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Study on the competitive adsorption thermodynamic and kinetic performance of methyl orange and fuchsin basic on expanded graphite adsorbent

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ABSTRACT

In this study, expanded graphite (EG) is prepared through chemical oxidation method with graphite as raw materials, potassium permanganate as oxidant, vitriol as intercalation compound and expanded at 900 °C. Methyl Orange (MO) with azo-structure and Fuchsin basic (FB) with tritane structure are selected as organic adsorbates, and their adsorption and competitive adsorption thermodynamic, kinetic characteristics on EG are investigated. The results are: In the adsorption and competitive adsorption of MO and FB on EG, the adsorption isotherms are all type I, and the existence of the other component MO or FB would decrease the adsorbance of EG for FB and MO due to the competitive adsorption of MO and FB for the same adsorbing site. But the total adsorbances in competitive adsorption are higher than adsorbance of MO or FB in single system because these adsorbates can also be adsorbed on different adsorbing site. Adsorption of MO or FB on EG is spontaneous, and the increase of ionic strength, temperature and specific surface area of EG would cause the increase of adsorbates adsorbance. No matter the adsorption of single component system, or the competitive adsorption of bi-component system, the kinetic models can all be described with pseudo second-order kinetic model. Adsorption rate increases with the increase in temperature. Physical adsorption is the main action between EG with adsorbates.

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KEYWORDS

Expanded graphite;
Methyl Orange;
Fuchsin basic;
Competitive adsorption;
Thermodynamics and
kinetics;
Replacement.

INTRODUCTION

Extensive use of color in industries such as textiles, paper, plastics, leather, food, cosmetic etc, often cause the formation of colored wastewater that require pre-treatment prior to disposal into receiving water bodies. The used dyes are normally resistant to biodegradation

and photodegradation. In wastewater treatment, adsorption is a kind of effective measure used for the elimination of these contaminants. Active carbon^[1-4], Mesoporous silica^[5,6], barrier discharge plasma^[7], ion exchange resin^[8] and organobentonite^[9] have been tested in the treatment of organic molecules.

Expanded graphite (EG) is a new kind of adsor-

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bent with abundant 4 levels pores with the size ranging from nanometer to micron^[10], and it has attracted attentions of scientists and engineers due to its high adsorption capacity for organic materials, such as heavy oil, dyes, aromatic sulfonates, PEG etc^[11-16]. Actually, pollutants rarely exist solely in single component, but the adsorption research for them on EG often carried in single component system. Study for the poly-component system can reveal characteristics of competitive adsorption on the same site, distribution and adsorbance difference caused by the physical or chemical interaction between the coexisting adsorbates. In the adsorption of atrazine on powdered activated carbon^[17], *p*-dichlorobenzene is found to significantly reduce atrazine adsorption capacity, but it has no effect on atrazine adsorption kinetics. In contrast, the effect of poly (styrene sulfonate) (PSS, MW=1800) on atrazine adsorption capacity is very small. In the competitive adsorption of Cu (II), Pb (II) and Cd (II)^[18], iminodiacetic acid chelating resin shows good selectivity toward Cu (II) over Pb (II) and Cd (II), interaction mechanism between the favorable component and other metal ions could mainly contribute to the direct displacement impact. The objective of the present research is to study bi-component system competitive adsorption characteristics on EG. Methyl Orange (MO) with azo-structure and Fuchsin basic (FB) with tritane structure are the selected references. Influence of dye concentration, ionic strength of solution, temperature and adsorbent specific surface area on adsorption and competitive adsorption capacities are investigated. The study not only can establish thermodynamic and kinetic models, give model parameter, but can also give some instruction for EG application as adsorbent.

EXPERIMENTAL

Adsorbent: Preparation and structure characteristics of EG adsorbent

The EG is prepared according to the mass ratio C : KMnO₄ : H₂SO₄ (98%) of 1.0 : 0.15 : 5.0 with different size of natural graphite of 0.3 mm, 0.18 mm and 0.15 mm as materials^[19]. The expansion volume (EV), surface area, pore size distribution and pore cubage

are detected and the results are listed in TABLE 1. In all the adsorption and competitive adsorption experiments, EG with an EV of 400 mL·g⁻¹ is used as adsorbent except for special illustration.

TABLE 1 : Structural parameter of EGs^a.

Materials size mm	EV mL·g ⁻¹	Pore volume cm ³ ·g ⁻¹	Surface area m ² ·g ⁻¹	Average pore Diameter 4V/A nm
0.3	400	0.1009	34.35	11.61
0.18	150	0.0698	23.84	11.61
0.15	35	0.06263	21.30	11.59

^a Instrument condition: adsorbate N₂; aperture ranges 1.7000 ~ 300.0000 nm; equilibration interval 10 s; maximum relative pressure $p/p_0 = 0.9858$

Adsorbate characteristics

Methyl Orange (MO) with azo-structure and Fuchsin basic (FB) with tritane structure are the selected references. The chemical structure and molecular weight are showed in TABLE 2.

Simulated wastewaters of MO and FB in single component and in bi-component are prepared by dissolving these adsorbates in de-ionized water at various concentrations. In quantitative analysis, T6 New Century UV spectrophotometer (Puxi Tongyong Instrument Limited Company of Beijing) is used. The absorption spectrum of MO and FB are detected as showed in Figure 1, quantitative equations of MO at 463 nm and quantitative equations of FB at 463 nm, 543 nm are founded and listed in TABLE 3.

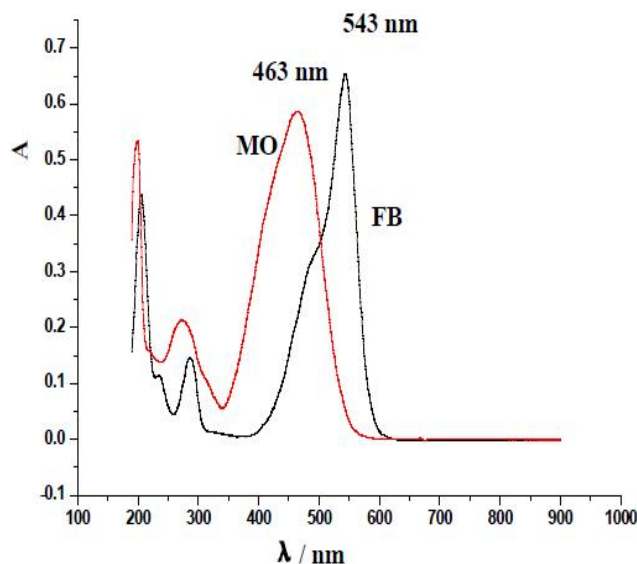


Figure 1 : Absorption wave of MO and FB.

TABLE 2 : Structures of MO and FB.

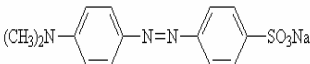
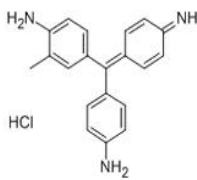
Adsorbates	Structure	Molecular weight
MO		327.33
FB		337.85

TABLE 3 : Working equations of DDB and MO^b.

Adsorbate	$\lambda_{max}(nm)$	Quantitative equations	r
MO	463	$Y = -0.00473 + 0.06765C$	0.9999
FB	543	$Y = -0.01052 + 0.12764C$	0.9998
	463	$Y = -0.00419 + 0.04285C$	0.9995

^b C—concentration of adsorbates, mg/L; Y—absorbance

Methods

(a) Static adsorption in single component system and bi-component system

0.20 g of EG is mixed in different conical glass flasks with 100.0 mL solution at the desired adsorbates concentration and ionic strength. Ionic strength is adjusted with NaCl or Na₂SO₄ solution. Mass of EG to volume of solution is standardized as $M/V = 0.200 / 0.1 = 2.0 \text{ g}\cdot\text{L}^{-1}$, the equilibrium time at 15 °C are about 25 h and 12 h for MO and FB, respectively; and it's not affected by adsorbate concentration. Absorbance and concentration changes of MO, FB are recorded with spectrophotometer and calculated according to equation listed in TABLE 3, and adsorbance q is calculated according to equation (1).

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

When the adsorption reaches equilibrium state, C can be written as C_e and q can be written as q_e .

(b) Adsorption capacity of EG under the influence of EV, ionic strength and temperature

EGs with different EV are used to detect the influence of adsorbent structure on adsorption capacity, mass of EG to volume of solution is standardized as $M/V = 0.200 / 0.1 = 2.0 \text{ g}\cdot\text{L}^{-1}$. NaCl and Na₂SO₄ are used to investigate influence of ionic strength on adsorbance.

Different temperature of 5 °C, 20 °C and 45 °C are controlled in kinetic studies. Adsorbance and equilibrium adsorbance are calculated according to equation (1).

RESULTS AND DISCUSSION

Investigation of adsorption isotherm and thermodynamic parameters

(a) Adsorption and competitive adsorption isotherms

As showed in Figure 2, typical I isotherms are observed under the tested condition, no matter in single component system or MO and FB bi-component system. But in bi-component system, the existence of competitive component can decrease FB or MO adsorbance, which indicates that MO and FB contest the same adsorption sites on EG.

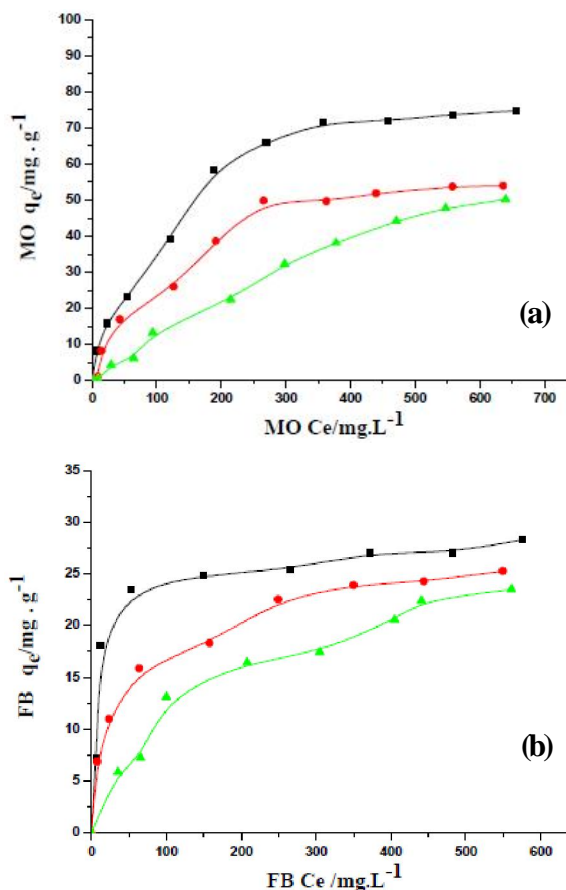


Figure 2 : Adsorption isotherm and competitive adsorption isotherm (a) MO (b)FB; (a) Concentration of FB (■) 0 mg·L⁻¹(●)50 mg·L⁻¹(▲)300 mg·L⁻¹; (b) Concentration of MO (■) 0 mg·L⁻¹(●)100 mg·L⁻¹(▲) 600 mg·L⁻¹

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To providing a description of adsorbate concentration and possible conformation in the interfacial region, Langmuir and Freundlich isotherm equations^[19] are used to treat the isotherm data. As showed in TABLE 4, these two models can all be used to describe the adsorption and competitive adsorption behaviors, and r is above 0.9. MO and FB saturation adsorbances q_0 in bi-component system are all smaller than that in single component system, and it decreases with the increase of competitive component concentration. The results illustrate again there are competitive adsorption for the same adsorbing site on EG and replacement between FB and MO.

TABLE 4 : Langmuir and freundlich isotherm constants at 15°C.

Adsorbates	Langmuir			Freundlich			
	$q_0(\text{mg}\cdot\text{g}^{-1})$	A	r	K_F	n	r	
Adsorption	FB	26.86	0.0169	0.998	7.479	4.482	0.967
	MO	64.35	0.163	0.983	3.163	1.936	0.987
Competitive adsorption	MO 100 mg·L ⁻¹	21.51	0.0515	0.984	4.046	3.32	0.989
	MO 600 mg·L ⁻¹	20.04	0.4047	0.983	1.007	1.972	0.975
	FB 50 mg·L ⁻¹	31.49	0.8664	0.989	0.4776	1.246	0.964
	FB 300 mg·L ⁻¹	30.99	0.9827	0.975	0.2317	1.175	0.99

Adsorption free energy changes (ΔG°) are calculated, and negative (ΔG°) (showed in TABLE 5) indicate that adsorption and competition adsorption of these reference compounds on EG are all spontaneous.

TABLE 5 : The gibbs energy of adsorption and competitive adsorption^c.

	Adsorption		Competitive adsorption			
	FB	MO	MO 100 mg·L ⁻¹	MO 600 mg·L ⁻¹	FB 50 mg·L ⁻¹	FB 300 mg·L ⁻¹
ΔG° kJ·mol ⁻¹	-9.775	-4.344	-7.101	-2.888	-0.343	-2.357

^c 1 atmosphere 15°C

(b) Comparison of adsorbances and competitive adsorbances

Under the same concentration condition, comparison of single component adsorbance and total adsorbance in single component system and bi-component system are carried. As showed in TABLE 6, there are relationships of single component adsorbance in competitive system less than single component adsorbance in single component system, single com-

ponent adsorbance in single component system less than total adsorbance of MO and FB in bi-component system, total adsorbance of MO and FB in bi-component system less than total adsorbance of MO and FB in single component system. The results testify there are competitive adsorptions for the same adsorbing site on EG and replacement between MO and FB, MO and FB can also adsorb on different adsorbing site as the same time. In competitive adsorption of FB and MO, the adsorbing site can be well utilized than that in single component adsorption.

TABLE 6 : Comparison of adsorbance and competitive adsorbance.

System	Concentration (mg·L ⁻¹)	Component	Adsorbance (mg·g ⁻¹)	Total adsorbance (mg·g ⁻¹)
Single component system	50	FB	18.12	45.84
	100	MO	27.72	
	300	FB	35.46	84.79
	600	MO	49.33	
Bi-component system	50	FB	17.82	42.31
	100	MO	24.49	
	300	FB	31.73	77.65
	600	MO	45.92	

Influence of EG particle size on adsorption and competitive adsorption capacity

Adsorption and competitive adsorption research are carried out using different EGs listed in TABLE 1 as adsorbent. As showed in Figure 3, the increase of EV of these adsorbents enhances the increase of adsorbance in single component system and bi-component system, but it has no influence on adsorption isotherm.

Influence of ionic strength on adsorption and competitive adsorption capacity

NaCl and Na₂SO₄ are used respectively to adjust solution ionic strength in the range of 0 to 0.45 mg·L⁻¹ with the concentration of MO keeping 100 mg·L⁻¹ and FB keeping 50 mg·L⁻¹. Influence of ionic strength on adsorbance (showed in Figure 4) indicate that presence of salt ions can improve the adsorption capacity of EG for these adsorbates, and it may be caused by increase of hydrophobic attraction of adsorbates due to the "salting-out" effect.

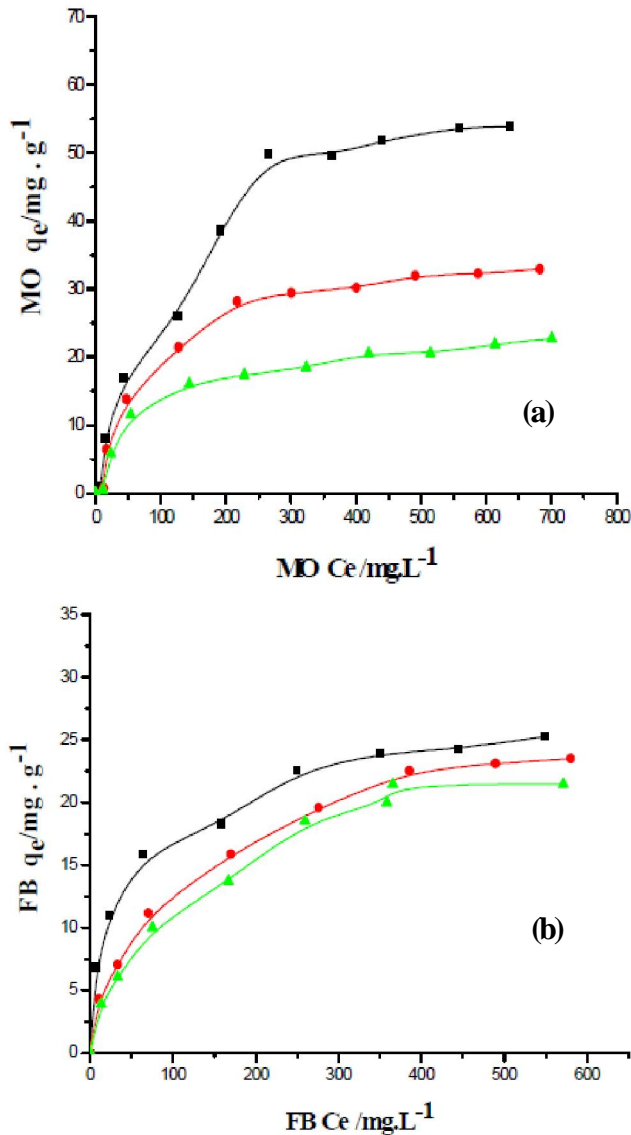


Figure 3 : Adsorption isotherms and competitive adsorption isotherms of MO and FB on different EG (a) MO (b) FB; (a) FB concentration $50 \text{ mg}\cdot\text{L}^{-1}$, EG size (\blacksquare) 0.3 mm (\bullet) 0.18 mm (\blacktriangle) 0.15 mm ; (b) MO concentration $100 \text{ mg}\cdot\text{L}^{-1}$, EG size (\blacksquare) 0.3 mm (\bullet) 0.18 mm (\blacktriangle) 0.15 mm

Investigation of kinetics parameters of adsorption and competitive adsorption

(a) Influence of adsorbate concentration and temperature on adsorption kinetics

MO and FB adsorbance on EG is a function of time, temperature and adsorbate concentration. As showed in Figure 5 and Figure 6, equilibrium times decrease with the increase of temperature, but they are not affected by adsorbate concentration. Equilibrium adsorbances increase with adsorbate initial concentration, and they have a slight increase with the increase of

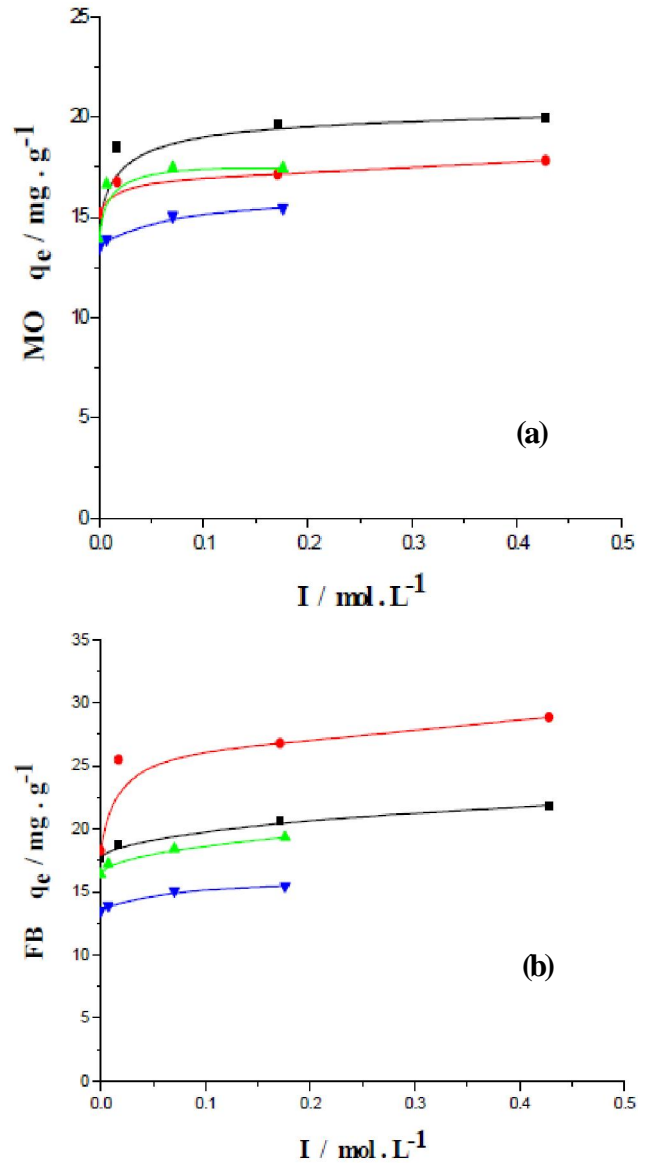


Figure 4 : Influence of ionic strength on adsorption and competitive adsorbances (a) MO (b) FB; (\bullet) (\blacktriangledown) single component system; (\blacktriangle) (\blacksquare) bi-component system; (\circ) (\blacksquare) NaCl (\blacktriangle) (\blacktriangledown) Na_2SO_4

temperature no matter for single component system or competitive system. The results might be caused by the decrease of MO and FB effective concentration in water with the increase of temperature.

(b) Adsorption and competitive adsorption kinetic models

The dynamics data of adsorption and competitive adsorption are characterized by pseudo First-order model (equation 2) and pseudo Second-order model (equation 3)^[20,21].

$$\text{First-order model : } \ln(q_e - q) = \ln q_e - kt \quad (2)$$

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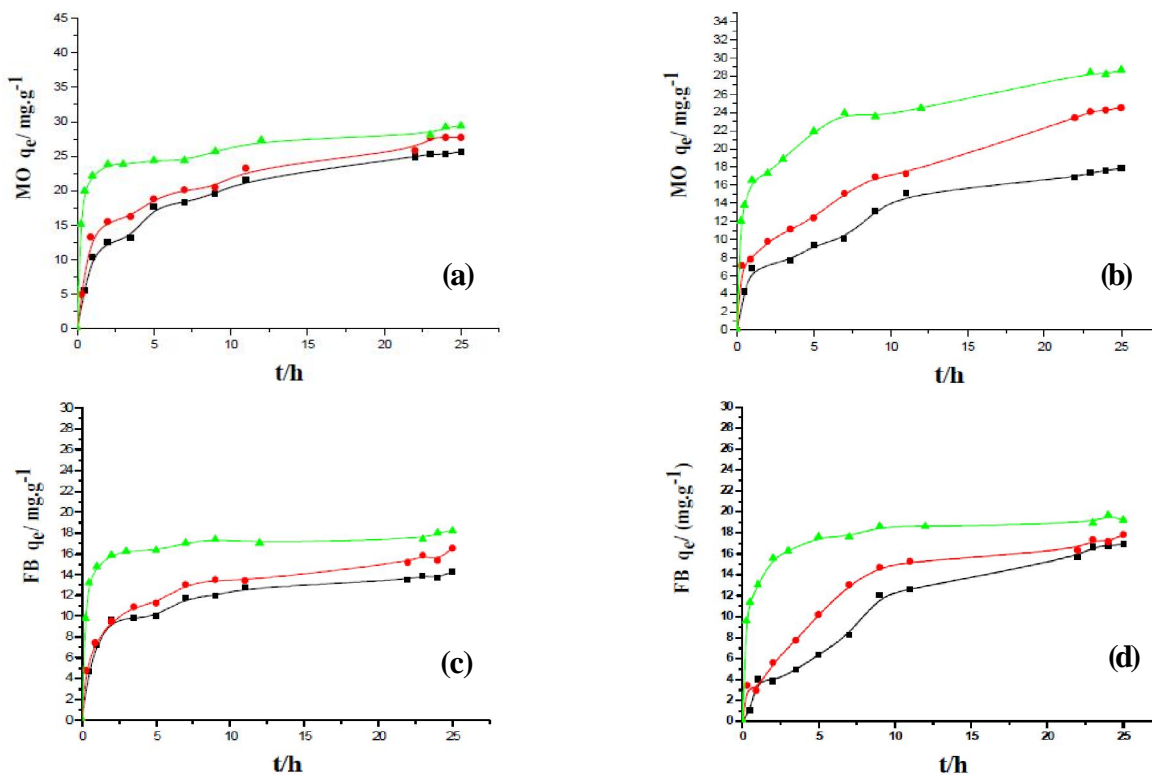


Figure 5 : Influence of temperature on adsorption time (MO initial concentration 100 mg·L⁻¹, FB initial concentration 50 mg·L⁻¹). (a) MO single component (b) competitive adsorption of FB for MO (c) FB single component (d) competitive adsorption of MO for FB; (■)5 °C, (●)20 °C, (▲)45 °C

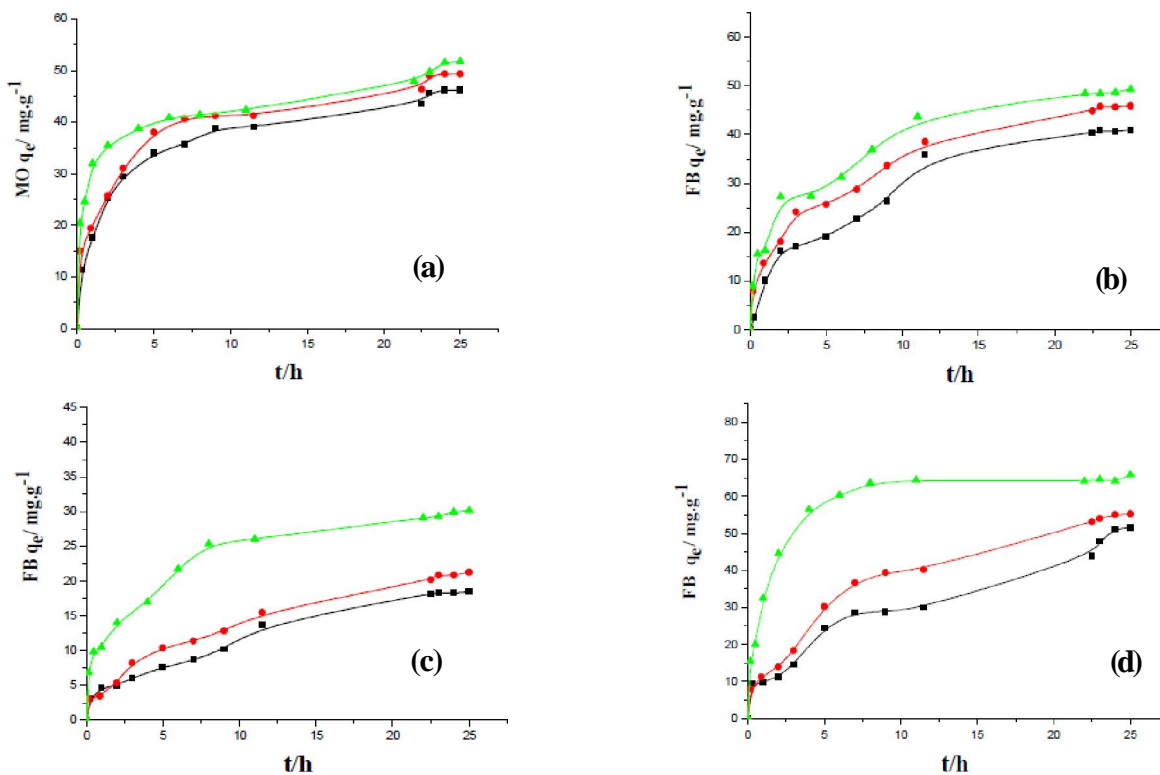


Figure 6: Influence of temperature on adsorption equilibrium time (MO initial concentration 600 mg·L⁻¹, FB initial concentration 300 mg·L⁻¹). (a) MO single component (b) competitive adsorption of FB for MO (c) FB single component (d) competitive adsorption of MO for FB; (■)5 °C, (●)20 °C, (▲)45 °C.

TABLE 7 : Comparison of the experimental results and the kinetic models of MO.

C_0 ($mg \cdot L^{-1}$)	T (°C)	$q_{e,exp}(mg \cdot g^{-1})$	First order			Second order		
			$q_{e,cal}(mg \cdot g^{-1})$	$k(h^{-1})$	R	$q_{e,cal}(mg \cdot g^{-1})$	$k(g \cdot (mg \cdot h)^{-1})$	r
100	5	25.68	20.30±1.079	0.1469	-0.972	28.03	0.0123	0.996
	20	27.72	22.57±1.102	0.1125	-0.964	29.77	0.0137	0.996
	45	29.39	25.79±1.197	0.1064	-0.865	31.35	0.0436	0.999
600	5	46.19	29.11±1.123	0.1196	-0.956	48.92	0.0102	0.998
	20	49.34	33.65±1.246	0.1535	-0.932	51.71	0.0109	0.998
	45	51.74	26.65±1.140	0.1036	-0.943	52.14	0.0287	0.997

TABLE 8 : Comparison of the experimental results and the kinetic models of FB.

C_0 ($mg \cdot L^{-1}$)	T (°C)	$q_{e,exp}(mg \cdot g^{-1})$	First order			Second order		
			$q_{e,cal}(mg \cdot g^{-1})$	$k(h^{-1})$	r	$q_{e,cal}(mg \cdot g^{-1})$	$k(g \cdot (mg \cdot h)^{-1})$	r
50	5	14.30	9.48±1.128	0.1696	-0.950	14.72	0.0106	0.999
	20	16.55	14.69±1.129	0.1022	-0.935	16.80	0.0116	0.997
	45	18.22	26.51±1.303	0.3005	-0.838	18.10	0.0220	0.999
300	5	18.41	22.77±1.213	0.1824	-0.949	22.09	0.0095	0.988
	20	21.25	20.90±1.058	0.1242	-0.990	22.78	0.0096	0.992
	45	30.16	22.51±1.081	0.1471	-0.985	32.12	0.0147	0.997

TABLE 9 : Comparison of the experimental results and the competitive adsorption kinetic models of FB for MO^d.

C_0 ($mg \cdot L^{-1}$)	T (°C)	$q_{e,exp}$ ($mg \cdot g^{-1}$)	First order			Second order		
			$q_{e,cal}(mg \cdot g^{-1})$	$K(h^{-1})$	R	$q_{e,cal}(mg \cdot g^{-1})$	$k(g \cdot (mg \cdot h)^{-1})$	R
50	5	18.35	14.15±1.100	0.1223	-0.970	20.03	0.0053	0.986
	20	24.49	23.26±1.133	0.1485	-0.974	25.91	0.0134	0.982
	45	28.66	18.50±1.131	0.1735	-0.971	29.52	0.0257	0.998
300	5	40.96	44.92±1.129	0.1815	-0.979	42.20	0.0030	0.999
	20	45.92	41.72±1.065	0.1565	-0.992	46.49	0.0073	0.994
	45	49.30	41.30±1.067	0.1720	-0.994	52.85	0.0199	0.998

^d FB is competitive component, its concentration is 50 $mg \cdot L^{-1}$ and 300 $mg \cdot L^{-1}$, respectively.

TABLE 10 : Comparison of the experimental results and the competitive adsorption kinetic models of MO for FB^e.

C_0 ($mg \cdot L^{-1}$)	T (°C)	$q_{e,exp}$ ($mg \cdot g^{-1}$)	First order			Second order		
			$q_{e,cal}(mg \cdot g^{-1})$	$k \cdot 10^{-3}(h^{-1})$	r	$q_{e,cal}(mg \cdot g^{-1})$	$k(g \cdot (mg \cdot h)^{-1})$	r
100	5	16.94	16.83±1.056	0.1180	-0.991	16.43	0.0072	0.993
	20	17.82	14.15±1.131	0.1211	-0.951	18.14	0.0087	0.993
	45	19.19	17.87±1.282	0.1696	-0.893	19.63	0.0190	0.999
600	5	51.61	48.25±1.089	0.0939	-0.971	52.77	0.0030	0.995
	20	55.23	61.73±1.092	0.1514	-0.988	56.43	0.0031	0.997
	45	65.81	74.82±1.109	0.3573	-0.989	67.11	0.0079	0.996

^e MO is competitive component, its concentration is 100 $mg \cdot L^{-1}$ and 600 $mg \cdot L^{-1}$, respectively.

Second-order model : $t/q = 1/(k q_c^2) + t/q_c$ (3) $0.9q_c$ are used for analysis. Plots of $\ln(q_c - q)$ versus t
 Since q reaches q_c at equilibrium, q values smaller than $0.9q_c$ and t/q versus t are used to test the first- and second-

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order models, and the fitting results are given in TABLE 7~10. Both line curve fit, and $q_{e,cal}$, second-order model gives more well results than first-order model. So the kinetics parameter of both adsorption and competitive adsorption can all be described by Second-order model. In addition, there is not obvious correlation between adsorption rate constant and the adsorption temperature.

Based on Second-order model, equation (4) and equation (5), adsorption rate and half adsorption time of these adsorbates are calculated.

$$u = kq_c^2 \quad (4)$$

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

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

As showed in TABLE 11~13, u is found to increase with the increase of adsorbates initial concentration and temperature, and $t_{1/2}$ decrease with the increase of temperature.

TABLE 11 : Kinetic parameters of MO for the second-order adsorption model.

C_0 ($mg \cdot L^{-1}$)	T ($^{\circ}C$)	u ($mg \cdot g^{-1} \cdot h^{-1}$)	$t_{1/2}$ (h)	E_a ($kJ \cdot mol^{-1}$)	r
	5	8.167	3.145		
100	20	10.534	2.631	24.07	-0.942
	45	37.70	0.780		
600	5	21.81	2.118		
	20	26.74	1.845	19.75	-0.938
	45	76.81	0.674		

TABLE 12 : Kinetic parameters of FB for the second-order adsorption model.

C_0 ($mg \cdot L^{-1}$)	T ($^{\circ}C$)	u ($mg \cdot g^{-1} \cdot h^{-1}$)	$t_{1/2}$ (h)	E_a ($kJ \cdot mol^{-1}$)	r
	5	2.16	6.610		
50	20	3.19	5.189	13.88	-0.957
	45	7.29	2.498		
300	5	3.23	5.706		
	20	4.32	4.921	8.352	-0.918
	45	13.36	2.258		

Second-order rate constants are used to calculate adsorption activation energy according to equation (6). Results listed in TABLE 11~13 show that the activation energy in adsorption are lower than 40 $kJ \cdot mol^{-1}$, which indicates that adsorption of the reference compounds on EG are mainly physical adsorption.

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

A : re-exponential factor, ($g \cdot mg^{-1} \cdot min^{-1}$); E_a : activation energy of adsorption, ($kJ \cdot mol^{-1}$)

TABLE 13 : Kinetic parameters of competitive adsorption for the second-order adsorption model.

C_0 ($mg \cdot L^{-1}$)	T ($^{\circ}C$)	u ($mg \cdot g^{-1} \cdot h^{-1}$)	$t_{1/2}$ (h)	E_a ($kJ \cdot mol^{-1}$)	r
	5	1.77	10.342		
50	20	8.04	3.048	28.48	-0.978
	45	21.13	1.356		
	5	5.06	8.100		
300	20	15.42	2.977	34.38	-0.997
	45	48.29	1.021		
	5	2.07	8.201		
100	20	2.756	6.468	18.34	-0.973
	45	7.014	2.737		
	5	7.86	6.569		
600	20	9.53	5.800	18.89	-0.934
	45	34.24	1.922		

f When FB is used as competitive component, its concentration is set as 50 $mg \cdot L^{-1}$ and 300 $mg \cdot L^{-1}$, respectively; When MO is used as competitive component, its concentration is set as 100 $mg \cdot L^{-1}$, 600 $mg \cdot L^{-1}$, respectively

CONCLUSIONS

This study has provided an insight into the adsorption and competitive adsorption isotherm, thermodynamic parameter, kinetic model and parameter of EG for MO and FB. The results are summarized as follows:

EG has adsorption capacity for MO and FB, the adsorption and competitive adsorption isotherm of these adsorbates on EG are all type I. In competitive adsorption of bi-component system, the existence of another component would decrease the adsorbance of EG for single adsorbate, which might be caused by the competitive adsorption for the same adsorbing site on EG. In competitive adsorption of FB and MO, the adsorbing site can be well utilized than that in single component adsorption because MO and FB can also adsorb on different adsorbing site as the same time. Adsorption and competitive adsorption of MO and FB on EG are all spontaneous, and the increase of ionic strength, temperature and EV of adsorbent would cause the increase of EG adsorption capacity. No matter single

adsorption or competitive adsorption of bi-component system, the adsorption kinetics models can all be well described with pseudo second-order kinetics model. Physical adsorption is the main action between EG with MO or EG with FB.

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