9. Polymer adsorption in the porous medium 4 after 5000 seconds. Concentration of polymer is 2000 ppm.

TABLE 1. Data of LGA Porous Media.

Porous medium	Porosity (fraction)	Surface Length (cm)
1	0.41	8.0
2	0.50	13.8
3	0.41	13.8
4	0.41	4.0

TABLE 2. Absorbance Level of Xanthan.

Concentrations (ppm)	Absorbance
0	0
200	0.014
500	0.033
1000	0.057
1500	0.072
2000	0.116

TABLE 3. Absorbed Amount of Xanthan.

Concentrations (ppm)	Absorbed Amount of xanthan	
	(mg/g)	molecules/cm
0	0	0
200	0.014	11110659
500	0.033	15043990
1000	0.057	18142380
1500	0.072	18142380
2000	0.116	18142380

were conducted for the porous media by channeling the polymer solution from left side continuously for 10000 seconds.

4. RESULTS AND DISCUSSION

A. Experiment and Simulation of Polymer Adsorption in Batch System Five batch experiments of xanthan adsorption process were conducted at room temperature, 27°C, for concentrations 200, 500, 1000, 1500, and 2000 ppm. The output readings from spectrophotometer in term of absorbance are shown in Table 2.

In order to determine the relationship between the concentration and the absorbance, the constants a and b of Equation (A.1) should be are calculated. Using linear regression analysis of the data of Table 2, one can find that a = 0.00005 and b = 0.002. By using the constants, the adsorbed amount, Q_e, is calculated by Eq. (A.3). Data between number of adsorbed polymer molecules and final concentrations of xanthan are shown in Table 3. Using Avogadro number and converting from surface area to surface length, the unit of molecules/cm can be obtained as given in the table.

Meanwhile, the simulation result of batch experiment using LGA model is given in Figure 10. The figure indicates that at 3 hours, the equilibrium condition has been attained where the
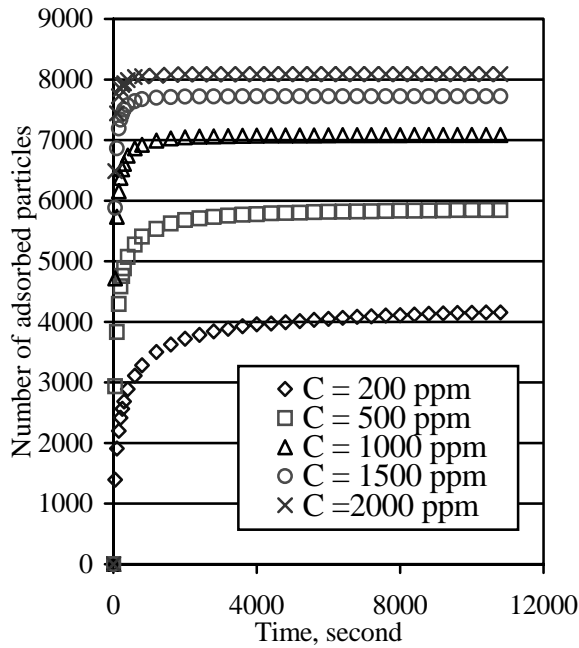
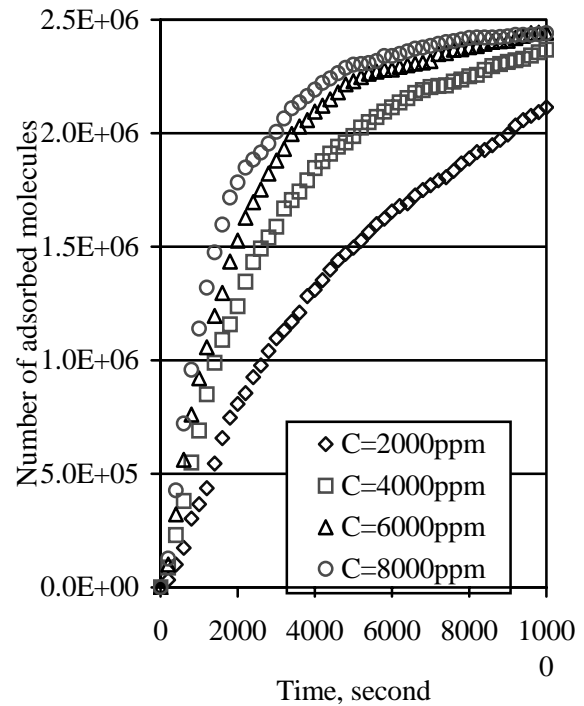**Figure 10**. Cumulative number of adsorbed polymer particles on simulation of batch experiment for 3 hours.

Figure 11. Comparisons of experimental, theoretical, and LGA simulation curves of adsorbed xanthan molecules for batch experiment.

Figure 12. Effect of polymer concentration to number of adsorbed polymer molecules in the porous medium 1 during 10000 seconds.
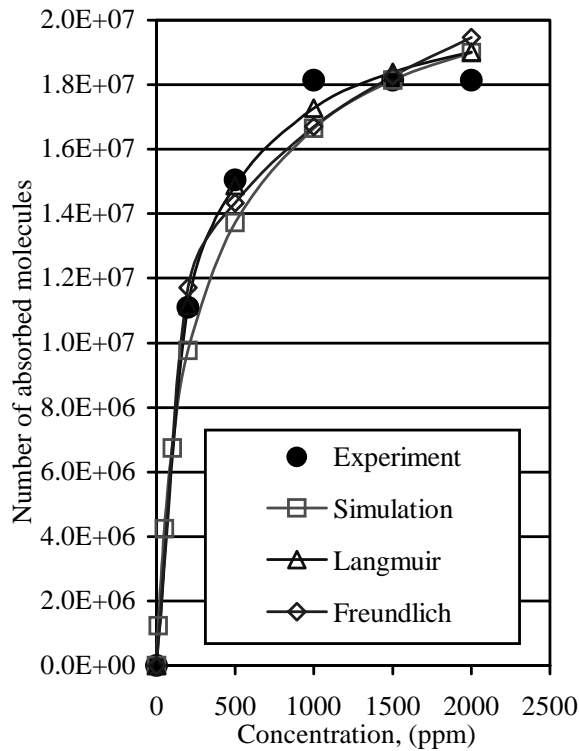
number of adsorbed particles is constant with time. The simulation result is then matched with experimental result. Both of them are then plotted in Figure 11. In this matching, 1 particle of LGA model represents 2349 molecules.

Besides the experimental and simulation curves, the curves of Langmuir, and Freundlich models are also depicted in Figure 11. The curves are constructed using Equations 2 and 4, whereas the constants of the equations are calculated using Equations of the straight-line form. As general, the LGA simulation curve gives a good match to the experimental and the theoretical isothermal adsorption curves.

B. Simulation of Polymer Adsorption in Continuous System The effect of polymer concentration on the number of adsorbed molecules for porous medium 1 is shown in Figure 12. The effect for this case is different from that for batch experiment. The figure shows that at the early time of the flow, the increasing rate

of adsorbed molecules is proportional to concentration. As the time goes on, the rate becomes slow. Moreover, the curves of various concentrations tend to pile. This means that the concentration does not affect the maximum number of adsorbed molecules of a porous medium.

Figure 13 shows how the surface length factor affects the polymer adsorption for a concentration. The number of adsorbed polymer particles increases up to a certain value for a medium. The descent of curve slopes in the figure can be explained as follows. The length of solid surface limits the number of adsorbed polymer particles. The definition of the proposed collision rules states implicitly that the probability of adsorption process will decrease as the available sites of solid surface decrease. So that, the smaller the surface length of porous media available the lower the level of adsorption that is observed. In monolayer adsorption, adsorbed polymer molecules occupy the available surface of solid material so that the maximum number of adsorbed molecules depends on surface area of porous media. In the figure, the cumulative number of adsorbed polymer molecules of the porous media 2 and 3, which have the longest surface length (13.8 cm) are higher than that of porous media 1 (8.0 cm) and 4 (4.0 cm).

Effect of porosity may be indicated by the curve of porous media 2 and 3. For the same surface length, porosity factor represents cross sectional area size of channel. Since it is easier for the wider channel to distribute polymer solution, the adsorption rate of porous medium 2 is higher than that of porous medium 3 during 10000 seconds.

In case of polymer solution flows through the porous medium 3, the decreasing of velocity of polymer solution and permeability of the porous medium is shown in Figures 14 and 15 respectively.

In LGA, each site evolves according to the rule, which depends only on the states of the site and the nearest neighbor sites, the direction and the velocity of fluid of each site may fluctuate. The situation affects the flow rate of whole system, as shown in Figure 14. Fundamentally, however, the flow rates for various concentrations tend to decrease with time. The velocity reduction is affected by constriction of channel due to adsorption. Meanwhile, the adsorption rate is
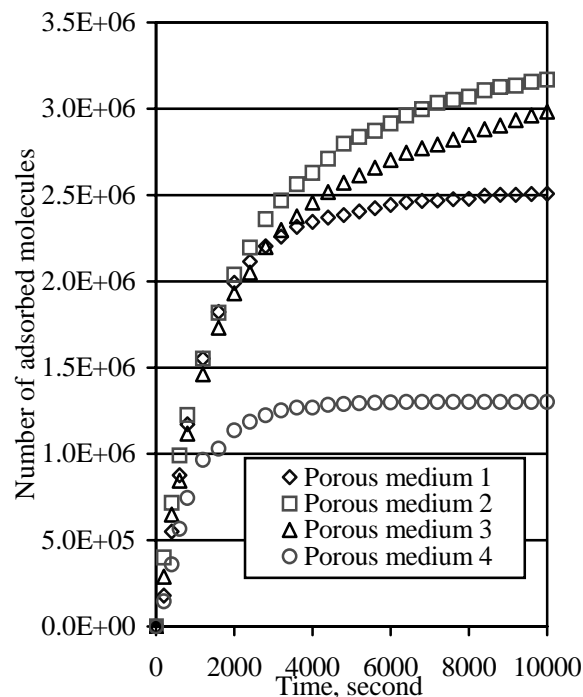

Figure 13. Cumulative number of adsorbed polymer molecules in the four porous media for concentration 10000 ppm during 10000 seconds.
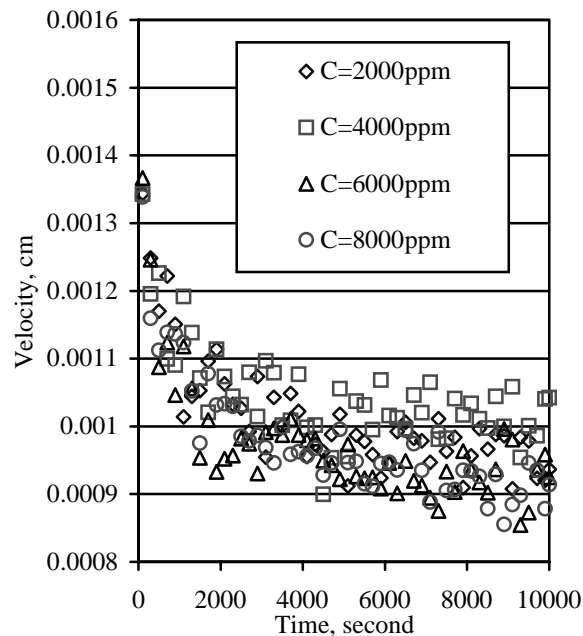

Figure 14. The effect of polymer concentration to fluid velocity reduction in the porous medium 3 during 10000 seconds.
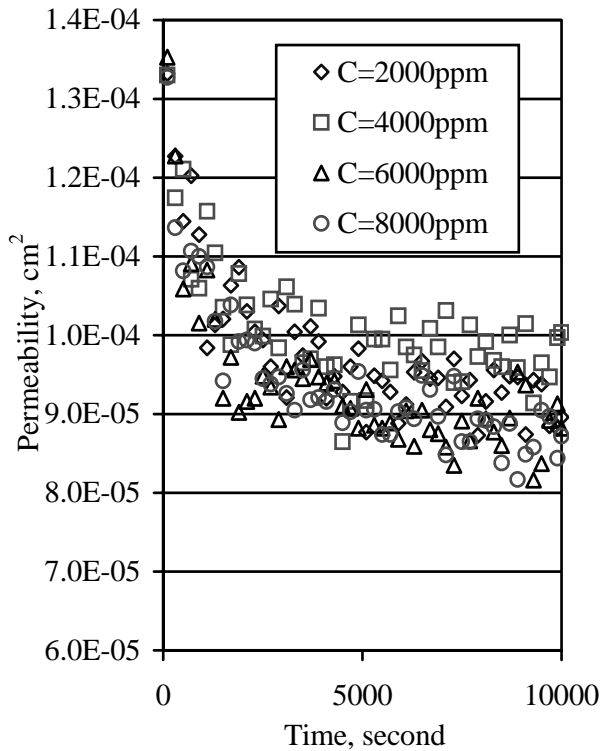
Figure 15. The effect of polymer concentration to permeability reduction in the porous medium 3 during 10000 seconds.

mainly affected by polymer concentration. However, other possible factor that also affects the velocity reduction is the distribution of adsorbed polymer. Since the adsorption happens randomly on any site and at any time, the rate of velocity reduction is not completely proportional to concentration factor.

Figure 15 shows the change of permeability due to adsorption process. The similar condition to velocity is experienced by the permeability. In general, the permeability decreases as the number of adsorbed particles increases for all concentration. In this case, the fluctuation of permeability is related to that of fluid velocity.

The decreasing of fluid velocity and permeability in this model is related to the level of adsorption. Hence, the decreasing will also achieve a certain level as time goes on.

5. CONCLUSIONS

This paper has established some fundamental

guidelines to apply LGA model to polymer adsorption process. The collision rules that used to simulate polymers adsorption are given.

The simulation results show that the model has good agreement to batch experiment and the equations of Langmuir and Freundlich models. The LGA model can describe the monolayer of adsorbed polymer particles on the solid surface as given in Figures 5 to 9.

In continuous polymer flow through porous media, the maximum number of adsorbed polymer molecules in a porous medium is mainly determined by the length of solid surface. Meanwhile, the concentration and porosity affect the adsorption rate in transient period of polymer flowing. The polymer adsorption in porous media can decrease its permeability and fluid velocity.

6. NOMENCLATURE

A   surface area, cm^2
C   concentration of particles in solution, ppm
d   diameter, cm
m   mass, g
P_{pa} the probability factor of polymer adsorption occurrence, fraction
q   number of molecules adsorbed on solid
S   surface area, cm^2
V_p volume of polymer solution, ml

8. APPENDIXES

A. Theory of Batch Experiment   The out put reading from spectrophotometer of batch experiment is in term of absorbents. The absorbance values should be converted to term of concentration where the concentration is required for calculating the amount of polymer adsorbed. Then, the relationship between the concentration and the absorbance is determined. The relationship usually takes the form:

$$A = a + bC \tag{A.1}$$

where A represents the absorbance The constants a and b are determined by linear regression analysis [10].

Concentration after adsorption, C_f can be calculated by rearranging the Equation A.1:

$$C_f = \frac{(A - a)}{b} \qquad (A.2)$$

Total amount of polymer adsorbed is calculated using the following relation:

$$q_e = \frac{(C_i - C_f)}{m_s} V_p \qquad (A.3)$$

where C_i (ppm) is initial polymer concentration, C_f (ppm) is polymer concentration after adsorption; q_e is the amount of absorbed polymer at equilibrium concentration; V is the volume of polymer solution; m is the mass of sand particles.

B. Determination of Surface Length Surface area (S) of a pack of sand grains may be estimated by the following equation:

$$S \approx 4\pi N_g \left(\frac{d_g}{2} \right)^2 \qquad (B.1)$$

where N_g is number of grains and d_g is average diameter of grain.

Meanwhile, the number of sand grains in a pack of sand may be obtained with dividing of the volume of sand grains by average volume of a sand grain. The relation is mathematically expressed by

$$N_g \approx \frac{3 \left(\frac{m_t}{\rho} \right)}{4\pi \left(\frac{d_g}{2} \right)^3} \qquad (B.2)$$

where m_t is total mass of sand grains and ρ is density of sand.

For two dimension porous media, the surface area should be converted in form of surface length. The surface length (S_l) of a porous medium can be defined as:

$$S_l \approx 2 \left(\frac{d_g}{2} \right) \sqrt{\pi N_g}$$

7. REFERENCES

1. Slejko, F.L., (Ed.), "Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application", Marcel Dekker Inc., New York, (1985), 3, 9.

2. Bondor, P. L., Hirasaki, G. J. and Tham, M. J., "Mathematical Simulation of Polymer Flooding in Complex Reservoir", *Society of Petroleum Engineering Journal, SPE 3524*, (1972), 369–382.

3. Todd, M. R. and Chase, C. A., "A Numerical Simulation for Predicting Chemical Flood Performance", *Society of Petroleum Engineering Journal, SPE 7689*, (1979), 161–174.

4. Gupta, A. D., Pope, G. A., Sepehrnoori, K. and Thrasher, R. L., "A Symmetric, Positive Definite Formulation of a Three-Dimensional Micellar/Polymer Simulator", *Society of Petroleum Engineering Journal, SPE 13504*, (1986), 622–632.

5. Masuda, Y., Tang, K. C., Miyazawa, M. and Tanakam S., "1D Simulation of Polymer Flooding Including the Viscoelastic Effect of Polymer Solution", *Society of Petroleum Engineering Journal, SPE 19499*, (1992), 247–252.

6. Rasmussen, S. and Smith, J. R., "Lattice Polymer Automata", *Berichte der Bunsen-Gesellschaft. Phys. Chem*. No. 9, (1994), 1185–1193.

7. Mayer, B., Kohler, G. and Rasmussen, S., "Simulation and Dynamics of Entropy-Driven, Molecular Self-Assembly Process," *Physical Review E*, Vol. 55, No. 4, (1997), 4489–4499.

8. Buick, J. M., "Lattice Boltzmann Methods in Interfacial Wave Modelling", Ph.D Thesis, University of Edinburgh, (1997), 19.

9. Sing, K. S. W., "Reporting Physisorption Data for Gas/Solid Systems", in Myers, A.L. and Belfort, G., (Eds.), *Fundamentals of Adsorption*, Engineering Foundation, New York, (1984), 567–583.

10. Taufiq Fathaddin, M., Awang, M. and Swadesi, B., "An Experimental Study on the Adsorption of Polyacrylamide, Xanthan, and Hydroxyethyl Cellulose on Sand Particles", *Regional Conference for Young Chemists*, Universiti Sains, Malaysia, Penang, (2004), 85.

11. Cal, M. P., "Characterization of Gas Phase Adsorption Capacity of Untreated and Chemically Treated Activated Carbon Cloths, Ph.D Thesis, University of Illinois, Urbana, Illinois, (1995), 16–19.

12. Beverloo, W. A., Pierik, G. M. and Luyben, K. C. A. M., "Adsorption Rate of Organics from Aqueous Solutions onto Granular Activated Carbon", Myers, A.L. and Belfort, G., (Eds.), Fundamentals of Adsorption, Engineering Foundation, New York, (1984), 95–104.

13. Suzuki, M., "Adsorption Engineering", Kodansha Ltd. and Elsevier, Tokyo and Amsterdam, (1990), 5.

14. Weilin Sun, Tiejun Wang, Yaqin Lin, and Qinggong Dang, "An Experimental Study on The Adsorption of Polyacrylamides on Clay Particles", *Society of Petroleum Engineering Journal, SPE 24407*, (1992), 1–22.

15. Lake, L. W., "Enhanced Oil Recovery", Prentice Hall, Englewood Cliffs, New Jersey, (1989), 324–326.

16. Galya, D. P. and Clark, A. B., "Modeling Transport and Fate of Contaminants in Ground Water", Cheremisinoff, N.P., (Ed.), Encyclopedia of Fluid Mechanics, Vol. 10, Gulf Publishing Co., Houston, (1990), 595–609.

17. Treybal, R. E., "*Mass-Transfer Operation*", 3rd Ed., McGraw-Hill, New York, (1980), 581–582.