Adsorption Characteristics of Polyvinyl Alcohols in Solution on Expanded Graphite

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Abstract: Expanded graphite (EG) adsorbent was prepared with 50 mesh graphite as raw materials, potassium permanganate as oxidant, and vitriol as intercalation compound. Three kinds of polyvinyl alcohol (PVA) with different degree of polymerization (DP) in aqueous solution were used as adsorbates. We have studied the influence of initial PVA concentration, temperature and ionic strength on adsorption capacity. Langmuir constants and Gibbs free energy change (ΔG°) were calculated according to experimental data respectively. Thermodynamic analysis indicates the equilibrium adsorbance of PVA on EG increase with the rise of SO_4^{2-} concentration. Adsorption isotherms of PVA with different degree of polymerization are all types and we deduce PVA molecules lie flat on EG surface. Adsorption processes are all spontaneous. 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 rise with the increasing of temperature and half-adsorption time decreases with the increasing of temperature. The adsorption activation energy of each PVA is less than $20 \text{ kJ}\cdot\text{mol}^{-1}$, physical adsorption is the major mode of the overall adsorption process.

Keywords: Expanded graphite, Polyvinyl alcohol, Adsorption kinetics, Adsorption thermodynamics, Gibbs free energy change, Physical adsorption

Introduction

Polyvinyl alcohol (PVA) is a sort of widely used polymer in industry and the molecular structure of $[-\text{CH}_2-\text{CH}(\text{OH})]_n$ makes it possess of well water solubility. PVA 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, papermaking, agriculture, polymer chemical industry¹. However, the wasted textile solution may become one of the major wastewater

sources of PVA, especially in sizing production process². The principal treatment methods of PVA wastewater are biodegradation^{3,5}, chemical coagulation⁶ and ultrafiltration technique^{7,8}. Lee *et al*³ isolated PVA-degrading bacteria (SB68+SB69) from various sources such as activated sludge from the water-course of textile and dyeing factories, cultivating soil and leaf mold. They showed high activity for PVA degradation so that 75% of PVA with an initial concentration of 0.01% was mineralized during 46 days of the modified Sturm test. A dyeing factory in Beijing⁶ made continuous condensation recycling of PVA slurry desizing water of polyester-cotton fabric with Na_2SO_4 (10~12 g/L) and Borax (1~1.5 g/L) under temperature 40~50 °C, both of PVA condensate recovery and wastewater COD removal rate achieved 80%. With hollow fiber ultra-filtration membrane equipment⁸, Dong studied the influence of liquid running time, pressure on both sides of membrane, liquid temperature and mainstream flow rate *et al* on filter flux and rejection rate, gained optimum conditions of PVA desizing wastewater.

In wastewater treatment, it is well known that adsorption process has been considered available method for eliminating organic pollutants. Adsorption of PVA on adsorbents such as silica, polystyrene particles, kaolin, fuller's earth, montmorillonite and powered activated carbon has been studied⁹⁻¹⁴. Adsorption of PVA on silica illustrated silanols and siloxane bonds were the main adsorption sites. Very low affinity was found between PVA and kaolin minerals. At fixed pH (4.8) and ionic strength of the medium, adsorption isotherm for PVA on fuller's earth surfaces resembles with LIII type. The maximum adsorbance of PVA (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 PVA 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 30 min 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 EG 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 molecules¹⁶⁻²¹. Pang *et al* have studied the adsorption capacities of EG for oil, dyes, aromatic sulfonates, polyethylene glycol (PEG)²²⁻²⁵, results indicated EG 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 PVA on EG in water solution. Investigate the effect of ionic strength, adsorbate 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. In the research, PVA with different PDs of 500, 700 and 1750 in aqueous solution are investigated.

Experimental

With the mass ratio of 1: 0.12: 5.0 of graphite (C): KMnO_4 : H_2SO_4 (96%), the definite amount of C, KMnO_4 and H_2SO_4 (diluted to a mass concentration of 50% with de-ionized before mixed with graphite) were mixed under room temperature. The reaction lasted 30 min under stirring, then products were washed with de-ionized water until pH reached to 6.0 ~ 7.0. After filtration and dryness under 80 °C, the solid scalelike grains were heated under 900 °C for about 10 sec and then EG could be gained. The pore distribution of the prepared EG is detected by autopore II 9220 mercury porosimeter (Micromeritics Inc. USA) under the condition of 0.58~1301PSIA. Results given in Table 1 show pores in EG are mainly micron pore.

Table 1. Structural parameter of EG

Bulk density, g/mL	Total pore area, m ² /g	Total volume, cm ³ /g	Distribution of pore volume, mL/g			
			~1037 nm	1037~10072 nm	10072~112689 nm	112689~313584 nm
0.0308	1044.99	30.11	1.3693	7.4544	15.8525	3.6583

Adsorbates characteristic

Adsorbates used in experiments are PVA with different DPs of 500, 700, 1750, respectively. PVA-1750 is general commercial, PVA (500, 700) of expected polymerization degree were prepared through the degradation of polyvinyl alcohol 1750 with H₂O₂ under different pH, and its molecular weight was detected with ubbelohde viscometer²⁶. Simulated PVA wastewaters are prepared by dissolving PVA in distilled deionized water at various concentrations. In quantitative analysis²⁷, H₃BO₃-I₂ in solution is used as colored reagent of PVA and absorbance of the colored complex (color 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 ($\lambda_{\max}$) (Table 2) and its solution is initially calibrated for concentration in terms of absorbance units.

Table 2. DP and maximum absorbance wavelength of PVA

PVA	500	700	1750
$\lambda_{\max}$, nm	646	646	646

Static adsorption of PVA

0.20 g of EG is mixed in different conical glass flasks with 100.0 mL solution at the desired PVA concentration and ionic strength. Ionic strength is adjusted with NaCl or Na₂SO₄ solution. Mass of EG to volume of solution is standardized as $M/V = 0.200 / 0.1 = 2.0$ g/L. PVA concentration changes are recorded with spectrophotometer at $\lambda_{\max}$ and equilibrium adsorbance is determined according to equation (1).

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

q_e : Equilibrium adsorbance of PVA on EG, mg/g; C_0 : Initial concentration of PVA in solution, mg/L; C_e : Equilibrium concentration of PVA in solution, mg/L; V : Volume of solution, L; M : Mass of EG, g

Adsorption kinetics of PVA

Adsorption kinetics experiments are carried out using a HZS-D shaking water bath (Donglian Haerbin, China). A series of desired PVA concentration and fixed 100.0 mL are placed in vessels, where they are brought into contact with EG at 25 °C, 35 °C and 45 °C, respectively. Amount of PVA captured by EG at different time is determined according to equation (2):

$$q_t = V(C_0 - C_t) / M \quad (2)$$

q_t : Accumulative adsorbance of adsorbate on EG at the moment of t , mg/g; C_t : concentration of PVA in solution at the moment of t , mg/L;

Results and Discussion

Adsorption isotherm and thermodynamic parameters

Static adsorption capacities of EG for PVA (500, 700, 1750) are measured. Figure 1 (a) and (b) illustrates a typical I type isotherm. Equilibrium adsorbances are less than 20 mg/g among the detected PVA solution and it decrease with the increase of PVA' DP. The results are just as the adsorption of linear PEG on EG²⁵. The planar structure and large molecules of PVA might form certain kinds of conformation on the surface of EG, which might reduce the adsorbed sites and make the further adsorption difficult.

Figure 1. Adsorption isotherm of PVA (500, 700, 1750) at 25 °C, (a) Unit of adsorbance is mg/g; (b) Unit of adsorbance is mmol/g

To providing a description of PVA concentration and possible conformation in the interfacial region, Langmuir and Freundlich isotherm equations (3) and (4) are used to treat the isotherm data. The molecule area (a) of PVA with different DP is calculated according to q_0 and total pore area. As showed in Table 3, Langmuir isotherm gives a better fit than Freundlich isotherm and the higher DP PVA possessed, the smaller A is gained, the lower equilibrium concentration of PVA corresponding to half saturation adsorbance. This might be caused by the lower water solubility of higher DP of PVA and then cause stronger appetency with EG. At the same time, there is an almost linear relationship between PVA DP and PVA molecule area (Figure 2). We can deduce PVA molecule lies flat on the EG surface²⁵.

$$\text{Langmuir equation}^{28}: 1/q_e = 1/q_0 + A/(q_0 \times C_e) \quad (3)$$

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

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

Table 3. Langmuir and Freundlich isotherm constants at 25 °C

DP	Langmuir				Freundlich		
	q_0	a	A	r	K_F	$1/n$	r
	mmol/g	nm ² /molecule	mmol/mL				
500	0.000863	402.286	0.00716	0.9910	0.2966	0.7587	0.9786
700	0.000534	650.136	0.00524	0.9739	0.1598	0.8221	0.8911
1750	0.000127	2733.644	0.00275	0.9918	0.2421	0.6599	0.9843

a : Area of PEG molecule, (nm)²/molecule; r : Linear related coefficient

Base on temperature and Langmuir constant, adsorption free energy change (ΔG°) of the adsorption process is calculated according to equation (5)²⁹, negative ΔG° (Table 4) indicates that adsorption of these reference compounds on EG are all spontaneous and the higher DP the PVA possessed, the easier adsorption is carried.

$$\Delta G^\circ = -RT \ln b \quad (5)$$

Where b = Langmuir equation constant, $b = 1/A$, mL/mg; ΔG° : The free energy change in the adsorption, kJ .

Figure 2. Relationship between PVA, DP and molecule area**Table 4.** Free energy change of PVA adsorption on EG at 25 °C

PVA	500	700	1750
$\Delta G^\circ/kJ$	-12.24	-13.02	-14.61

Influence of ionic strength on adsorption capacity

At room temperature, the influence of ionic strength on adsorption capacity is investigated using a 100 mg/L PVA (500, 700,) solutions which contain NaCl or Na₂SO₄ with ionic strength ranging from 0 to 0.6 mol/L. The results showed in Figure 3 indicate that the presence of SO₄²⁻ can improve the adsorption capacity of EG for PVA and it may be caused by the electrostatic interaction between PVA and adsorbent, hydrophobic attraction of PVA increases due to the “salting-out” effect.

Figure 3. Influence of ionic strength on adsorption capacity of EG for PVA, (a) PVA 500; (b) PVA 700

Adsorption kinetic

Influence of PVA concentration and temperature on adsorption kinetics

The influence of PVA (500, 700) concentration and temperature on adsorption equilibrium time is detected and showed in Figure 4 & 5. Results suggest that adsorbance is the function of PVA concentration, temperature and adsorption time. Equilibrium adsorbances and adsorption rate increase with the increasing of temperature, which might be caused by the change of solution viscosity under different temperature.

Figure 4. Influence of PVA (500) concentration and temperature on adsorbance, (a) 50 mg/L, (b) 100 mg/L, (c) 200 mg/L; (■)25 °C, (●)35 °C, (▲)45 °C

Figure 5. Influence of PVA (700) concentration and temperature on adsorbance, (a) 50 mg/L, (b) 100 mg/L, (c) 200 mg/L; (■)25 °C, (●)35 °C, (▲)45 °C

Adsorption kinetic models

Both pseudo first- and second-order adsorption models are used to describe the adsorption kinetics data^{30,31}. In both models, all the steps of adsorption such as external diffusion, internal diffusion and adsorption are lumped together and it is assumed that the difference between the average solid phase concentration and the equilibrium concentration is the driving force for adsorption and the complete 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).

$$\text{First-order model : } \ln(q_e - q) = \ln q_e - kt \quad (6)$$

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

K : Adsorption rate constant (min^{-1} for first-order adsorption, $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ for second-order adsorption); t : Adsorption time (min)

Since q reaches q_e at equilibrium, q values smaller than $0.9q_e$ are used for analysis. Plots of $\ln(q_e - q)$ versus t and t/q versus t are used to test the first- and second-order models and the fitting results are given in Table 5 and Table 6. Both line curve fit and $q_{e,\text{cal}}$, second-order model gives more well results than first-order model. Second-order model is more suitable to describe the adsorption kinetics data. Similar results were observed in the adsorption of PEG on EG²⁵.

Table 5. Comparison of the adsorption kinetic models of PVA (500) on EG

C_0 mg	$T, ^\circ\text{C}$	$q_{e,\text{exp}}$ mg/g	First-order			Second-order		
			$q_{e,\text{cal}}$ mg/g	k , 1/min	r	$q_{e,\text{cal}}$ mg/g	k , g/g·min	r
50	25	4.88	4.00 ±1.083	0.176 ±0.008	-0.992	5.102± 0.067	0.093±0.0148	0.999
	35	5.997	3.453 ±1.028	0.199 ±0.027	-0.940	6.172± 0.067	0.129±0.026	0.999
	45	7.113	4.838 ±1.125	0.190 ±0.012	-0.986	7.209±0 .061	0.137±0.011	0.999
100	25	7.671	4.467 ±1.176	0.109 ±0.012	-0.953	8.012 ±0.056	0.503±0.003	0.999
	35	8.508	5.486 ±1.135	0.135 ±0.010	-0.980	8.863±8. 56E-4	0.530±0.004	0.999
	45	8.926	5.093 ±1.165	0.135 ±0.011	-0.972	9.213± 0.043	0.065±0.004	1.000
200	25	7.810	6.338 ±1.099	0.138 ±0.007	-0.989	8.384 ±0.132	0.034 ±0.004	0.999
	25	9.484	6.381 ±1.153	0.143 ±0.011	-0.978	9.967 ±0.142	0.042±0.006	0.999
	45	10.600	6.381 ±1.152	0.194± 0.011	-0.988	11.08± 0.113	0.043± 0.005	0.999

Table 6. Comparison of the adsorption kinetic models of PVA (700) on EG

C_0 , mg/L	T , °C	$q_{e,exp}$, mg/g	First-order			Second-order		
			$q_{e,cab}$, mg/g	k , 1/min	r	$q_{e,cab}$, mg/g	k , g/g·min	r
50	25	3.674	2.821 ±1.083	0.097 ±0.008	-0.983	3.952 ±0.067	0.059 ±0.015	1.000
	35	5.994	5.735 ±1.028	0.229 ±0.027	-0.983	6.297 ±0.067	0.073 ±0.026	0.999
	45	7.154	6.508 ±1.125	0.290± 0.012	-0.989	7.390 ±0.061	0.099 ±0.019	0.999
	25	7.153	2.451 ±1.062	0.116± 0.005	-0.994	7.836± 0.184	0.025 ±0.003	0.998
	35	8.121	2.811 ±1.185	0.117 ±0.030	-0.993	8.968 ±0.111	0.0872 ±0.019	0.999
	45	9.281	3.661 ±1.295	0.118 ±0.020	-0.905	9.443± 0.035	0.098 ±0.005	1.000
100	25	8.507	7.115 ±1.060	0.179 ±0.006	-0.996	8.934 ±0.094	0.049 ±0.005	1.000
	35	9.087	7.437 ±1.064	0.191 ±0.006	-0.996	9.498 ±0.103	0.052 ±0.006	0.999
	45	10.247	9.246 ±1.117	0.194 ±0.011	-0.988	10.792 ±0.164	0.055 ±0.012	0.999

Based on the second-order model, initial adsorption rate and half-adsorption time are estimated according to equations (8) and (9). As showed in Table 7 and Table 8, u is found to increase with the increase of temperature and $t_{1/2}$ decrease with the increase of temperature.

$$u = kq_e^2 \quad (8)$$

$$t_{1/2} = 1/(kq_e) \quad (9)$$

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

Second-order rate constants are used to calculate activation energy of PVA adsorption on EG using Arrhenius equation³²:

$$\ln k = \ln A - Ea/(RT) \quad (10)$$

A : The re-exponential factor, (g·mg⁻¹·min⁻¹); Ea : The activation energy of adsorption, (kJ/mol)

Slope of $\ln k$ versus $1/T$ is used to evaluate Ea , which is found less than 20.0 kJ·mol⁻¹ (as showed in Table 7 and Table 8). So, the adsorption is mainly physical adsorption.

Internal diffusion analysis

Among the external diffusion, internal diffusion and actual adsorption of the adsorption process, the long adsorption equilibrium time of PVA on EG (20~60 min corresponding to adsorption temperature of 25~45 °C) 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 step³³:

$$q = k_{id}t^{1/2} \quad (11)$$

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

Table 7. Kinetic parameters for the second-order adsorption model of PVA (500)

C_0 , mg/g	T , °C	u , mg/g·min	$t_{1/2}$, min	E_a , kJ/mol	r
50	25	2.415	2.209	15.61±5.63	0.941
	35	3.299	1.297		
	45	4.677	1.043		
100	25	3.230	2.590	9.81±3.53	0.941
	35	4.164	2.167		
	45	5.488	1.733		
200	25	2.396	2.755	8.85±4.07	0.908
	35	4.155	2.521		
	45	5.233	2.215		

Table 8. Kinetic parameters for the second-order adsorption model of PVA (700)

C_0 , mg/g	T , °C	u , mg/g·min	$t_{1/2}$, min	E_a , kJ/mol	r
50	25	0.915	4.468	20.52±1.94	0.996
	35	2.912	2.271		
	45	5.388	1.417		
100	25	1.517	5.656	23.6±7.7	0.910
	35	7.009	1.319		
	45	8.762	1.097		
200	25	3.875	2.422	5.01±0.032	1.000
	35	4.678	2.122		
	45	6.418	1.772		

According to the internal diffusion model, the 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 of PVA (500, 700) and $t^{1/2}$ at different temperature are showed in Figure 6 and Figure 7. In the range of the tested temperature, a linear relationship between q versus $t^{1/2}$ with a zero intercept is found when the adsorption temperature is high. Increase of temperature can decrease the viscosity of PVA solution and reduce the external diffusion and then internal diffusion is control step.

Figure 6. Plot of q vs. $t^{1/2}$ in internal diffusion model of PVA (500), (a) 50 mg/L, (b) 100 mg/L, (c) 200 mg/L; (■) 25 °C, (●) 35 °C, (▲) 45 °C

Figure 7. Plot of q vs. $t^{1/2}$ in internal diffusion model of PVA (700), (a) 50 mg/L, (b) 100 mg/L, (c) 200 mg/L; (■) 25 °C, (●) 35 °C, (▲) 45 °C

Conclusion

Adsorption of EG for PVA with different DPs have been investigated. The results are summarized as follows:

- Adsorption isotherms of EG for PVA can be well described with Langmuir equation, and the present of SO_4^{2-} can improve the adsorbance.
- Adsorption of EG for PVA is spontaneous, adsorption isotherms of PVA (500, 700, 1750) are all type I and PVA molecule lies flat on EG surface.
- Adsorption kinetics of EG for PVA can be described by pseudo-second-order model equation. Equilibrium time and half-adsorption time $t_{1/2}$ decreases with the increase of temperature. The adsorption belongs to physical adsorption and internal diffusion is tested to be the rate-limiting step of the complete adsorption process.

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