Adsorption Kinetics and Thermodynamics Characteristics of Expanded Graphite for Poly(vinyl alcohol)

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In the present study, expanded graphite processing of an expanded volume of 400 mL/g is prepared through chemical oxidation intercalation and its adsorption kinetics and thermodynamics characteristics for poly(vinyl alcohol) with polymerization degree of 1750 in aqueous solution is investigated. We studied the influence of initial poly(vinyl alcohol) concentration, temperature and ionic strength on adsorption capacity. Langmuir constants and Gibbs free energy change (ΔG°) are calculated according to the experimental data. Kinetic studies are carried out with a series of poly(vinyl alcohol) concentration under different temperatures and the data are simulated with pseudo first-order and second-order kinetic model, respectively. Thermodynamic study indicates that ionic strength has no obvious influence on the equilibrium adsorbance. Adsorption isotherm of expanded graphite for poly(vinyl alcohol) with a polymerization degree of 1750 is type I; Adsorption processes are all spontaneous. Kinetic studies show that the kinetic data can be delineated by pseudo second-order kinetic model. Second-order rate constants and the initial adsorption rate increase with the increasing of temperature. Adsorption activation energy of expanded graphite for poly(vinyl alcohol) with a polymerization degree of 1750 is less than 20 kJ·mol^{-1}, physical adsorption is the major mode of the overall adsorption process.

Key Words: Expanded graphite, Poly(vinyl alcohol), Adsorption kinetics, Adsorption thermodynamics, Activation energy.

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a sort of widely used polymer in industry and the molecular structure of [-CH$_2$-CH(OH)]$_n$ makes it possess of well water solubility. Poly(vinyl alcohol) has many unique characteristics such as strong adhesion, film flexibility, smoothness, oil resistance, solvent resistance, protective colloid, obstruction of gas and abrasion resistance, so it has extensive use in food, medicine, textile, paper making, agriculture and polymer chemical industry[1]. However, the wasted textile solution may become one of the major wastewater sources of poly(vinyl alcohol), especially in sizing production process[2]. The principal treatment methods of poly(vinyl alcohol) wastewater are biodegradation[3-5], chemical coagulation[6] and ultrafiltration technique[7,8]. Lee *et al.*[3] isolated poly(vinyl alcohol)-degrading bacteria (SB68 + SB69) from various sources such as activated sludge from the watercourse of textile and dyeing factories, cultivating soil and leaf mold. They showed high activity for poly(vinyl alcohol) degradation so that 75 % of poly(vinyl alcohol) with an initial concentration of 0.01 % was mineralized during 46 days of the modified sturm test. A dyeing factory in Beijing[6] made continuous condensation recycling of poly(vinyl alcohol)

slurry desizing water of polyester-cotton fabric with Na$_2$SO$_4$ (10-12 g/L) and borax (1-1.5 g/L) under temperature 40-50 ℃, both of poly(vinyl alcohol) condensate recovery and wastewater COD removal rate achieved 80 %. With hollow fiber ultra-filtration membrane equipment[8]. Dong *et al.*[8] studied the influence of liquid running time, pressure on both sides of membrane, liquid temperature and mainstream flow rate on filter flux and rejection rate, gained optimum conditions of poly(vinyl alcohol) desizing wastewater.

In wastewater treatment, it is well known that adsorption process has been considered available method for eliminating organic pollutants. Adsorption of poly(vinyl alcohol) on adsorbents such as silica, polystyrene particles, kaolin, Fuller's earth, montmorillonite and powered activated carbon has been studied[9-14]. Adsorption of poly(vinyl alcohol) on silica illustrated silanols and siloxane bonds were the main adsorption sites. Very low affinity was found between poly(vinyl alcohol) and kaolin minerals. At fixed pH (4.8) and ionic strength of the medium, adsorption isotherm for poly(vinyl alcohol) on Fuller's earth surfaces resembles with L-III type. The maximum adsorbance of poly(vinyl alcohol) (pH = 6) on montmorillonite Ca-Mt was 151.2 mg/g, which is considerably lower than that on Na-Mt(496.2 mg g^{-1}). Adsorption isotherm of poly(vinyl

alcohol) on powered active carbon was similar with H-type and the maximum removal of 92 % was obtained at a pH of 6.3 and contact time of 0.5 h for an adsorbent dose of 5 g/L.

Expanded graphite (EG) is a kind of porous adsorbent; it can be easily prepared with chemical method or electrical chemical method through oxidation and intercalation reaction. The pore in expanded graphite ranges from several nm to hundreds μm[15], it has been used as absorbent for its high adsorption capacity for organic materials, such as heavy oil and biomedical molecules[16-21]. Pang *et al.*[22-25] have studied the adsorption capacities of expanded graphite for oil, dyes, aromatic sulfonates, polyethylene glycol (PEG), results indicated expanded graphite show definite adsorption capability for these organic substances, especially for oils. Both adsorbates molecular weight and molecular structure affected adsorption type, saturation adsorbance.

The aim of this work is to study the adsorption thermodynamics and adsorption kinetics characteristics of poly(vinyl alcohol) on expanded graphite in water solution. The effect of ionic strength, concentration, temperature on adsorption capacity and do further evaluation of applicability of common isotherm model (*i.e.*, Langmuir and Freundlich) and pseudo-second-order rate model were also investigated. In the study, the poly(vinyl alcohol) with a polymerization degree (PD) of 1750 in aqueous solution is investigated.

EXPERIMENTAL

Preparation and structure characteristics of expanded graphite: Expanded graphite is prepared according to the literature[26]. Its pore distribution is detected with Micromeritics Instrument Corporation TriStar II 3020 V1.02 and pore structure parameters are calculated with BET method. Table-1 shows expanded graphite possess lower pore area and pore volume in N_2 adsorption than that of mercury adsorption method[27].

TABLE-1
STRUCTURAL PARAMETERS OF EXPANDED GRAPHITE

Detection method	Bulk density (g/mL)	Total volume (cm^3/g)	Total pore area (m^2/g)	Adsorption average pore width (4V/A) (nm)
N_2 adsorption	1.0000	0.1010	34.30	11.61
Mercury adsorption	0.0308	30.1145	1044.99	115.30

Adsorbate characteristic: Adsorbate used in experiment is poly(vinyl alcohol) with a polymerization degree of 1750. Simulated poly(vinyl alcohol) wastewaters are prepared by dissolving poly(vinyl alcohol) 1750 in distilled deionized water at various concentrations. In quantitative analysis[28], H_3BO_3-I_2 is used as coloured reagent of poly(vinyl alcohol) and absorbance of the coloured complex (colour reaction lasted 15 min) is detected with T6 New Century UV spectrophotometry (Puxi Tongyong Instrument Limited Company of Beijing). Absorbance values are recorded at the wavelength for maximum absorbance (λ_{max}) (Table-2) and its solution is initially calibrated for concentration in terms of absorbance units.

Static adsorption of poly(vinyl alcohol): 0.20 g of expanded graphite is mixed in conical glass flasks with 100 mL

solution at the desired poly(vinyl alcohol) concentration and ionic strength. Ionic strength is adjusted with NaCl or Na_2SO_4 solution. Mass of expanded graphite to volume of solution is standardized as M/V = 0.200/0.1 = 2.0 g/L. Poly(vinyl alcohol) concentration changes are recorded with spectrophotometer at λ_{max} and adsorbance is determined according to equation (1):

$$q_e = V (C_0 - C_e)/M \qquad (1)$$

where, q_e-equilibrium adsorbance of poly(vinyl alcohol) on expanded graphite; mg/g; C_0- initial concentration of poly(vinyl alcohol) in solution, mg/L; C_e- equilibrium concentration of poly(vinyl alcohol) in solution, mg/L; V- volume of solution, L; M- mass of expanded graphite, g.

TABLE-2
WORKING CURVE AND MAXIMUM ABSORBANCE WAVELENGTH OF POLY(VINYL ALCOHOL)

Poly(vinyl alcohol)	λ_{max}/nm	Working curve equation	r
1750	646.2	Y = - 0.01367 + 0.02803x	0.9998

Adsorption kinetics experiments of poly(vinyl alcohol): Adsorption kinetics experiments are carried out using a HZS-D shaking water bath with a shaking speed of 100 rpm/min (Donglian Haerbin, China). A series of desired poly(vinyl alcohol) concentration and a fixed volume of 100.0 mL are placed in vessels, where they are brought into contact with 0.2 g expanded graphite at 35, 45 and 60 ºC, respectively. Amount of poly(vinyl alcohol) captured by expanded graphite at different time is determined as equation (2):

$$q = V(C_0 - C_t)/M \qquad (2)$$

where, q - accumulative adsorbance of poly(vinyl alcohol) on expanded graphite at the moment of t, mg/g; C_t- concentration of poly(vinyl alcohol) in solution at the moment of t, mg/L.

RESULTS AND DISCUSSION

Adsorption thermodynamics

Investigation of adsorption isotherm and thermodynamic parameters: Static adsorption capacity of poly(vinyl alcohol) 1750 is measured. Fig. 1 illustrates a typical I type isotherm just as the adsorption of polyethylene glycol on expanded graphite[25]. Long molecule structure of poly(vinyl alcohol) might form certain kinds of conformation on the surface of expanded graphite, which might reduce the adsorbed sites and make the further adsorption difficult.
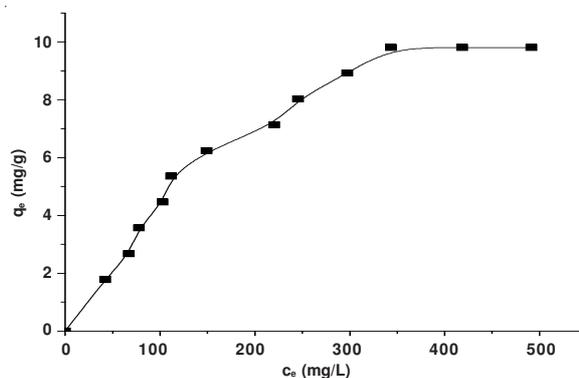

Fig. 1.　Adsorption isotherm of poly(vinyl alcohol) with a polymerization degree of 1750 on expanded graphite at 25 ºC

A considerable number of studies have been made on the polymer adsorption theory, providing a description of the polymer concentration and possible conformation in the interfacial region. For the adsorption of poly(vinyl alcohol) on expanded graphite, Langmuir and Freundlich isotherm equations (3) and (4) are used to treat the isotherm data.

Langmuir equation[29,30]: $1/q_e = 1/q_0 + A / (q_0 \times C_e)$ (3)

Freundlich equation: $\ln q_e = \ln K_F + (1/n) \ln C_e$ (4)

where, q_0 - maximum adsorption amount of poly(vinyl alcohol) in forming complete monolayer coverage on expanded graphite pore surface, mg/g; A- equilibrium concentration of poly(vinyl alcohol) corresponding to half saturation adsorbance, mg/mL; K_F - freundlich equation constant; 1/n: adsorption intensity for Freundlich equation.

As showed in Table-3, Langmuir isotherm gives a better fit than Freundlich isotherm. It is just the same as the results of expanded graphite for polyethylene glycol[25].

TABLE-3
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS OF POLY(VINYL ALCOHOL) 1750 at 25 ºC

PVA	Langmuir			Freundlich		
	q_0 (mg/g)	A (mg/mL)	r	K_F	1/n	*r*
1750	9.80	211.75	0.9918	0.2421	0.6599	0.9843

r: Linear related coefficient; PVA: Poly(vinyl alcohol)

At the same time, adsorption free energy change (ΔG^o) is calculated according to equation (5)[30], the value is -14.61 kJ/mol, negative ΔG^o indicates that adsorption of poly(vinyl alcohol) 1750 on expanded graphite is spontaneous.

$$\Delta G^o = \Delta RT \ln b \qquad (5)$$

b- Langmuire equation constant; ΔG^o- the free energy change in the adsorption, kJ/mol.

Influence of ion strength on adsorption capacity: Influence of ion strength on adsorption capacity is investigated using 100 mg/L poly(vinyl alcohol) solutions which contain NaCl or Na_2SO_4 with concentration ranging from 0 to 25 mg/L. Fig. 2 shows that the presence of NaCl or Na_2SO_4 has no obvious influence on adsorption capacity and change of ionic strength can not influence solubility of poly(vinyl alcohol) with a polymerization degree of 1750 in water.
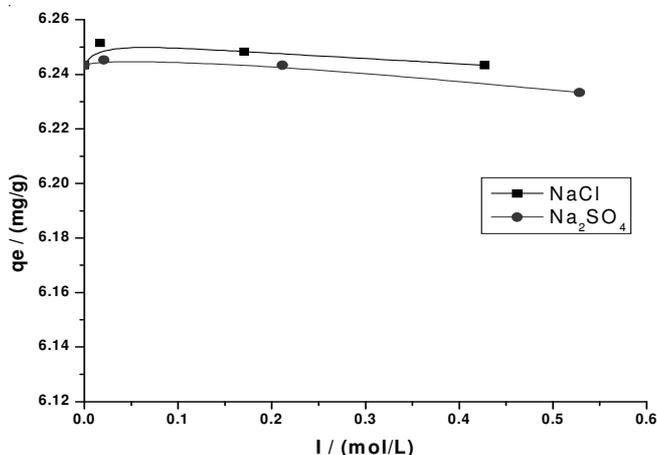

Fig. 2.   Influence of ionic strength on adsorption capacity of poly(vinyl alcohol) with a polymerization degree of 1750 at 25°C

Adsorption kinetics

Equilibrium time: The influence of concentration of poly(vinyl alcohol) and temperature on adsorption equilibrium time is detected (Fig. 3). Results suggest that the adsorbance is the function of poly(vinyl alcohol) concentration, temperature and adsorption time. Adsorption rate increases with the increasing of temperature, which might be caused by the change of solution viscosity under different temperature. In kinetic experiment, different adsorption equilibrium times are used for poly(vinyl alcohol) under different temperature. All adsorption can reach adsorption equilibrium within 1 h.

Adsorption kinetic models: Both pseudo first- and second-order adsorption models are used to describe the adsorption kinetics data according to eqns. (6) and (7)[31-33].

First-order model: $\ln(q_e - q) = \ln q_e - k_t$ (6)

Second-order model: $t/q = 1/(k\, q_e^2) + t/q_e$ (7)

where, K - adsorption rate constant (min^{-1} for first-order adsorption, g·mg^{-1}·min^{-1} for second-order adsorption); t - adsorption time, min.

Since q reaches q_e at equilibrium, q values smaller than 0.9 q_e are used for analysis. Plots of $\ln(q_e - q)$ *versus* t and t/q
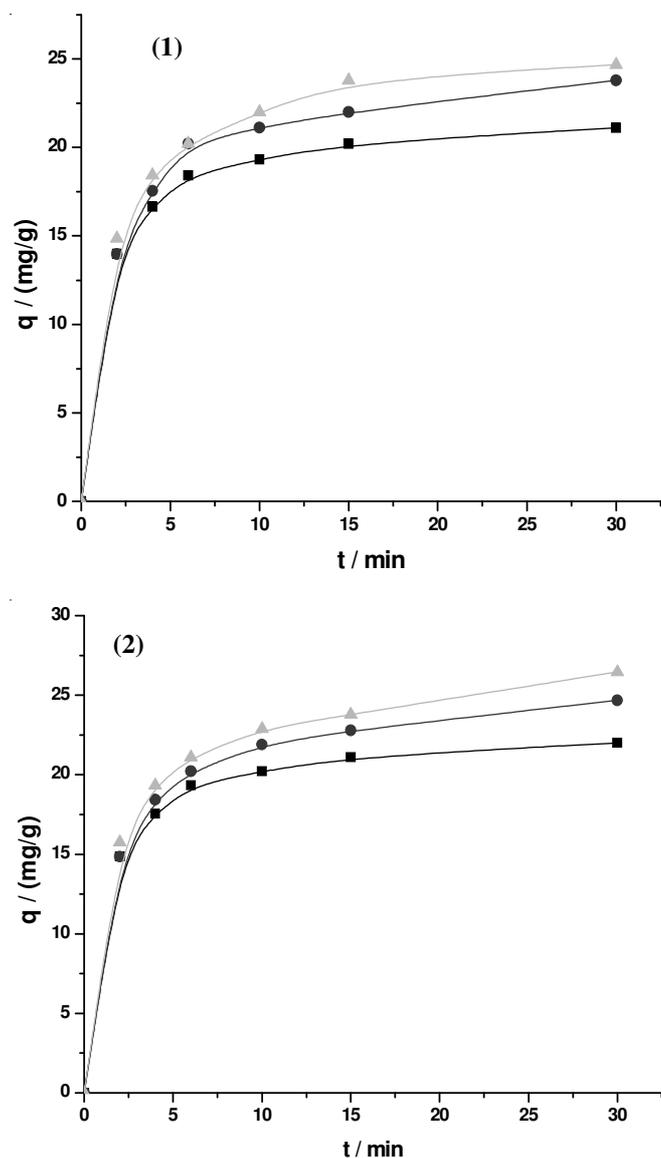
TABLE-4
COMPARISON OF THE ADSORPTION KINETIC MODELS OF POLY(VINYL ALCOHOL) ON EXPANDED GRAPHITE

| C_0 (mg/L)	Temperature (ºC)	$q_{e,exp}$ (mg/g)	First-order			Second-order		
			$q_{e,cal}$ (mg/g)	k (1/min)	r	$q_{e,cal}$ (mg/g)	k [g/(g min)]	r
200	35	8.919	8.552 ± 1.094	0.156 ± 0.011	-0.990	9.08 ± 0.002	0.0213 ± 5.77E-03	0.999
	45	11.595	10.703 ± 1.142	0.130 ± 0.017	-0.969	12.337 ± 0.002	0.0243 ± 1.82E-03	0.999
	60	12.487	13.086 ± 1.065	0.174 ± 0.008	-0.996	12.87 ± 0.002	0.0273 ± 4.18E-03	0.999
300	35	9.811	8.898 ± 1.102	0.160 ± 0.012	-0.987	10.369 ± 0.002	0.018 ± 586. E-03	0.998
	45	12.487	12.388 ± 1.108	0.113 ± 0.013	-0.975	12.548 ± 0.002	0.0242 ± 1.82E-03	0.999
	60	14.270	15.864 ± 1.257	0.142 ± 0.029	-0.927	14.997 ± 0.002	0.028 ± 1.73E-03	0.998
400	35	12.487	12.613 ± 1.056	0.172 ± 0.007	-0.997	12.574 ± 0.002	0.0223 ± 3.75E-03	0.998
	45	13.379	13.194 ± 1.076	0.181 ± 0.0009	-0.995	13.41 ± 0.0016	0.0278 ± 5.5E-03	0.999
	60	15.162	15.595 ± 1.045	0.186 ± 0.006	-0.998	15.352 ± 0.002	0.029 ± 3.03 E-03	0.998
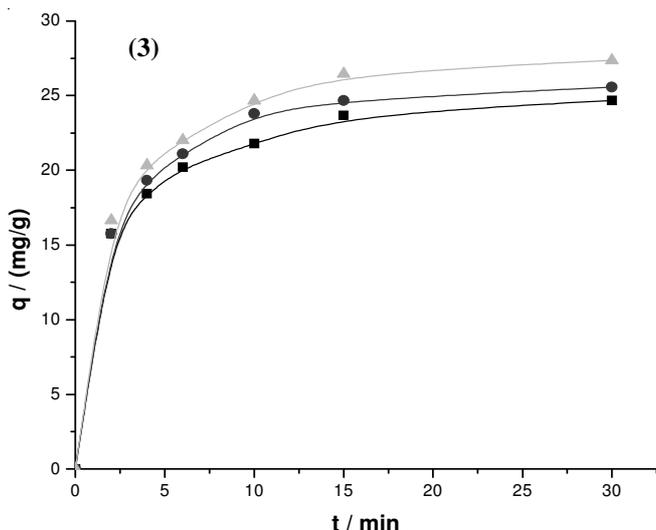
Fig. 3.   Influence of poly(vinyl alcohol) with a polymerization degree of 1750 concentration and temperature on adsorption kinetics (1) 200 mg/L, (2) 300 mg/L, (3) 400 mg/L; (■) 25 ºC, (●) 35 ºC, (▲) 45 ºC

TABLE-5
KINETICS PARAMETERS FOR THE SECOND-ORDER ADSORPTION MODEL OF POLY(VINYL ALCOHOL) WITH A POLYMERIZATION DEGREE OF 1750

C_0 (mg/g)	T (°C)	u (mg/(g·min))	$t_{1/2}$ (min)	E_a (kJ/mol)	r
200	35	1.756	5.264		
	45	3.2688	3.748	8.367±1.087	0.992
	60	4.522	2.933		
300	35	1.935	5.663		
	45	3.810	3.309	14.798±4.274	0.961
	60	6.320	2.494		
400	35	3.526	3.591		
	45	5.008	2.680	9.191±4.091	0.914
	60	6.958	2.234		

versus t are used to test the first- and second-order models and the fitting results are 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 poly(vinyl alcohol) with a polymerization degree of 1750 kinetics data. Similar results were observed in the adsorption of active carbon for poly(vinyl alcohol)[14].

Based on the second-order model, initial adsorption rate and half-adsorption time are estimated according to eqns. (8) and (9). As showed in Table-5, initial adsorption rate u is found to increase with the increase of initial poly(vinyl alcohol) 1750 concentration and temperature and half-adsorption time $t_{1/2}$ decrease with the increase of temperature.

$$u = kq_e^2 \qquad (8)$$
$$t_{1/2} = 1/(kq_e) \qquad (9)$$

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

Second-order rate constants are used to estimate activation energy of poly(vinyl alcohol) adsorption on expanded graphite using Arrhenius equation[34]:

$$\ln k = \ln A - E_a/(RT) \qquad (10)$$

where, A- the re-exponential factor, (g mg^{-1} min^{-1}); E_a - the adsorption activation energy, kJ/mol.

Slope of ln k *versus* 1/T is used to evaluate E_a, which is found less than 20 KJ mol^{-1} (as showed in Table-6). So, the adsorption is mainly physical adsorption. Similar results were observed in adsorption of expanded graphite for polyethylene glycol[25].

Conclusion

According to the adsorption thermodynamics and kinetics experiments of expanded graphite for poly(vinyl alcohol) 1750, the results can be summarized as follows:

(1) Adsorption thermodynamics data can be well described with Langmuir equation. Ionic strength has no obvious influence on adsorption capacity.

(2) Adsorption of expanded graphite for poly(vinyl alcohol) with a polymerization degree of 1750 is spontaneous, adsorption isotherm is type I.

(3) Adsorption kinetics data can be described by pseudo-second-order model. Initial adsorption rate increases with the increase of solution temperature and the adsorption belongs to physical adsorption.

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