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## Kinetics and thermodynamics of the anthraquinone-2, 6-disulfonate adsorption on expanded graphite

Xiu-Yan Pang\*, Fei Gong, Hai-Li Ren, Ting-Ting You

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, (P.R.CHINA)

E-mail : pxy833@163.com

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### ABSTRACT

Expanded graphite (EG) is a kind of important adsorbent for organic compound such as oil and dyes. We investigate the adsorption kinetic and thermodynamic characteristics of anthraquinone-2, 6-disulfonate (AQS) on EG which is prepared with 50 mesh crude graphite through chemical oxidation. We study the influence of initial AQS concentration, temperature, pH, ionic strength and EG expanded volume on the adsorption capacity of AQS from aqueous solution. The equilibrium adsorbance is found to increase with the increase in initial AQS concentration, ionic strength and expanded volume of EG, respectively. But temperature and solution acidity do not have an obvious effect. Adsorption type of AQS on EG is type II. The adsorption isotherms can be described with Langmuir equation. Kinetic studies show that the kinetic data can be described by pseudo second-order kinetic model. Second-order rate constants and the initial adsorption rate increase with the increasing of temperature. Physical adsorption is the major adsorption of the overall adsorption process.

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### KEYWORDS

Expanded graphite;  
Anthraquinone-2,  
6-disulfonate;  
Adsorption kinetics;  
Adsorption thermodynamics;  
Physical adsorption.

### INTRODUCTION

Expanded graphite (EG) is a kind of eco-material and it holds abundant porous structure ranging from several nm to hundreds  $\mu\text{m}$ <sup>[1,2]</sup>. EG has attracted attentions of scientists and engineers as an absorbent with a high sorption capacity for organic materials, such as heavy oil<sup>[3-9]</sup>, biomedical molecules<sup>[10]</sup> and dyes<sup>[11,12]</sup>.

Aromatic sulfonates like benzene-, naphthalene-, anthraquinone- and stilbene sulfonates are widely used in industrial and domestic processes. Because of their widely use, they often present in high concentrations in wastewaters originating from textile or curatorial factories. Though their aquatic toxicity appears to be small,

they can easily cause pollution of surface waters and pass through water treatment process for their high mobility and good solubility in the aquatic system.

In treatment of aromatic sulfonates waste water, advanced oxidation, complexation extraction<sup>[13,14]</sup> and polymeric resins adsorption<sup>[15,16]</sup> are normally used. Gao studied the adsorption capacity of active carbon for benzene sulfonic acid<sup>[17]</sup>, a balance adsorbance of 60 mg/g was obtained, which corresponding to a initial adsorbate concentration of 100 mg/L. But the research about the adsorption characteristics of aromatic sulfonates on EG has not been reported so much. In this work, EG was prepared by the research group. An aromatic sulfonate, AQS was used as a reference ad-

sorbate to study the adsorption kinetics and thermodynamics under various experimental conditions.

## EXPERIMENTAL

### The EG adsorbent

EG was firstly prepared according to literature<sup>[18]</sup>. Structural parameters of EG are characterized by expanded volume, surface area, pore cubage. The detection results are listed in TABLE 1.

### Aromatic sulfonates

Aromatic sulfonic acids are strong acid ( $pK_a < -1$ ), biologically persistent compounds<sup>[19]</sup>, and it often possess strong hydrophilicity. In the experiments, anthraquinone-2, 6-disulfonate (AQS) is selected as referenced adsorbate. Its chemical structure, molecular weight and  $\lambda_{max}$  are listed in TABLE 2. The  $\lambda_{max}$  is independent of the solution pH (2.0~11.0) and ionic strength (0~100.0 g/L).

### Adsorption studies

In the adsorption experiments, 0.20 g of EG was mixed with 100.0 mL solution at the desired AQS concentration, pH, ionic strength and temperature. Solution pH was adjusted with dilute HCl or NaOH solutions, and the ionic strength was adjusted with  $KNO_3$  solution. AQS concentration change was recorded by a New Century -T6- spectrophotometer (Pgenera, China) at the maximum wavelength of AQS absorption. The amount of AQS adsorbed onto the EG was calculated according to equation (1):

$$q = V(C_0 - C)/M \quad (1)$$

When  $C_e$  is used instead of C in Eq.(1),  $q_e$  is obtained. where:  $q$ - adsorption amount of AQS on EG, mg/g;  $q_e$ - equilibrium adsorption amount of AQS on EG, mg/g;  $V$ - volume of the AQS solution, mL;  $C_0$ - initial concentration of AQS in solution, mg/L;  $C$ - concentration of AQS in solution corresponding to a definite adsorption time, mg/L;  $C_e$ - equilibrium concentration of AQS in solution, mg/L;  $m$ - mass of EG, g

## RESULTS AND DISCUSSION

### Adsorption thermodynamics

At equilibrium state, the adsorption process is considered to be at dynamic state in which the rate of the adsorption process equals that of the desorption pro-

TABLE 1 : Structural parameter of EG

Expanded volume $mL \cdot g^{-1}$	Specific surface area $m^2 \cdot g^{-1}$	Pore volume $cm^3 \cdot g^{-1}$
90	24.03	28.67
180	43.31	30.4
240	79.92	66.73

TABLE 2 : Chemical structure molecular weight and  $\lambda_{max}$  of AQS

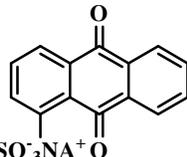
Structure	Molecular weight	$\lambda_{max}$ (nm)
 Anthraquinone-2,6-disulfonate	412.30	327.2

TABLE 3: Langmuir and freundlich isotherm constants at 25°C

Langmuir <sup>a</sup>			Freundlich <sup>b</sup>		
$q_m$ $mg \cdot g^{-1}$	$K_L$ $L \cdot mg^{-1}$	$r$	$K_F$	$1/n$	$r$
166.1±43.9	21.6±1.1	0.991	35.1±1.2	0.248±0.009	0.963

a-Linear Langmuir equation:  $C_e/q_e = 1/(K_L q_m) + C_e/q_m$ ; b-Linear Freundlich equation:  $\ln q_e = \ln K_F + (1/n) \ln C_e$ , where:  $K_F$ - Freundlich equation constant;  $K_L$ - Langmuir equation constant ( $L \cdot mg^{-1}$ );  $q_m$ - maximum adsorption amount ( $mg \cdot g^{-1}$ );  $1/n$ - adsorption intensity for Freundlich equation

cess. Adsorption equilibrium is governed by several factors such as the nature of adsorbates and adsorbents as well as the solution composition and temperature.

### 1. Effect of AQS concentration-adsorption isotherms

The adsorption isotherms of AQS on EG at 25°C are shown in figure 1.

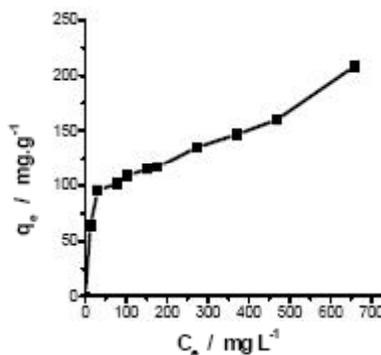


Figure 1: The influence of AQS concentration on adsorption (25°C expanded volume of EG is 240mL/g pH=6.0 ionic strength 0.0)

Langmuir and Freundlich isotherm equations are used to treat the isotherm data. The results are listed in TABLE 3. Langmuir isotherm gives a better fit than

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Freundlich isotherm. Similar results were reported for the adsorption of brilliant blue on mesoporous hybrid xerogel<sup>[20]</sup>, and acids dye, actives dye, direct dye on chitosan<sup>[21]</sup>.

### 2. Effect of solution pH

The effect of solution pH on the equilibrium adsorption amount is shown in figure 2. It demonstrates that the pH doesn't have an obvious influence because of the strong acid of sulfonic acids.

### 3. Effect of ionic strength

The effect of ionic strength on the equilibrium adsorbance is demonstrated in figure 3. It is shown that the adsorption increases with the increase in solution ionic strength. That is the result of the "salting-out" effect. For the adsorption of brilliant blue on hybrid xerogel<sup>[20]</sup>, adsorbance was also found to increase with increasing ionic strength.

### 4. Effect of expanded volume of EG

The effect of expanded volume of EG on the equilibrium adsorbance is shown in figure 4. In the detected range of expanded volume, the adsorbances increase with increasing expanded volume. It is because of the increase of specific surface areas and pore volumes with the increasing expanded volume.

### 5. Influence of temperature on adsorbance

Influence of temperature on AQS adsorbance is shown in figure 5, and no obvious change is observed.

## Adsorption kinetics

### 1. Equilibrium time

Adsorption occurs more rapidly at higher tempera-

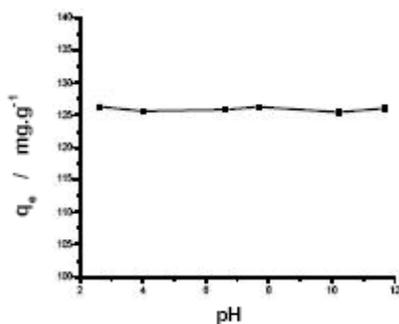


Figure 2: Effect of pH on the adsorption (25°C, initial concentration of AQS is 250 mg L<sup>-1</sup>, ion strength 0.0)

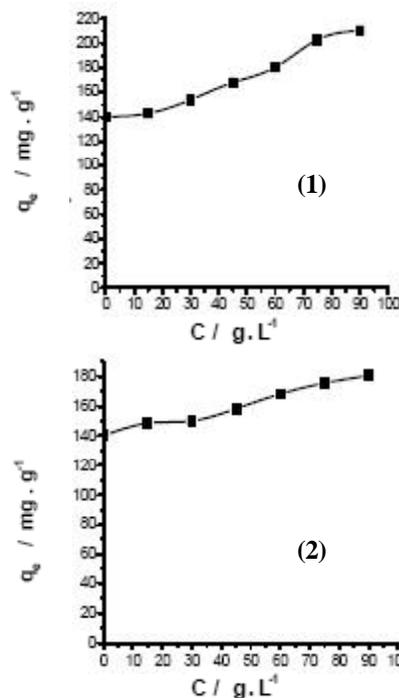


Figure 3: Effect of ionic strength on adsorbance (25°C, Initial AQS concentration is 300mg L<sup>-1</sup>, pH=6.0, (1) NaCl (2) Na<sub>2</sub>SO<sub>4</sub>)

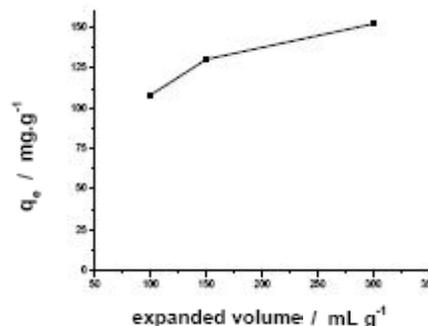


Figure 4: Effect of expanded volume of EG (25°C, initial concentration of AQS is 300mg L<sup>-1</sup>, pH=6.0, ion strength is 0.0)

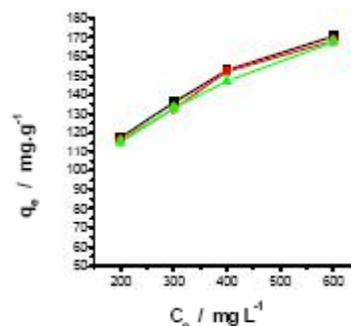


Figure 5: Effect of temperature (pH=6.0, ion strength is 0.0, temperature is (■) 5°C (●) 25°C (▲) 45°C)

TABLE 4: Comparison of the kinetic models

C <sub>0</sub> mg·L	T°C	q <sub>e,exp</sub> mg·g <sup>-1</sup>	First-order			Second-order		
			q <sub>e,cal</sub> mg·g <sup>-1</sup>	K min <sup>-1</sup>	r	q <sub>e,cal</sub> mg·g <sup>-1</sup>	k ×10 <sup>-3</sup> mg·L <sup>-1</sup> ·min <sup>-1</sup>	r
200	5	117.5	107.9±1.1	0.312±0.013	0.995	137.4±7.4	7.28±0.39	0.993
	25	116.0	90.6±1.1	0.286±0.020	0.985	121.2±3.8	8.25±0.26	0.998
	45	115.2	47.0±1.1	0.212±0.029	0.965	109.5±4.2	9.13±0.35	0.997
300	5	132.9	90.7±1.0	0.312±0.060	0.933	160.5±9.1	4.02±0.19	0.992
	25	132.7	117.3±0.88	0.291±0.020	0.988	153.9±8.3	4.16±0.22	0.994
	45	136.0	115.4±0.88	0.195±0.017	0.977	150.7±8.6	4.25±0.24	0.992
400	5	152.8	140.57±0.86	0.284±0.020	0.990	175.1±11.6	3.66±0.24	0.994
	25	147.1	104.2±0.93	0.270±0.034	0.962	148.7±0.96	4.30±0.03	1.000
	45	152.1	86.3±1.2	0.415±0.133	0.875	143.1±0.85	4.47±0.04	1.000
600	5	170.5	156.8±0.69	0.286±0.013	0.996	203.8±13.0	2.07±0.13	0.994
	25	168.3	148.1±0.71	0.402±0.024	0.995	192.3±2.4	2.20±0.03	1.000
	45	167.4	125.4±0.90	0.58±0.113	0.964	173.8±2.7	2.43±0.04	1.000

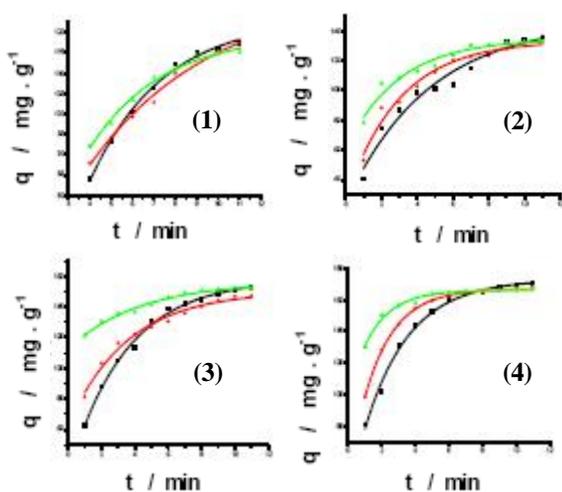


Figure 6: Effect of the initial AQS concentration and temperature on adsorption kinetics (Initial AQS concentration is (1)200mg/L, (2) 300mg/L, (3) 400mg/L and (4) 600mg/L, Ion strength is 0.0; pH=6.0; Temperature (■)5°C (●)25°C and (▲)45°C)

TABLE 5 : Kinetic parameters for the second-order adsorption model

C <sub>0</sub> mg·g <sup>-1</sup>	T°C	u mg·g <sup>-1</sup> ·m <sup>2</sup>	t <sub>1/2</sub> min	E <sub>a</sub> kJ·mol <sup>-1</sup>	r
200	5	109.53±0.006	1.17±0.06		
	25	121.21±0.004	1.04±0.03	4.20±0.07	0.999
	45	137.36±0.021	0.95±0.04		
300	5	96.42±0.018	1.87±0.09		
	25	98.46±0.015	1.81±0.10	1.01±0.09	0.996
	45	103.67±0.016	1.73±0.10		
400	5	91.59±0.001	1.79±0.12		
	25	95.17±0.001	1.58±0.01	3.78±1.17	0.955
	45	112.04±0.032	1.47±0.01		
600	5	73.43±0.001	2.83±0.18		
	25	81.25±0.001	2.71±0.03	2.92±0.59	0.980
	45	86.09±0.022	2.46±0.04		

ture: it takes only 5 minutes to reach the adsorption equilibrium at 45°C, while it will take a little more at 5°C. Thus, 12 minutes was set for the adsorption thermodynamics experiments. The amount of AQS adsorbed is shown as a function of time in figure 6.

## 2. Adsorption kinetic models

Both pseudo first- and second-order adsorption models were used to describe the adsorption kinetics data, and the overall adsorption rate is supposed proportional to either the driving force or the square of the driving force.

First-order model:  $\ln(q_e - q) = \ln q_e - kt$  (2)

Second-order model:  $t/q = 1/(k q_e^2) + t/q_e$  (3)

where: k-adsorption rate constant (min<sup>-1</sup> for first-order adsorption, g·mg<sup>-1</sup>·min<sup>-1</sup> for second-order adsorption), t-adsorption time (min)

Since q reaches a plateau (q<sub>e</sub>) at equilibrium, q values smaller than the 0.9q<sub>e</sub> were used for analysis. The plots of ln(q<sub>e</sub> - q) versus t and t/q versus t were used to test the first- and second-order models, and the fitting results are given in TABLE 4. As for the line curve fit, second-order model gives higher correlation coefficients. And the q<sub>e,cal</sub> corresponding to second-order model, agrees more well with the experimental data except at 5°C. Thus, the second-order model is more suitable to describe the adsorption kinetics data, and the adsorption rate constant increases with the increase of temperature.

Based on the second-order model, the initial adsorption rate and half-adsorption time are estimated in TABLE 5 according to the following equations:

$u = kq_e^2$  (4)

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$$t_{1/2} = 1/(kq_e) \quad (5)$$

where:  $u$  - initial adsorption rate mg/(g·min)  $t_{1/2}$  - half-adsorption time(min)

Half-adsorption time,  $t_{1/2}$ , is defined as the time required for the adsorption to take up half as much AQS as its equilibrium value. As showed in TABLE 5, normally, the initial adsorption rate is found to increase with the increase of temperature, and the half-adsorption time  $t_{1/2}$  decrease with the increase of temperature.

The second-order rate constants listed in TABLE 4 are used to estimate the activation energy of AQS adsorption on the EG using Arrhenius equation:

$$\ln k = \ln A - E_a/(RT) \quad (6)$$

The slope of plot of  $\ln k$  versus  $1/T$  is used to evaluate  $E_a$ , which was found to be 1.01~4.20 kJ·mol<sup>-1</sup> depending on the initial AQS concentration (TABLE 5). Physical adsorption may be the major adsorption, and it can be deduced from the short adsorption equilibrium times, small active energy  $E_a$  and weak influence of temperature on adsorption rate constants.

## CONCLUSIONS

The adsorption characteristics of EG for AQS have been investigated. The results are summarized as follows:

1. The adsorption type of AQS on EG is type II, equilibrium adsorption amount is found to increase with the increase in initial AQS concentration. Adsorption isotherm can be described with Langmuir equation. pH doesn't have an obvious influence on equilibrium adsorbance, but it increases with the increase in solution ionic strength and the expanded volume of EG.
2. The adsorption kinetics can be described by the pseudo second-order kinetic model. Normally, the second-order adsorption rate constant and initial adsorption rate increase with the increasing of temperature.

The physical adsorption is the major adsorption of the overall adsorption process.

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