

A General Isotherm Model for Activated Carbon Adsorption of Typical Natural Organic Matters

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Abstract—The activated carbon adsorption isotherms of organic matters in natural water were type II and III isotherms, which cannot fitted accurately by the Langmuir and Freundlich models. It is investigated on the different kinds of activated carbon adsorption characteristics for humic, lignin and tannic acid and the fit of the modified SR equation. Results show that the modified SR model has a high degree of fit to all types of isotherms (Coefficient of determination >0.95) compared with the two classical models. In order to make the predicted value of the modified SR model having practical significance, the limiting adsorption capacity, which is related to the pore structure of activated carbon and organic molecular size, is introduced. Limiting equilibrium concentrations are calculated by the modified SR equation and the limiting adsorption capacity.

Keywords—natural organic matters; adsorption isotherm; the modified SR model

I. INTRODUCTION

Natural organic matters (NOM) are a complex mixture of various organic compounds with different molecular weight and physico-chemical characteristics dissolved in surface water, ground water and soil water[1].

Adsorption by activated carbon is a common method for NOM removal from waters. The theoretical foundation of adsorption process design is adsorption isotherm, which is usually described by two classical models, Langmuir and Freundlich models [2,3]. Langmuir-type adsorption is considered to be a monolayer homogeneous process with no interactions among adsorbates⁴. Freundlich-type adsorption is considered to be a multi-layer process with two parameters used to characterize the adsorption process[2]. Investigations indicated that fitting degree of the two classical models depended on adsorbent dosage and equilibrium concentration C_e ⁵. Freundlich model showed better fitting degree than

Langmuir under lower C_e ; under higher C_e , a significant deviation was observed for Freundlich model, while Langmuir model usually achieved a good fitting results; the two models were both unsuitable under the conditions with C_e approaching initial concentrations.

In this study, a general model was introduced to fit different types of adsorption isotherms obtained by different activated carbons with humic acid, lignin and tannic acid, three typical NOMs, as adsorbate. The limiting adsorption capacity related to pore structure and organic matter molecular weights was also put forward to make the predicted value of the general model more practical. The results obtained in this study are expected to provide an insight for analysis and design of adsorption process for NOM removal from natural water by activated carbon.

II. MATERIALS AND METHOD

Major headings should be typeset in boldface with the first letter of important words capitalized.

A. Sources of NOM

Preparation of humic acid. NOM in natural waters was adsorbed by resin firstly, and then the resin was immersed in 4% NaOH and 15% NaCl for 24 hours at 40 °C. Then pH of the soak solution was adjusted to 1~2, and the obtained precipitates were dissolved in 0.1 mol/L NaOH and filtrated. The filtrate was filtered through a hydrogen type cation exchange column and eluted by desalinated water. The elution was humic acid samples from natural waters.

Preparation of lignin. The lignin complex was precipitated by adding 0.1% H₂SO₄ into filtrate of papermaking wastewater to adjust pH of 6.0, and then filtered. The harvested precipitate was dissolved in 0.1% NaOH and filtered. The filtrate was precipitated by 0.1%

H₂SO₄, and the harvested precipitate was dried to prepare solid lignin sample.

The tannic acid (analytical grade) was purchased from Chinese Medicine Group Chemical Reagent Co., Ltd.

B. Pretreatment of Activated Carbon

Characteristics of the five types of activated carbon used in this study are shown in Table I. The activated carbon was

immersed in 5% HCl for 8 h firstly, then soaked in the solution adjusted to neutral pH, and then dried at 60 °C. The dried activated carbon was ground to 200 mesh and stored in a desiccator.

TABLE I. CHARACTERISTICS OF ACTIVATED CARBON USED IN THIS STUDY

Materials	Pore size (nm)	Pore volume (cm ³ /g)				Iodine adsorption value (mg/g)	Methylene blue adsorption value (mg/g)
		Total pore	Macropore	Mesopore	Micropore		
Coconut shell	2.57	0.4304	0.0002	0.0985	0.3321	1085	208
Apricot shell	3.69	0.5736	0.0065	0.2451	0.3220	980	183
Chitin	4.80	0.7216	0.0000	0.5162	0.2354	950	126
Coal	3.13	0.4896	0.0221	0.2298	0.2377	1000	165
Nut shell	3.60	0.5615	0.0082	0.3388	0.2145	896	95

C. Determination of Adsorption Isotherm

The activated carbon samples with different weights were added into 150 ml solutions with NOM concentrations of 20~30 mg/L, and then continuously vibrated for 4 h at 25 °C. Then samples were taken out of solutions under adsorption equilibrium and filtered through 0.45 μm membrane. The absorbance at 254 nm were measured for filtrate and used to calculate the NOM concentrations.

The adsorption capacity q_e (mg/g) was calculated as in Eq. (1).

$$q_e = V(C_0 - C_e)/m \quad (1)$$

Where, C_0 is initial NOM concentration, mg/L; C_e is the residual (equilibrium) NOM concentration, mg/L; m is the weight of activated carbon, g; V is the volume of NOM solution, L.

D. Adsorption Isotherm Models

The linear expressions of Langmuir and Freundlich models are shown in Eq. (2) and (3).

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

Where, b is Langmuir constant, and q_m is saturated adsorption capacity, mg/g.

$$\ln(q_e) = \ln(k_f) + 1/n \ln(C_e) \quad (3)$$

Where, k_f is Freundlich constant, L^{1/n} mg^(1-1/n)/g, and 1/n is Freundlich index.

SR model (Eq. (4)) was a general isotherm model built by Summers and Roberts to describe the influence of adsorbent dosage on NOM adsorption[6-9].

$$q_e = K(C_e/C_C)^{1/n} \quad (4)$$

Where, K is SR adsorption parameter, C_C is adsorbent dosage, and 1/n is isotherm index. Of the NOM isotherm models in the literature, the SR equation appears to be most suitable for practical use as it requires the fewest parameters. However, when applied to a fixed-bed adsorber, Eq. (4) is problematic as the C_C approaches zero, which corresponds to C_e approaching C_0 , q_e becomes infinitely large¹⁰.

In order to avoid the problems in classical SR model, a mass balance equation for adsorption process was built as shown in Eq. (5):

$$q_e = (C_0 - C_e)/C_C \quad (5)$$

And thus a modified SR model was built by combining Eq. (4) with Eq. (5)^[11].

$$\ln q_e = \frac{1}{n-1} \ln\left(\frac{C_e}{C_0 - C_e}\right) + \ln K_n \quad (q_e \leq q_{lim}) \quad (6)$$

Where, q_{lim} is limiting adsorption capacity of adsorbent, mg/g.

III. RESULTS AND DISCUSSION

A. Adsorption isotherm curves for Different Adsorbates

The relative molecular weight (MW) of different adsorbates are listed in Table II. The MW of humic acid extracted from natural water was higher than 6 kDa, indicating that humic acid represented 30~50% medium molecular and macromolecular NOM. Lignin was mainly macromolecular substances with MW higher than 50 kDa accounting for 84.5%. The tannic acid with MW of 1.7 kDa represented about 40~60% small-molecular NOM in natural water. The adsorption isotherm curves of five types of

activated carbon on the three representative NOMs are illustrated in Fig. 1.

TABLE II. RELATIVE MOLECULAR WEIGHT OF THREE REPRESENTATIVE NOMS

MW (kDa)	>50	20~50	10~20	6~10	4~6	2~4	<2
Humic acid	40.38	46.15	9.62	3.85	0	0	0
Lignin	84.5	9.71	1.86	0.41	1.24	0.83	1.45
Tannic acid	Relative MW of 1.701 kDa						

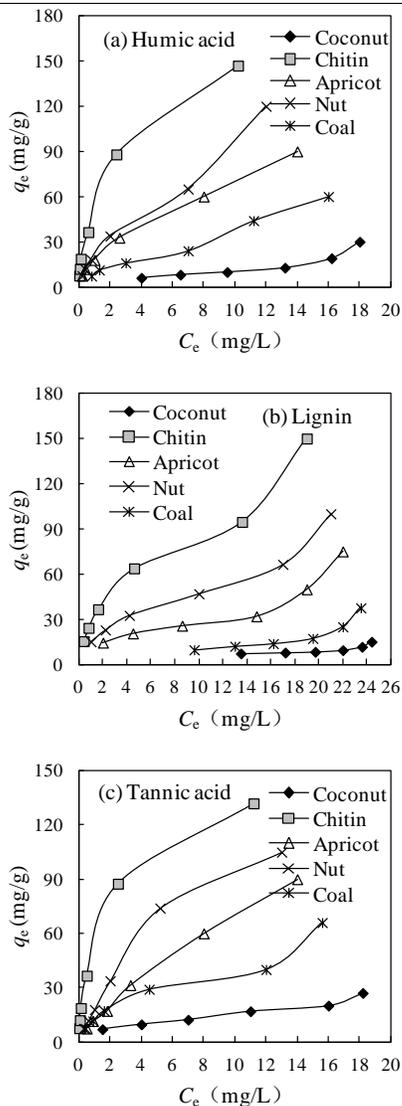


Figure 1. Adsorption isotherm data of 5 kinds of activated carbon on different adsorbents.

The coconut shell activated carbon had the highest iodine adsorption value and methylene blue adsorption value, but illustrated the lowest adsorption performances on the three NOMs. This was mainly attributed to that the two adsorption values characterized adsorption performances of micropore

¹¹, which accounted for 77.2% in total pores for pore volume in the coconut shell activated carbon, but the three NOMs were difficult to be adsorbed by micropore. Therefore, the adsorption isotherm showed Type III with worse adsorption performance.

The adsorption isotherm curves of the other four types of activated carbon on humic acid and tannic acid all belonged to Type II and between Type II and III. For lignin with higher MW, the activated carbon showed the lowest adsorption efficiency. The adsorption isotherm curves of chitin and nut shell activated carbon on lignin were Type II, while the other three types on lignin were all Type III.

B. Isothermal Data Fitting of Humic Acid

The fitting results of humic acid adsorption isotherm by Freundlich, Langmuir and the modified SR models are illustrated in Fig. 2 and Table III.

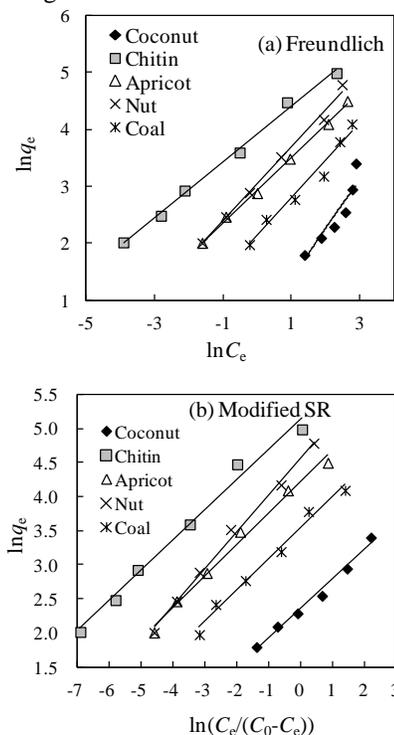


Figure 2. Fitting of humic acid adsorption with different models.

Freundlich model describes the adsorption data more precisely than the Langmuir equation, but it appears to be not suitable for Type III isotherm as well ($R^2 < 0.92$). That is because q_e of Langmuir equation has limit value and the increase of q_e with C_e slows down gradually in Freundlich equation [12,13], which does not coincide with Type III.

The modified SR model predicts that q_e depends on the relative equilibrium concentration C_e/C_0 . The type of adsorption isotherm (Type II or III) exclusively depends on the exponent $1/n$ defined by the modified SR equation, the fitting results of which are better than Freundlich and Langmuir ($R^2 > 0.98$). Physically, K_n is the adsorption capacity at $C_e = C_0/2$, which can express the adsorption

capacity of adsorbent for adsorbate. It is proved by the positive correlations between them in Table III.

TABLE III. THE FITTING PARAMETERS OF THREE KINDS OF MODEL FOR THE ADSORPTION ISOTHERM OF HUMIC ACID BY ACTIVATED CARBON

Activated Carbon	Coconut shell	Apricot shell	Chitin	Coal	Nut shell	
Freundlich	k_f	1.40	18.85	50.25	8.35	21.08
	n	1.06	1.74	2.04	1.50	1.53
	R^2	0.874	0.998	0.995	0.972	0.994
Langmuir	b	0.03	0.80	9.00	0.21	0.61
	q_m	51.02	52.08	46.30	51.02	65.79
	R^2	0.914	0.968	0.912	0.971	0.976
Modified SR	K_n	10.58	68.38	170.20	34.50	97.80
	n	3.32	3.18	3.25	3.18	2.84
	R^2	0.986	0.984	0.987	0.984	0.995

C. Isothermal Data Fitting of Lignin

The fitting results of lignin adsorption isotherm by Freundlich, Langmuir and modified SR model are illustrated in Fig. 3 and Table IV.

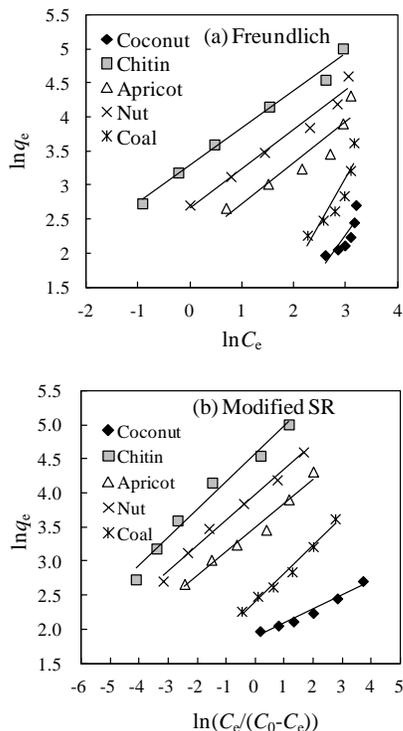


Figure 3. Fitting of lignin adsorption process by different models.

The deviation between predicted value by Freundlich model and experimental data of lignin adsorption isotherm was higher than the Langmuir model for activated carbons except for chitin and nut shell types. This was because macromolecular lignin was difficult to adsorb by activated carbon and the obtained Type III isotherm curve was unsuitable for the fitting by both Freundlich and Langmuir models. The modified SR model showed better fitting results than the two models with $R^2 > 0.97$, and the obtained

parameter K_n was also positively correlated with practical adsorption performance of activated carbon.

TABLE IV. THE FITTING PARAMETERS OF THREE KINDS OF MODEL FOR THE ADSORPTION ISOTHERM OF LIGNIN BY ACTIVATED CARBON

Activated Carbon	Coconut shell	Apricot shell	Chitin	Coal	Nut shell	
Freundlich	k_f	0.42	8.40	26.74	0.40	14.42
	n	0.95	1.67	1.82	0.75	1.62
	R^2	0.724	0.868	0.987	0.836	0.972
Langmuir	b	0.01	0.17	0.42	-0.01	0.24
	q_m	96.15	53.19	104.17	-113.64	74.07
	R^2	0.740	0.875	0.983	0.893	0.958
Modified SR	K_n	6.58	33.13	97.51	11.18	53.49
	n	5.82	3.82	3.44	3.42	3.67
	R^2	0.970	0.974	0.977	0.984	0.991

D. Isothermal Data Fitting of Tannic Acid

The fitting results of tannic acid adsorption isotherm by the three models are illustrated in Fig. 4 and Table V.

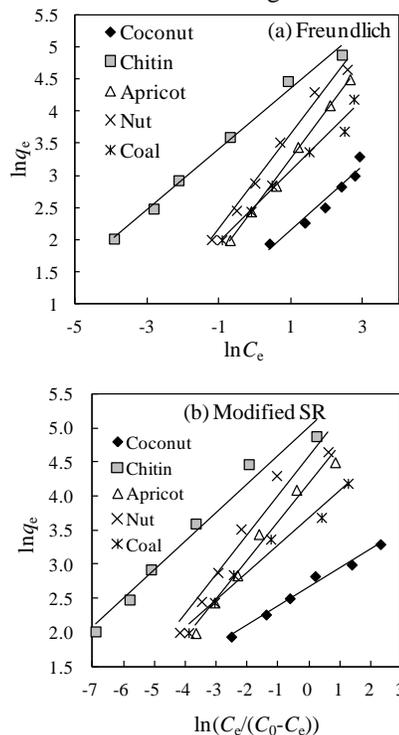


Figure 4. Fitting of tannins adsorption process by different models.

The adsorption isotherm of coconut shell activated carbon on tannic acid was between Type II and Type III, and the fitted R^2 value was 0.94 and 0.98 by Freundlich and Langmuir model, respectively, which were both lower than the other activated carbon. The tannic acid with small molecule was easy to adsorb by activated carbon.

At lower C_e , the adsorption capacity q_e increased quickly with rising C_e because organic substances can be directly contact with activated sites owing to the lower coverage on the surface of activated carbon. The increase of q_e was slower

at higher C_e with organic molecules associated in the adsorption pores [11]. Although representing small NOM, the tannic acid was also unable to enter the micropores ($d < 0.8\text{nm}$) with the most activated sites; therefore, the modified SR model also obtained better fitting results.

TABLE V. THE FITTING PARAMETERS OF THREE KINDS OF MODEL FOR THE ADSORPTION ISOTHERM OF TANNINS BY ACTIVATED CARBON

Activated Carbon		Coconut shell	Apricot shell	Chitin	Coal	Nut shell
Freundlich	k_f	5.09	12.11	48.59	12.42	18.30
	n	1.95	1.31	1.37	1.81	1.35
	R^2	0.940	0.990	0.990	0.970	0.980
Langmuir	b	0.29	0.19	9.00	0.47	0.27
	q_m	21.83	80.65	46.30	44.44	93.46
	R^2	0.880	0.980	0.910	0.970	0.939
Modified SR	K_n	14.36	65.87	151.44	39.76	97.81
	n	4.59	2.75	3.38	3.51	2.72
	R^2	0.990	0.980	0.980	0.970	0.950

IV. CONCLUSIONS

(1) Lignin, humic acid and tannic acid represent macromolecular, medium molecular and small molecular NOMs in natural water, respectively. Different types of activated carbon showed different adsorption isotherm curves. The coconut shell activated carbon illustrated Type III adsorption isotherm for the three NOMs with the worst adsorption performances, while the other activated carbon demonstrated Type II isotherm.

(2) The fitting degree of Freundlich model was higher than Langmuir model for adsorption isotherm curves of the

five types of activated carbon on the three typical NOMs, but the fitting of Type III isotherm by Freundlich model significantly deviated from the experimental data. The modified SR model showed good fitting performance for both Type II and III isotherms.

ACKNOWLEDGMENTS

This work was financially supported by Chinese National Natural Foundation Project (51408352).

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