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Fractal–Like Kinetics Study of Adsorption on Multi–Walled Carbon Nanotube

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ABSTRACT

The fractal degree of adsorption on the carbon nanotube has been investigated. The fractal-like Langmuir kinetics model has been used to obtain the fractal degree of ion adsorption on carbon nanotube. The behavior of the fractal-like kinetics equation was compared with some famous rate equations like Langmuir, pseudo-first-order and pseudo-second-order equations. It is shown that the kinetic of adsorption onto carbon nanotube can be used to obtain its spectral dimension, successfully.

1. INTRODUCTION

Physical, chemical and adsorption properties of adsorbents depend on its surface. The highly inhomogeneous surface structure of solid particles is difficult to characterize using simple geometry. Fractals, whose structures repeat themselves in all dimensions and on all length scales, are often used to depict the structure of solid particles and their surfaces. Adsorption is a method frequently used to determine the surface fractal dimension of porous media. It can be expected that adsorption processes involving solid–liquid interfaces could be of high heterogeneity.

The wide applicability of the fractal approach to adsorption systems and at the same time its limited utility in almost every case, brings one to the following conclusion: solid surfaces are never perfectly regular or irregular. Real solid surfaces represent an

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intermediate case. Several different theories have been developed to analyze adsorption data and obtain the surface fractal dimension [1, 2]. Avnir and Pfeifer [3] applied fractal geometry concepts to describe the general features of surface geometric heterogeneity in adsorption systems showing a small degree of surface organization. Ismail and Pfeifer [4] demonstrated three variants of the gas adsorption method for measurement of the surface fractal dimension, using carbon fibers as a test material. Ozek [5] provided methods to estimate pore and surface structures of activated carbon fiber by adsorption of dyes on the surface of and determined its fractal dimension. Lopez et al [6] presented a fractal kinetic model for adsorption at solid/solution interface.

2. PROBLEM STATEMENT

Carbon nanotube has brought on plenty of research in different scientific fields due to its special physical and chemical properties. The purpose of this study is to use this rate equation to analyze adsorption data of ions on some modified multi-walled carbon nanotubes. We are going to obtain the spectral dimension of some modified multi-walled carbon nanotubes by analysis of kinetic data.

3. PRELIMINARIES

There are famous kinetics model to describe rate of adsorption including pseudo-first-order, pseudo-second-order and Langmuir models. The Langmuir equation is the simplest adsorption isotherm with sound theoretical foundations that is considered a good approximation of the real adsorption systems. The Langmuir model is based on a kinetic principle. This model took into account the limited capacity of a flat and homogeneous surface as well as both adsorption and desorption processes [7]. The Langmuir rate equation is:

$$\frac{d\theta}{dt} = k_a\ c\ (1-\theta) - \ k_d\ \theta \qquad (1)$$

where k_a is the adsorption rate coefficient, k_d is the desorption rate coefficient, $\theta = q/q_m$ is the relative surface coverage, q_m is the adsorption capacity and c is the concentration. By equating the rates of adsorption and desorption, the famous Langmuir isotherm will be obtained.

In 1998, Kopelman [8] considered that in most heterogeneous phases, the rate constant k_{obs} of reaction depends on reaction time:

$$k_{obs} = k'\ t^{-h} \qquad 0 \le h \le 1 \qquad (t \ge 1) \qquad (2)$$

where k' is a constant not dependent on time and h is a parameter measuring the degree of local heterogeneity [9]. When h=0, k_{obs} is time-independent; however, when $h \neq 0$, k_{obs} is time-dependent at all times.

The rate constant and the order of reaction are associated with the spectral dimension d_s. The spectral dimension d_s for fractal objects is a kind of dimension. It means the degree of local heterogeneity. Increase of d_s value implies more local heterogeneous, more remarkable time-dependent rate coefficient. For a single reactant bimolecular reaction (A+A), there should be the following relation:

$$h = 1 - \frac{d_s}{2} \tag{3}$$

The adsorption of the molecules on the active surface sites on can be written as:

$$B + mA \rightarrow B–mA \tag{4}$$

where B is the adsorbate, A is the active site on surface and B−*m*A is the product of above reaction. Wang et al [10] developed the relations among the parameters of *m*, *h* and d_s to the adsorption kinetics of molecules onto fractal surfaces as:

$$d_s = 2(1 - \frac{h}{m}) \tag{5}$$

Recently, we developed a fractal-like kinetics equation for adsorption according to the Langmuir kinetic equation and fractal-like kinetics model [11]. This model studied the adsorption of some ions onto graphene surface, successfully.

4. PROPOSED METHOD

We proposed that rate coefficient of adsorption is time-dependent but rate coefficient of desorption is not [11]. This new rate equation is:

$$\frac{d\theta}{dt} = k_a t^{-h} c(1 - \theta) - k_d \theta \tag{6}$$

The value of $k_a t^{-h}$ changes over time until equilibrium that the rate constant of adsorption reaches to $k_a^{'}$:

$$k_a^{'} = k_a t_e^{-h} \tag{7}$$

where t_e is the time in which system reaches to equilibrium. Therefore, the Langmuir constant (K_L) equals to:

$$K_L = \frac{k_a t_e^{-h}}{k_d} \tag{8}$$

The analytical solution of equation (6) led to a complex expression. One powerful technique for numerical simulations is stochastic simulation. For this purpose, we applied the CKS package developed by Houle and Hinsberg [12]. Recently, we have used it to solve some rate equations, numerically [13, 14].

In this method, the adsorption mechanism is considered as reaction (4). Since fractal-like Langmuir equation was used, the value of "m" in this reaction was considered equals to one. The input data for simulation are the rate constants, the value of *h*, and the initial concentrations of adsorbates in the bulk and the active sites on carbon nanotube. The rates of adsorption and desorption steps (R_i), are taken to be proportional to the probability, P_i, and calculated based on equation (6). The time step Δt between

occurrences of any of the reaction steps is the mean time for a system obeying Poisson statistics:

$$\Delta t = \frac{-\ln \rho}{\sum R_i} \tag{9}$$

where ρ is a random number between 0 and 1. The simulation is propagated by repetitively selecting at random among the probability-weighted steps in the mechanism, and updating the reactant and product populations according to the stoichiometry of the selected step, system state variables, and reaction rates. The result is a set of concentration versus time curves that may be compared directly to experiment.

In the next section, this numerical solution method will be used to obtain the spectral dimension of multi-walled carbon nanotubes.

5. ILLUSTRATIVE EXAMPLES

In this section, the fractal-like Langmuir equation (equation (6)) will be used to determine the spectral dimension of multi-walled carbon nanotube. In addition, equation (6) will be compared with Langmuir kinetic model, pseudo-first-order and pseudo-second-order kinetic models. In order to determine the spectral dimension of multi-walled carbon nanotube, some experimental systems that have studied ion adsorption on the carbon nanotube were chosen [15, 16].

As an example, we have selected the system adsorption of Pb^{2+} on modified multi-walled carbon nanotube. Vukovic et al [15] studied Pb^{2+} ion adsorption on diethylenetriamine and triethylenetetramine modified multi-walled carbon nanotubes (e-MWCNT and d-MWCNT, respectively), experimentally. The experimental data were analyzed according to the Langmuir isotherm and the obtained values of K_L and q_m are shown in Table 1. Equilibrium data agree well with Langmuir isotherm. From the results, it is clearly seen that the equilibrium adsorption is much close to the experimental data, suggesting application of the kinetic Langmuir model. The curve fitting and statistical analyses were performed with CKS package. Having determined the parameters of Langmuir kinetic model, we used input data (temperature, concentration of adsorbent in solution and q_m) to fit the experimental kinetic plots by adjusting the value of the parameter k_a. The kinetic constants and correlation coefficient of this model were calculated and given in Table 2. Empirical (open diamond) and calculated data by kinetic Langmuir model (solid line) of Pb^{2+} ion adsorption on d-MWCNT are shown in Figure 1(a). As seen in Figure 1(a), the calculated data by kinetic Langmuir model are not in good agreement with empirical data.

Table 1: The initial concentration and Langmuir parameters for the adsorption of Pb^{2+} and Ni(II) onto modified multi-walled carbon nanotube.

Systems	$c_(\text{mol}/\ell)$	q_m (mg/g)	K_L (ℓ/mg)	R^2
Pb/d-MWCNT	2.40×10^{-5}	4.80×10^{1}	1.35	0.9879
Pb/e-MWCNT	2.40×10^{-5}	3.02×10^{1}	0.43	0.9885
Ni/MWCNT	1.00×10^{-3}	1.01×10^{1}	0.22	0.9879

The worse agreement between theory and experiment can be related to the fractal dimension of surface. Equation (6) was solved by CKS package and the values of k_a and h were obtained as adjustable parameters. The value of k_d was calculated by using equation (8). Figure 1(b) shows the agreement between theory and experiment, along with the values of the best-fit parameters (Table 2). There is noise in this fitting because of limited performance of the software. Figures 1(a) and 1(b) show the comparison of empirical kinetic data and calculated kinetic data fitted equations (1) and (6). A good fitting quality is obvious by equation (6) (see Table 2).

Table 2: The constant parameters of Langmuir and fractal-like Langmuir rate equations for the adsorption of Pb^{2+} and Ni(II) onto modified multi-walled carbon nanotube at 298 K.

Systems	Langmuir rate equation			Fractal-like Langmuir rate equation				
	k_a (ℓ/mol.min)	k_d (1/min)	R^2	k_a (ℓ/mol.min)	k_d (1/min)	h	d_s	R^2
Pb/d-MWCNT	4.00×10^{4}	0.14	0.9695	1.58×10^{4}	0.39×10^{-1}	0.67×10^{-1}	1.87	0.9899
Pb/e-MWCNT	2.70×10^{4}	0.30	0.9144	7.30×10^{3}	0.19×10^{-1}	0.28	1.44	0.9808
Ni/MWCNT	8.00×10^{2}	0.61×10^{-1}	0.9228	5.68×10^{2}	0.27×10^{-1}	0.10	1.80	0.9848

The pseudo-first-order and pseudo-second-order models are extensively used in the literatures. Azizian [17] showed that both pseudo-first- and pseudo-second-order equations are treated as special cases of Langmuir kinetic model. The pseudo-first-order equation is [18]:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{10}$$

where k_1 is the pseudo-first-order rate coefficient.

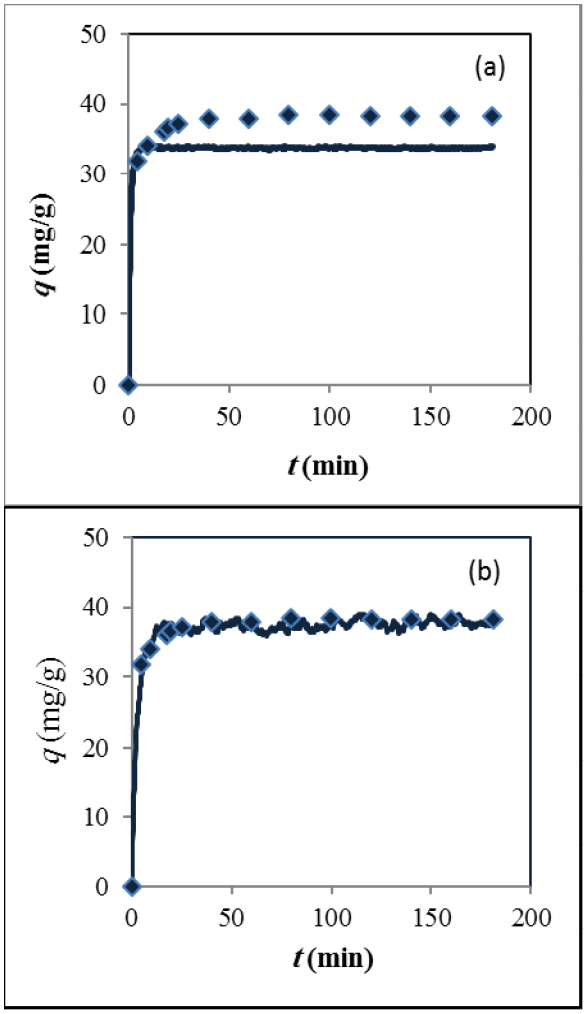

Figure 1. Kinetic data of Pb^{2+} adsorption on d-MWCNT surface; empirical [15] (diamonds) and calculated data (line) by a) Langmuir and b) the fractal-like Langmuir rate equations.

The pseudo-second-order kinetic equation is [19]:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{11}$$

where k_2 is the pseudo-second-order rate coefficient.

To compare equation (6) with pseudo-first-order and pseudo-second-order equations, empirical data of Pb^{2+} ion adsorption on d-MWCNT were fitted by them. Kinetic parameters along with correlation coefficients of the kinetic models are shown in Table 3. As can be seen from Tables 2 and 3, higher correlation coefficients (R^2) of equation (6) indicates that this kinetic model is suitable to describe adsorption of Pb^{2+} ion adsorption on d-MWCNT. Therefore, the fractal-like Langmuir equation was used to determine the spectral dimension of d-MWCNT and the result was shown in Table 2.

Table 3: The pseudo-first-order and pseudo-second-order parameters for the adsorption of Pb^{2+} and Ni(II) onto modified multi-walled carbon nanotube at 298 K.

Systems	Pseudo-first-order		Pseudo-second-order		
	k_1(1/min)	R^2	q_e(mg/g)	k_2(g/mg.min)	R^2
Pb/d-MWCNT	7.92×10^{-2}	0.8400	3.88×10^{1}	4.04×10^{-2}	0.9675
Pb/e-MWCNT	7.48×10^{-2}	0.9053	2.87×10^{1}	1.35×10^{-2}	0.9775
Ni/MWCNT	1.80×10^{-1}	0.9362	5.14	2.98×10^{-2}	0.9291

Now let us consider the experimental data of Pb^{2+} ion adsorption on e-MWCNT. For this purpose, we have applied the procedure described in the previous sections. The results of that fitting are shown in Figures 2(a) and 2(b) (solid lines), whereas the related best-fit parameters are collected in Table 2. When looking through Figures 2(a) and 2(b) one can state that equation (6) offers a better fit of kinetic data than kinetic Langmuir model.

A comparison of the kinetic models and the empirical kinetic data of Pb^{2+} ion adsorption on e-MWCNT was best described by equation (6). The obtained parameters of kinetic models are presented in Table 3. It was found that equation (6) is superior to other three ones for the description of kinetic data. Thus, the fractal-like Langmuir equation was used to determine the spectral dimension of e-MWCNT (Table 2).

In continuous, another experimental system was studied. This empirical system was presented by Chen et al [16] has studied Ni(II) adsorption on a kind of modified multi-walled carbon nanotube. In the first step, we fitted the empirical kinetic data by using equations (1) and (6) (Tables 2 and 3). The calculated data by equation (1) are shown in Figure 3(a). Figure 3(b) shows that equation (6) can correlate very well the behavior Ni(II) adsorption on modified multi-walled carbon nanotube. By looking at Figures 3(a) and 3(b), we observe a good suitability of equation (6) rather the kinetic Langmuir equation.

Finally, empirical data Ni(II) adsorption on modified multi-walled carbon nanotube were studied by pseudo-first-order and pseudo-second-order equations. The estimated model parameters with the correlation coefficient (R^2) for the different models are shown in Table 3. The correlation coefficients, R^2, given in the Tables 2 and 3 also show that equation (6) can be satisfactorily described empirical data of Ni(II) adsorption on a modified multi-walled carbon nanotube. The obtained value of spectral dimension of modified multi-walled carbon nanotube was shown in Table 2.

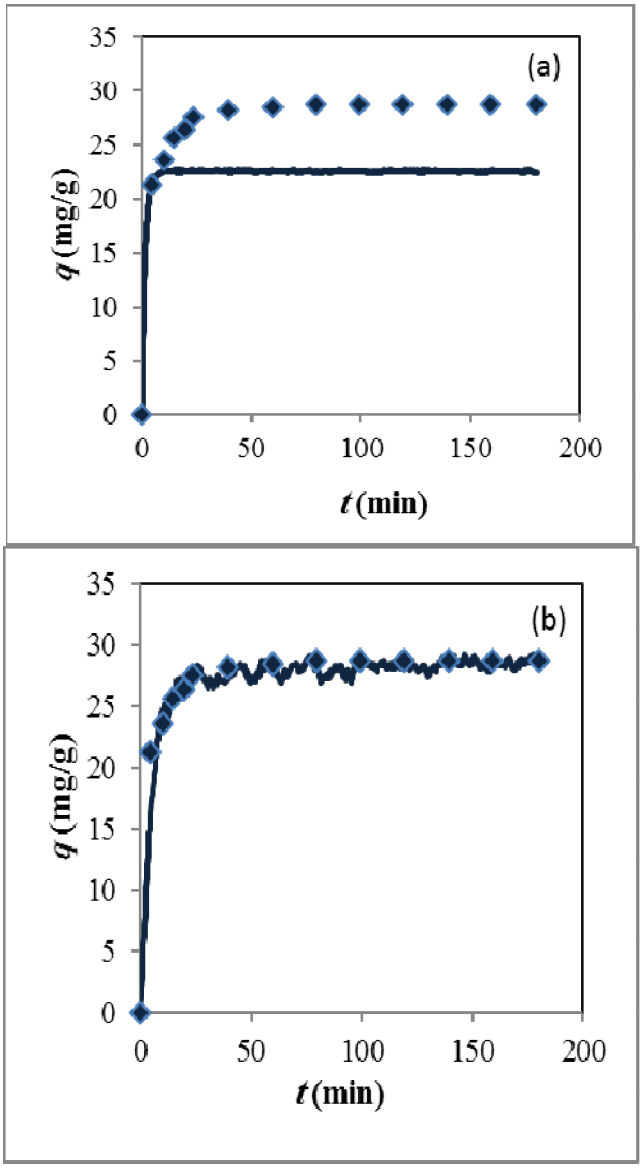

Figure 2. Kinetic data of Pb^{2+} adsorption on e-MWCNT surface; empirical [15] (diamonds) and calculated data (line) by a) Langmuir and b) the fractal-like Langmuir rate equations.

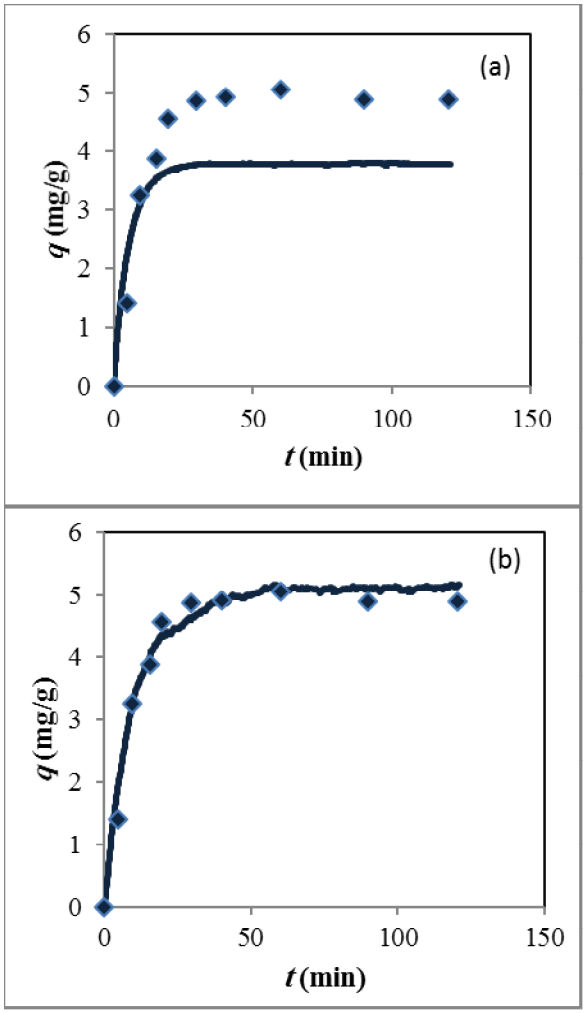

Figure 3. Kinetic data of Ni(II) adsorption on MWCNT surface; empirical [16] (diamonds) and calculated data (line) by a) Langmuir and b) the fractal-like Langmuir rate equations.

In summary, the presented model investigation seems to suggest that equation (6) is a very good equation to correlate kinetic data of adsorption on carbon nanotube surfaces and can be used to obtain the spectral dimension of surfaces.

6. CONCLUSION

By applying empirical data of Pd(II) and Ni(II) adsorption on carbon nanotube surfaces, it was shown that the fractal-like Langmuir model can be applied with good success in many adsorption systems. The best description of kinetics was obtained with the fractal-like Langmuir equation corresponding to Langmuir, pseudo-first-order and pseudo-second-order rate equations. By using of empirical data of ion adsorption on multi-walled carbon

nanotube, the fractal degree of adsorption (*h*) was obtained. The spectral dimensions of some multi-walled carbon nanotubes were obtained.

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