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Adsorption thermodynamics and kinetics of expanded graphite for oxamine blue GN

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ABSTRACT

In order to investigate the adsorption thermodynamic and kinetic characteristics of expanded graphite (EG) for oxamine blue GN, EG was prepared with 50 mesh crude graphite after chemical oxidation intercalation of potassium permanganate and vitriol. The adsorbent was characterized by expanded volume, specific surface area and pore cubage. In thermodynamic study, adsorption isotherm and free energy change (⊿G°) were detected and calculated, respectively. Influence of pH on absorbency and adsorbance, and impact of ion strength on adsorbance were investigated. In kinetic study, adsorption model and rate-limiting step for the adsorption process were discussed, adsorption rate and activation energy are calculated. Results illustrate: adsorption of oxamine blue GN on EG is a spontaneous process, and adsorption isotherm is type I. The presence of salts and the proper adjustment of pH would improve adsorption capacity. Kinetic studies show that the kinetic data can be well described by the pseudo second-order kinetic model. The internal diffusion appears to be the rate-limiting step for the adsorption process.

KEYWORDS

Expanded graphite;
Oxamine blue GN;
Adsorption thermodynamics;
Adsorption kinetics;
Ion strength;
Rate-limiting step.

INTRODUCTION

Expanded graphite (EG) is a kind of porous material, and can be prepared through chemical oxidation or electric chemical oxidation[1,2]. For its porous structure, EG is attracting attention of scientists and engineers as an adsorbent of organic substance, such as heavy oil[3-7]. As for the systemic adsorption study for dyes, it has been reported not so much. Wang pressed the worm-like particles into low-density plate of 0.1g/cm^3[8], then the plate was used to treat dye waste-water from woolen mill, and the optimum applying condition was tested. Research group of Hebei Normal University investigated the influence factors in adsorption process and indicated that the adsorption capacity was influenced by various factors, not only the expanded volume, primary concentration of dyes, contact time, but also the amount of EG, pH and temperature[9]. But they neglected the influence of pH both on absorbency and adsorption capacity, and improper pH was used. At the same time, too high dosage of EG or too low initial dyes concentration caused adsorption isotherms of the tested dyes were all type I. So, as the main source of wastewater, a systemic adsorption thermodynamics and kinetics studies of dyes on EG is need to carry out in order to predict their adsorption characteristics.

Oxamine blue GN is one kind of azoic dye, it is widely used in printing and dyeing then causes plenty of wastewater. As an adsorbate, its adsorption thermodynamic and kinetic characteristics on EG are studied in this paper.

EXPERIMENTAL

Adsorbent

Expandable graphite was prepared with 50 mesh crude graphite (C) as material, $KMnO_4$ as oxidant ($KMnO_4$: C = 0.15:1, mass ratio) and vitriol as intercalation compound (H_2SO_4: C = 5:1, mass ratio, the mass concentration of vitriol was 50%). EG was prepared with expandable graphite expanded in KSW heating oven at 900 °C. Structural parameters of EG were characterized by expanded volume, specific surface area and total pore volume. These data were detected with BET N_2 adsorption by Micromeritics Instrument Corporation TriStar II 3020 V1.02. Porosity characteristics of EG are showed as TABLE 1.

TABLE 1 : Structural parameter of EG[a]

Expanded volume (Ml/ g)	Specific surface area (m^2/g)	Pore volume (cm^3/g)
330	34.3458	0.100941

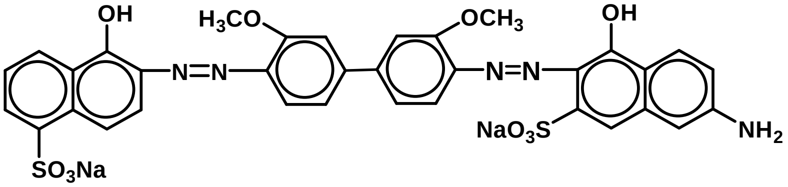
a -- Detection condition:
Analysis adsorptive: N_2; Sample mass: 0.1451 g; Equilibration interval: 10 s; Surface area or pore volume of pores between 1.7000 nm and 300.0000 nm diameter

Adsorbate

An azoic dye of oxamine blue GN was selected as reference compound, its molecular structure and molecular weight is showed in TABLE 2.

Simulated dye wastewater was prepared by dissolving the dye in distilled deionized water at various concentrations. Color measurements were made with T6 New Century UV spectrophotometry (Puxi Tongyong Instrument Limited Company of Beijing) operating in the visible range on absorbance mode. Absorbance values were recorded at the wavelength for maximum absorbance (λ_{max}), and oxamine blue GN solution was initially calibrated for concentration in terms of absorbance units.

TABLE 2 : Chemical structure and molecular weight of oxamine blue GN

	Structure	Molecule weight	λ_{max}(nm)
Oxamine blue GN		773.7	560

Methods

Static adsorption and equilibrium adsorption amount

Batch equilibrium experiments were undertaken. A series of desired dye concentration and of fixed volume 100.0 mL were placed in vessels where they were brought into contact with 0.2000 g EG at 5 °C, 25 °C and 45 °C, respectively. The jars were sealed and placed in a shaker for definite time until equilibrium reached. Samples were then analysed using standard spectrophotometry techniques. The amount of adsorbate captured by the adsorbant was determined as equation (1):

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

Q -- Adsorbance, mg/g; C_0 -- Initial concentration of dye, mg/L; C -- Equilibrium concentration of dye, mg/L; M -- Mass of adsorbent, g

Adsorption capacity of EG in the influence of ion strength and pH

NaCl and Na_2SO_4 were used to investigate the influence of ion strength on adsorption capacity. Batch equilibrium experiments were undertaken by using a 150 mg/L of oxamine blue GN solutions which corresponding to different ion strength ranging from 0 to 100 g/L. Equilibrium adsorption amount was calculated according to equation (1).

In the range of 2 to 12, pH of oxamine blue GN solution with a concentration of 150 mg/L was adjusted by HCl or NaOH, and then detected with pHS-3C acidimeter (Weiye Instrument Company of Shanghai). The absorbencies under different pH were detected. pH which had no influence on absorbency was chosen to study the influence of pH on adsorption capacity.

RESULTS AND DISCUSSION

Adsorption thermodynamics

Investigation of adsorption isotherm and thermodynamic parameters

Static adsorption capacities of EG corresponding to different equilibrium concentrations of oxamine blue GN were measured. As a plot of solid phase equilibrium adsorbance versus liquid phase equilibrium concentration, Figure 1 gives a typical I type adsorption isotherm. In the adsorption research of organic molecules on EG[10,11], such as linear herring sperm DNA and anthraquinone-2, 6-disulfonate, similar results were obtained. Planar or linear structure of organic molecules might form certain kinds of conformation on EG surface, which might reduce the adsorbed sites and make the further adsorption difficult.

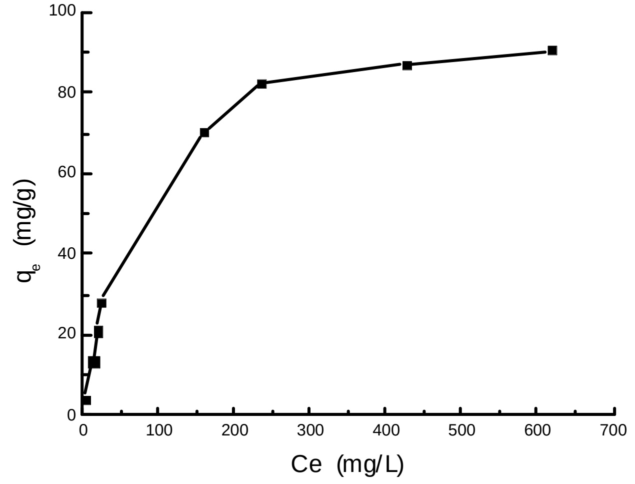


Figure 1 : Adsorption isotherm of oxamine blue GN at 25°C

In the condition of monolayer adsorption, adsorption constant can be obtained from Langmuir equation[12]:

$$Q = Q_0 \cdot C/(A+C) \qquad (2)$$

Q_0 -- The maximum adsorption amount of dye on EG in forming complete monolayer coverage on the surface, mg/g; A -- The equilibrium concentration of dye corresponding to half saturation adsorbance, mg/L

Equation (2) could be changed as equation (3). Based on equation (3), Q_0 and A could be calculated from the intercept and slope of the straight line.

$$1/Q = 1/Q_0 + A\cdot/(Q_0 \times C) \qquad (3)$$

Adsorption free energy change ($\triangle G^\circ$) could be calculated according to equation (4)[13].

$$\triangle G^\circ = -RT\ln b \qquad (4)$$

b -- Langmuir equation constant, mL/mg, b = 1/A; $\triangle G^\circ$ -- Free energy change in adsorption.

Based on experimental data, Langmuir constants for oxamine blue GN were shown in TABLE 3. Negative $\triangle G^\circ$ indicated that adsorption is spontaneous.

TABLE 3 : Adsorption constants and thermodynamic parameter of oxamine blue GN

	Saturation adsorbance in monolayer coverage Q_0 (mg/g)	Quilibrium concentration corresponding to half saturation adsorbance A (mg/L)	Gibbs energy $\triangle G^\circ$ (kJ/mol)
Oxamine blue GN	93.11	26.83	−8.81

Influence of ion strength on adsorption capacity

Influence of ion strength on adsorption capacity of EG for oxamine blue GN are showed in Figure 2. It indicates that the presence of NaCl, Na_2SO_4 and the increasing ion strength can improve adsorbance. Under the same mass concentration, influence of NaCl is higher than Na_2SO_4.

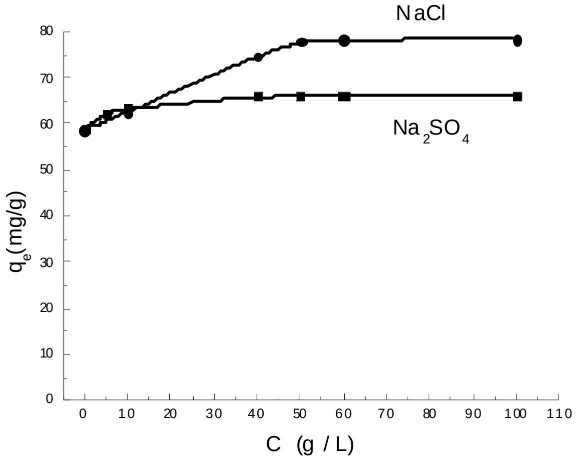


Figure 2 : Influence of ion strength on adsorption capacity

Influence of pH on absorbency and adsorption capacity

Ionic dyes upon dissolution release colored dye anions/cations in solution, and their absorbency changes along with the existence form, which is influenced by pH. So it is important to know how the pH influence absorbency and what the range of pH is before the study of pH on adsorption capacity. Figure 3 and 4 indicates that acidity has no noticeable impact on absorbency and adsorption capacity. The coexistence of functional group of OH and NH_2 in oxamine blue GN molecule causes the amount of non-dissociative molecules do not change with the changing of pH, and then pH has no influence on adsorption capacity.

Adsorption kinetics

Equilibrium time

As showed in Figure 5, adsorbance is showed as a function of time, and adsorption occurs more rapidly at higher temperature: it takes about 4.0 h to reach equilibrium at 45 °C, and 24.0 h at 5 °C. Oxamine blue GN initial concentration do not have significant effect on the equilibrium time.

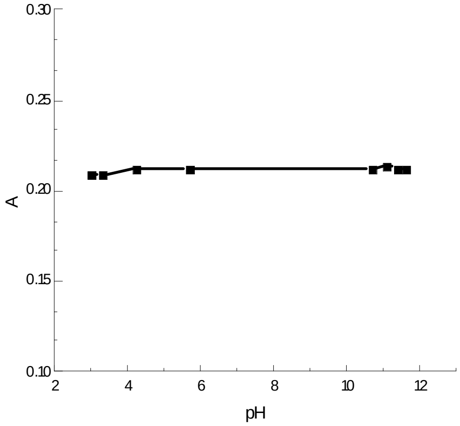


Figure 3 : Influence of pH on absorbency

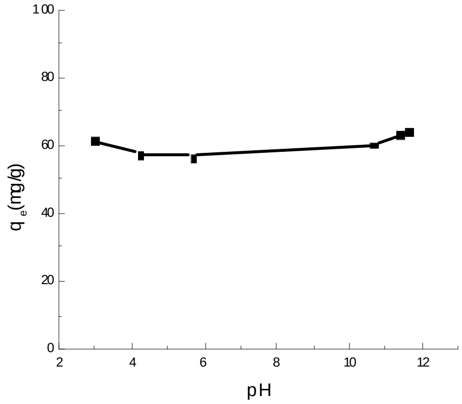
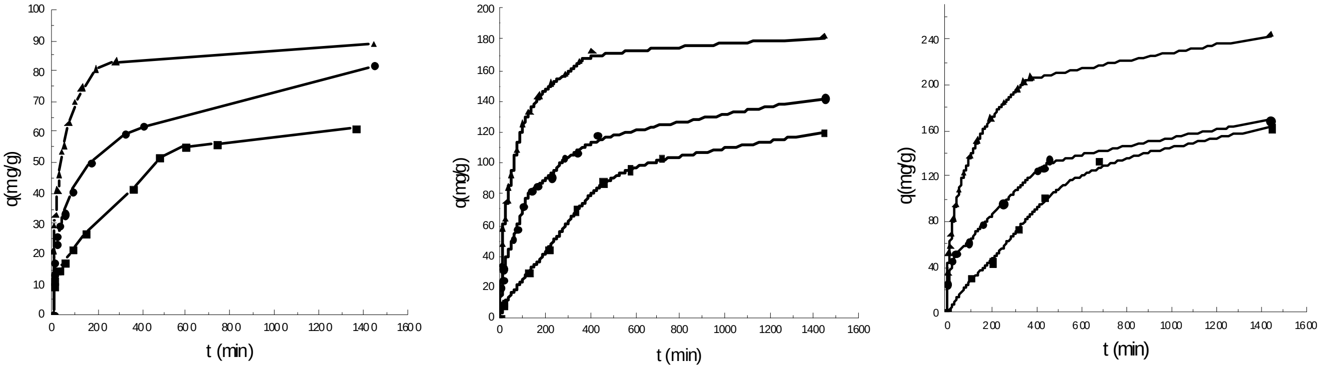


Figure 4 : Influence of pH on adsorption capacity



(a) **(b)** **(c)**

Oxamine blue GN initial concentration (a) 100 mg/L, (b) 200 mg/L; (c) 600mg/L (■) 5 °C, (●) 25 °C, (▲) 45 °C

Figure 5 : Influence of initial concentration and temperature on adsorption kinetics.

Adsorption kinetic models

Both pseudo first- and second-order adsorption models were used to describe the adsorption kinetics data[14,15]. In both models, all the steps of adsorption such as external diffusion, internal diffusion, and adsorption are lumped together. The overall adsorption rate is proportional to either the driving force (as in the pseudo first-order equation) or the square of the driving force (as in the pseudo second-order equation).

First-order model:

$$\mathrm{Ln}(q_e-q)=\mathrm{Ln}q_e-k_1t \quad (5)$$

Second-order model:

$$t/q=1/(k_2\,q_e^2)+t/q_e \quad (6)$$

k -- Adsorption rate constant (min^{-1} for first-order adsorption, g/(g·min) for second-order adsorption); *t*— Adsorption time (min)

Since q reaches a plateau (q_e) at equilibrium, q values smaller than the $0.9q_e$ were used for analysis. The plots of $\ln(q_e-q)$ 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. According to the correlation coefficients, second-order model gives satisfactory fits. At the same time, the $q_{e,cal}$ of second-order model agrees well with the experimental data.

Thus, the second-order model is more suitable to describe the adsorption kinetics data. Similar result was observed in the adsorption of anthraquinone-2, 6-disulfonate on EG[11].

TABLE 4 : Adsorption kinetic model comparison of oxamine blue GN on EG

C_0 mg / L	T ℃	$q_{e,exp}$ mg / g	First-order			Second-order		
			$q_{e,cal}$ mg / g	$k_1 \times 10^{-3}$ / min^{-1}	r	$q_{e,cal}$ mg / g	$k_2 \times 10^{-5}$ / g / (g·min)	r
200	5	67.69	52.30±1.07	1.80±0.14	-0.969	68.30±1.02	9.80±0.15	1.000
	25	81.66	58.88±1.04	2.96±0.21	-0.976	70.60±2.98	21.10±0.89	0.997
	45	88.65	61.41±1.03	10.90±0.37	-0.995	93.00±1.63	32.90±0.58	0.999
400	5	119.65	137.37±1.08	3.03±0.63	-0.996	123.60±3.95	4.80±0.79	0.999
	25	141.92	112.40±1.03	3.68±0.16	-0.990	134.80±2.13	8.30±0.27	0.999
	45	181.22	135.60±1.03	8.05±0.37	-0.991	190.10±2.56	9.90±0.13	0.999
600	5	173.79	162.00±1.07	1.90±0.14	-0.979	194.20±1.67	1.80±0.16	0.996
	25	168.99	134.60±1.05	3.36±0.16	-0.994	189.40±2.31	3.20±0.08	1.000
	45	243.23	182.90±1.03	4.45±0.15	-0.993	260.40±5.15	3.80±0.08	0.999

Based on the second-order model, initial adsorption rate and half-adsorption time are estimated in TABLE 5 according to the equation (7) and (8). Initial adsorption rate is found to increase with the increase in temperature, but oxamine blue GN initial concentration has no obvious influence on for it. Then, second-order rate constants listed in TABLE 5 are used to estimate adsorption activation energy according to Arrhenius equation (9). Sope of plot of ln*k* versus 1/*T* is used to evaluate *E*a. Results of 13. 48–22.58kJ/mol is higher than that of anthraquinone-2, 6-disulfonate on EG[11], and this might be cause by bigger molecule area of oxamine blue GN possessed.

$$u = kq_e^2 \qquad (7)$$

$$t_{1/2} = 1/(kq_e) \qquad (8)$$

u -- Initial adsorption rate, mg/(g·min); $t_{1/2}$ -- Half-adsorption time, min

$$Lnk = LnA - Ea/(RT) \qquad (9)$$

A -- Pre-exponential factor, g /(mg·min); Ea -- Activation energy of adsorption, kJ/mol

TABLE 5 : Kinetic parameters for second-order adsorption model

C_0 mg/g	Temperature °C	u mg/(g·min)	$t_{1/2}$ min	E_a kJ/mol	r
200	5	0.456	124.631	22.58	-0.994
	25	1.053	77.547		
	45	2.849	31.117		
400	5	0.740	172.518	13. 48	-0.971
	25	1.512	84.671		
	45	3.598	55.439		
600	5	0.692	313.683	13. 69	-0.963
	25	1.166	182.065		
	45	2.582	107.983		

Internal diffusion analysis

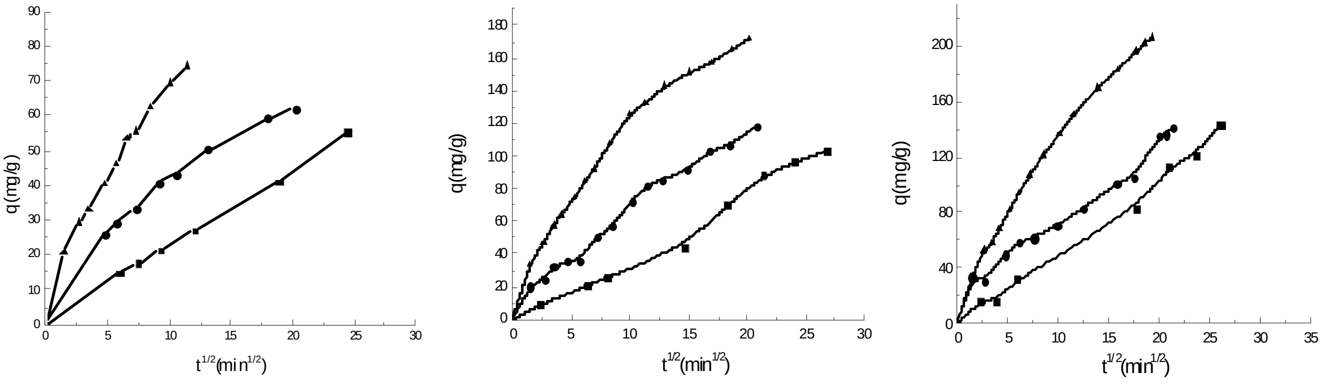
The adsorption process on a porous adsorbent generally involves three stages: (i) external diffusion; (ii) internal diffusion (or intra-particle diffusion); (iii) actual adsorption[16]. Quantitative treatment of experimental data may reveal the predominant role of a particular step among the three that actually governs the adsorption rate. The adsorption step is usually very fast for the adsorption of organic compounds on porous adsorbents compared to the external or internal diffusion step[17], and it is known that the adsorption equilibrium is reached within several minutes in the absence of internal diffusion[18]. Thus, the long adsorption equilibrium time in experiments (4.0–24.0 h) suggests that the internal diffusion may dominate the overall adsorption kinetics.

To provide definite information on the rate-limiting step, an internal diffusion model based on Fick's second law is used to test if the internal diffusion step is the rate-limiting step[19]:

$$q = k_{id} t^{1/2} \qquad (10)$$

k_{id} -- Internal diffusion constant, mg/(g·min$^{1/2}$)

According to the internal diffusion model, a plot of q versus $t^{1/2}$ should give a straight line with a slope k_{id} and an intercept of zero if the adsorption is limited by the internal diffusion process. The relationships between q and $t^{1/2}$ at different temperature are showed in Figure 6. Initially in all the cases studied, a linear relationship between q versus $t^{1/2}$ with a zero intercept is found, suggesting that the internal diffusion step dominates the adsorption process before the equilibrium is reached.



(a) **(b)** **(c)**

Initial oxamine blue GN concentration is (a) 200 mg/l, (b) 400 mg/l, (c) 600mg/l; (■) 5°C, (●) 25°C, (▲) 45°C

Figure 6 : Plot of *q* vs. $t^{1/2}$ in internal diffusion model.

CONCLUSIONS

This study has provided an insight into the adsorption thermodynamic and kinetics of EG for oxamine blue GN.

Thermodynamics study illustrates: adsorption of oxamine blue GN on EG is a spontaneous process, and the adsorption isotherm is type I. Adsorption process is influenced by multifactor, not only the initial concentration, the amount of EG, but also the ion strength of solution. High amount of EG, oxamine blue GN initial concentration and ion strength are propitious to adsorbance.

Kinetic study illustrates: adsorption kinetics can be well described by the pseudo second-order kinetic model. The second rate constant and initial adsorption rate increase with the increase of temperature. Active energy of adsorption is less than 40 kJ / mol, and internal diffusion step dominates the adsorption process before the equilibrium is reached.

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