Scientific Research

Adsorption Capacity of Expansion Graphite for Xylenol Orange[*]

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Abstract

Expansion graphite (EG) processing of an expanded volume of 400 mL/g was prepared with 50 mesh crude graphite after chemical oxidation intercalation of potassium permanganate and vitriol, and its adsorption kinetics and thermodynamics characteristics for xylenol orange (XO) was investigated. In thermodynamic study, adsorption isotherm and free energy change ($\triangle G°$) were detected and calculated, respectively. Influence of ionic strength on adsorbance was investigated. Kinetic studies were carried out with a series of XO concentration under different temperatures, and the data were simulated with pseudo first-order and second-order kinetic model, respectively. Results illustrate: adsorption of EG for XO is a spontaneous process, and adsorption isotherm is type II; equilibrium adsorbance increases with the increase of ionic strength. Kinetic studies show that the kinetic data can be delineated by pseudo second-order kinetic model. Initial adsorption rate increases with the increase of temperature. Adsorption activation energy is less than 20 kJ/mol; physical adsorption is the major mode of the overall adsorption process.

1. Introduction

Expansion graphite (EG) is a kind of porous material prepared through chemical oxidation or electric chemical oxidation [1,2]. EG had attracted attention of scientists and engineers as an adsorbent of organic substance, such as heavy oil [3-7]. As for the adsorption study for dyes, Wang pressed the worm-like particles into a low-density plate of 0.1g/cm³ [8], then the plate was used to treat dye waste-water from woolen mill, and the optimum applying condition was tested. Wang investigated the influence factors in adsorption process [9], and concluded that the adsorption capacity was affected by EG expansion volume and dosage, primary concentration of dyes, contact time, pH and temperature. But they neglected the influence of pH both on absorbency and adsorption capacity, and improper pH was used. At the same time, high EG dosage along with dyes low initial concentration caused adsorption isotherms of the tested dyes were all type I. Pang investigated the adsorption kinetic characteristics of Acid Red 3B on EG [10], and the kinetic data could be delineated by pseudo second-order kinetic model.

Xylenol orange (XO) is one kind of dye with triphenylmethane structure, it is widely used as chemical indicator and dye, and then causes plenty of wastewater. In its decoloration with coal powder [11] as adsorbent, the influence of adsorbent dosage, XO primary concentration, contact time and pH was investigated. Under the condition of pH 4, dosage of coal powder 8.0 g/L and XO initial concentration of 7.6 mg/L, A decoloration rate of 85% was gained after a 2.0 h decoloration treatment. With chitosan microsphere as adsorbent [12], the optimum decoloration condition of XO was gained as: pH 5, 2.0 h, dosage of chitosan microsphere with a diameter of 74 μm 0.3 g/L and XO initial concentration of 32 mg/L. As an adsorbent, EG adsorption capacity for XO has not been reported. The aim of the study is to investigate the adsorption characteristics of EG-XO system in water solution, and discuss the effect of ionic strength, concentration, temperature, and do further evaluation of applicability of common isotherm model (i.e., Langmuir and Freundlich) and pseudo-second-order rate model.

2. Experimental

2.1. Adsorbent

EG was prepared according to [13]. Its pore distribution was detected with Micromeritics Instrument Corporation

TriStar II 3020 V1.02, and pore structure parameters were calculated with BET method and shown in **Table 1**.

2.2. Adsorbate

XO molecular structure and molecular weight is shown in **Table 2**. Its simulated 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 XO solution was initially calibrated for concentration in terms of absorbance units.

2.3. Methods

Static adsorption of XO: 0.200 g of EG is mixed in conical glass flasks with 100 mL solution at the desired XO concentration and ionic strength. Ionic strength is adjusted with NaCl or Na_2SO_4 solution. Adsorption adsorbance was calculated according to Equation (1).

$$q = V(C_0 - C_t) / M \qquad (1)$$

q: Accumulative adsorbance of XO on EG at the moment of t, mg/g; C_t: Concentration of XO in solution at the moment of t, mg/L; *M*: mass of EG

Adsorption kinetics experiments of XO: Adsorption kinetics experiments were carried out using a HZS-D shaking water bath with a shaking speed of 100 rpm/min. A series of desired XO concentration and a fixed volume of 100 mL were placed in vessels, where they were brought into contact with 0.200 g EG at 15 °C, 25 °C and 35 °C, respectively. Amount of XO captured by EG at different time is determined according to Equation (1).

Table 1. Structural parameter of EG[a].

Expansion volume	Total volume cm³/g	Total pore area m²/g	Adsorption average pore width (4V/A) nm
400 mL/g	0.101	34.3	11.61

a. 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

Table 2. Chemical structure and quantitative method of XO.

Structure	λ_{max}/nm	Working curve equation
	436	Y= 0.01922+ 0.01501x

3. Results

3.1. Adsorption Thermodynamics

Investigation of adsorption isotherm and thermodynamic parameters: Static adsorption capacity of XO was detected as **Figure 1**. It is a typical II type isotherm, multilayer adsorption occurs on EG surface. In the condition of monolayer adsorption, the thermodynamic data were treated with Langmuir and Freundlich isotherm Equations (2) and (3), respectively. As shown in **Table 3**, Langmuir isotherm gives better results than Freundlich isotherm, and the monolayer saturation adsorbance of XO is 18.15 mg/g. But the total adsorbance increase with the increase of XO initial and equilibrium concentration due to its multilayer adsorption.

Langmuir equation: $1/q_e = 1/q_0 + A/(q_0 \times C_e)$ (2)

Freundlich equation: $\ln q_e = \ln K_F + (1/n)\ln C_e$ (3)

q_0: Saturation adsorption amount of XO in forming complete monolayer coverage on EG pore surface, mg/g; *A:* Equilibrium concentration of XO corresponding to half saturation adsorbance, mg/mL; K_F: Freundlich equation constant; *1/n:* Adsorption intensity for Freundlich equation
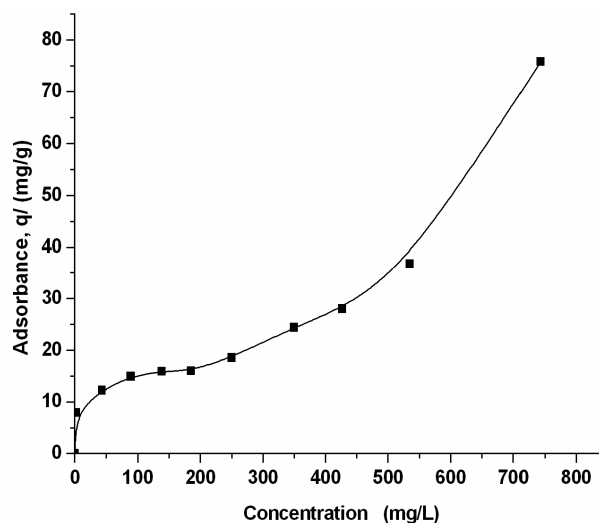

Figure 1. Adsorption isotherm of XO at 15°C.

Table 3. Langmuir and Freundlich isotherm constants of XO at 15 °C.

	Langmuir			Freundlich		
q_0 mg/g	A	r		K_F	1/n	r
18.15	0.0301	0.999		4.1915	0.3197	0.84

At the same time, adsorption free energy change ($\Delta G°$) is calculated according to Equation (4), the value is -8.388 kJ/mol, negative $\Delta G°$ indicates that adsorption of XO on EG is spontaneous.

$$\Delta G°= - RTlnb \qquad (4)$$

b: Langmuire equation constant; $\Delta G°$: The free energy change in the adsorption, kJ/mol

Influence of ion strength on adsorption capacity: NaCl and Na_2SO_4 were used respectively to adjust solution ionic strength in the range of 0 to 0.6 mol/L with MO concentration keeping 200 mg/L and 500 mg/L, respectively. Influence of ionic strength on adsorbance (shown in **Figure 2**) indicates that presence of salt ions can improve the adsorption capacity of EG for XO, and it might be caused by the increase of hydrophobic attraction of XO due to the "salting-out" effect. Under the same mass concentration, the influence of Na_2SO_4 is higher than that of NaCl.
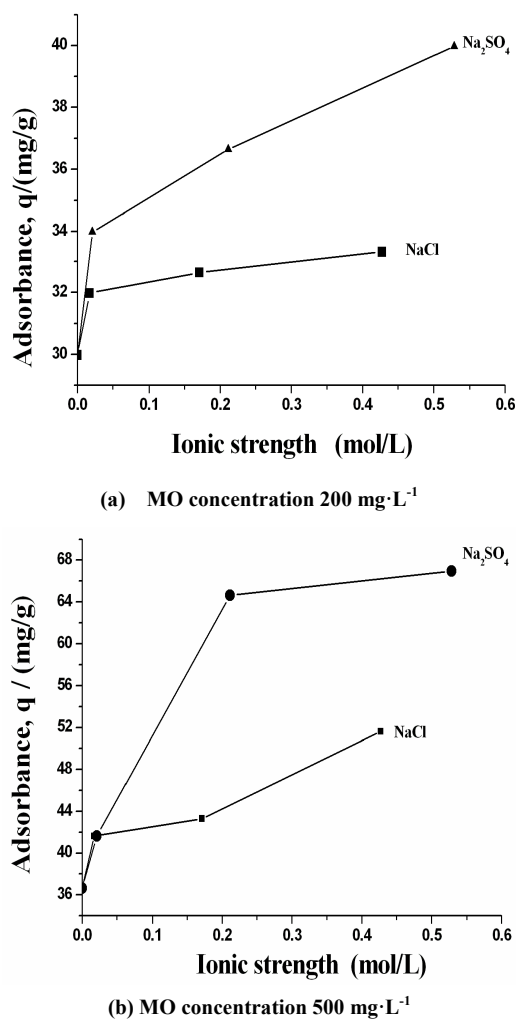
3.2. Adsorption Kinetics

Equilibrium time: Influences of XO concentration and temperature on adsorption equilibrium time were detected and shown in **Figure 3**. Results suggest that adsorbance is the function of XO concentration, temperature and adsorption time. In the beginning, adsorption rate increases with the increase of temperature, but temperature has no obvious influence on adsorption equilibrium time. In kinetic experiment, all adsorption could reach equilibrium within 24.0 h.
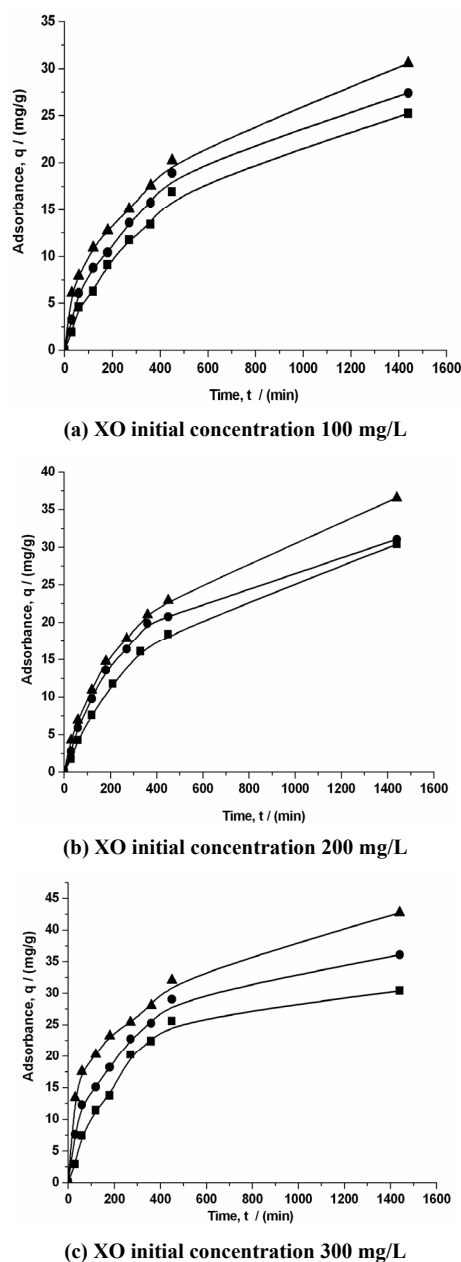

(a) XO initial concentration 100 mg/L

(b) XO initial concentration 200 mg/L

(c) XO initial concentration 300 mg/L

Figure 3. Influence of initial concentration and temperature on adsorption kinetics

(a)   MO concentration 200 mg·L^{-1}

(b) MO concentration 500 mg·L^{-1}

Figure 2. Influence of ionic strength on adsorption capacity of EG for XO.

Adsorption kinetic models: Both pseudo first- and second-order adsorption models were used to describe the adsorption kinetics data according to Equation (5) and (6) [14, 15].

First-order model： $\ln(q_e - q) = \ln q_e - kt$　(5)

Second-order model： $t/q = 1/(k\, q_e^2) + t/q_e$　(6)

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

Since q reached q_e at equilibrium, q values smaller than $0.9 q_e$ were used for analysis. 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 were given in

Table 4. Not only the line curve fit, but also $q_{e,cal}$, second-order model agrees more well with experimental data than first-order model. Second-order model is more suitable to describe XO kinetics data. Similar results were observed in the adsorption of EG for Acid Red 3B [10].

Based on the second-order model, initial adsorption rate and half-adsorption time were estimated according to Equations (7) and (8). As shown in **Table 5**, initial adsorption rate u increases with the increase of initial XO concentration and temperature. But there is no obvious relativity between half-adsorption time $t_{1/2}$ and temperature, XO concentration, respectively. The results are consistent with experiment data.

Table 4. Adsorption kinetics model comparison of EG for XO.

C_0 mg/L	T ℃	$q_{e,exp}$ mg/g	First-order			Second-order		
			$q_{e,cal}$ mg/g	k min^{-1}	r	$q_{e,cal}$ mg/g	$k/10^{-5}$ g/(mg·min)	r
	15	25.24	21.88	0.0028	-0.985	24.77	6.9	0.996
100	25	27.40	22.95	0.123	-0.977	26.38	8.7	0.993
	35	30.57	30.89	0.12	-0.979	30.33	10.0	0.984
	15	30.40	28.31	0.118	-0.979	31.39	4.5	0.999
200	25	31.07	28.77	0.118	-0.970	32.69	6.0	0.999
	35	36.56	35.74	0.138	-0.983	35.02	7.2	0.999
	15	30.40	32.63	0.211	-0.986	30.43	10.6	0.995
300	25	36.06	36.95	0.147	-0.987	36.23	14.0	0.997
	35	42.73	33.19	0.152	-0.943	43.34	14.0	0.992

Table 5. The second-order model parameters of EG for XO.

C_0 mg/L	T °C	u mg/(g·min)	$t_{1/2}$ min	E_a kJ/mol	r
	15	0.0743	572.96		
100	25	0.0976	416.67	14.28	-0.994
	35	0.1219	321.43		
	15	0.0783	719.41		
200	25	0.1081	445.97	17.50	-0.999
	35	0.1219	454.59		
	15	0.1218	307.77		
300	25	0.2231	201.07	9.059	-0.991
	35	0.2932	171.39		

$$u = kq_e^2 \tag{7}$$

$$t_{1/2} = 1/(k\, q_e) \tag{8}$$

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

To judge the sorption belongs to physical adsorption or chemical adsorption, the second-order rate constants are used to estimate activation energy of XO adsorption on EG using Arrhenius Equation (9). Plots of *lnk* versus *1/T* is used to evaluate Ea, and it is found less than 20.0 kJ/mol (as shown in Table 5). So, the adsorption between EG and XO is mainly physical adsorption.

$$Lnk = LnA - Ea/(RT) \tag{9}$$

A: The re-exponential factor, g/(mg·min); Ea: The adsorption activation energy, kJ/mol

4. Conclusion

This study has provided an insight into the adsorption characteristics of EG for XO.

Thermodynamics study illustrates: adsorption of XO on EG is a spontaneous process, and the adsorption isotherm is type II. Adsorption process is affected by multifactor, not only the initial concentration, temperature, but also the ionic strength of solution. High XO initial concentration and ionic strength are propitious to adsorbance.

Kinetic study illustrates: adsorption kinetics can be well described by the pseudo second-order kinetic model. Initial adsorption rate increases with the increase of temperature. Active energy of adsorption is less than 20 kJ/mol; and the sorption between EG and XO belongs to physical adsorption.

REFERENCES

[1] M. L. Xue, Y. L. Yu, Z. H. Ren and J. S. Zhang, "Improvement in Electrochemical Synthesis of Expanded Graphite," *Fine Chemicals*, Vol. 19, No. 10, 2002, pp. 567-570.

[2] J. H. Li, Q. Y. Liu, M. Li and Z. R. Liu, "Preparation of Low-sulphur Expandable Graphite," *Fine Chemicals*, Vol. 20, No. 6, 2003, pp. 341-342.

[3] M. Toyoda, K. Moriya, J. I. Aizawa, H. Konno and M. Inagaki, "Sorption and Recovery of Heavy Oils by Using Exfoliated Graphite Part I: Maximum Sorption Capacity," *Desalination*, Vol. 128, No. 3, 2000, pp. 205-211. doi:10.1016/S0011-9164(00)00034-5

[4] M. Inagaki, H. Konno, M. Toyoda, K. Moriya and T. Kihara, "Sorption and Recovery of Heavy Oils by Using Exfoliated Graphite Part II: Recovery of Heavy Oil and Recycling of Exfoliated Graphite," *Desalination*, Vol. 128, No. 3, 2000, pp. 213-218. doi:10.1016/S0011-9164(00)00035-7

[5] M. Inagaki, K. Shibata, S. Setou, M. Toyoda and J. I. Aizawa, "Sorption and Recovery of Heavy Oils by Using Exfoliated Graphite Part III: Trials for Practical Applications," *Desalination*, Vol. 128, No. 3, 2000, pp. 219-222. doi.:10.1016/S0011-9164(00)00036-9

[6] M. Toyoda, Y. Nishi, N. Iwashita and M. Inagaki, "Sorption and Recovery of Heavy Oils Using Exfoliated Graphite Part IV: Discussion of High Oil Sorption of Exfoliated Graphite," *Desalination*, Vol. 151, No. 3, 2003, pp. 139-144. doi:10.1016/S0011-9164(02)00992-X

[7] M. Inagaki, T. Nagata, T. Suwa and M. Toyoda, "Sorption Kinetics of Various Oils onto Exfoliated Graphite," *New Carbon Materials*, Vol. 21, No. 2, 2006, pp. 97-102.

[8] L. N. Wang, X. Chen, Y. P. Zheng, F. Y. Kang, J. F. Chen and W. C. Shen, "Application of Expansion Graphite on the Treatment of Woolen Mill Waste-water," *Guide Journal of Chinese Non-metal Mine Industry*, No. 5, 2004, pp. 59-62.

[9] L. N. Yang, "Study on the Adsorption of Expansion Graphite for Dyes," Master of Science, Thesis, Hebei Normal University, Shijiazhuang, 2004.

[10] X. Y. Pang and F. Gong, "Study on the Adsorption Kinetics of Acid Red 3B on Expanded Graphite," *E-Journal of Chemistry*, Vol. 5, No. 4, 2008, pp. 802-809. doi:10.1155/2008/786025

[11] Q. K. Hu and W. Jie, "Study on Removal of Xylenol Orange from Water by Fly-ash," Shanghai Chemical Industry, Vol. 31, No. 9, 2006, pp. 5-7.

[12] S. Wang, M. Y. Zheng, G. H. Ye and J. C. Guo, "Preparation of Chitosan Microspheres for Adsorptive Removal of Xylenol Orange," *Environmental Pollution & Control*, Vol. 30, No. 12, 2008, pp. 43-46.

[13] L. J. Xu, "Study on the Adsorption and Competitive Adsorption Capacities of Expanded Graphite for Environmental Pollutants," Master of Science, Hebei University, Baoding, 2011.

[14] Z. Aksu, "Biosorption of Reactive Dyes by Dried Activated Sludge: Equilibrium and Kinetic Modeling," *Biochemical Engineering*, Vol. 7, No. 1, 2001, pp. 79-84. doi:10.1016/S1369-703X(00)00098-X

[15] Z. J. Wu, H. Joo and K. Lee, "Kinetics and Thermodynamics of the Organic Dye Adsorption on the Mesoporous Hybrid Xerogel," *Chemical Engineering Journal*, Vol. 112, No. 1-3, 2005, pp. 227-236. doi:10.1016/j.cej.2005.07.011