



Effect of Solution pH and Isotherm Study on Adsorption of PVA Using Activated Carbon Fibre

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ABSTRACT

Polyvinyl alcohol (PVA) is a widely used water-soluble polymer, though it is difficult to degrade by biotreatment. Dyeing wastewater contains a lot of PVA, which has become one of the most important water pollution sources. In this research, PVA was efficiently removed by activated carbon fibre (ACF) in a batch adsorption system. Effect of solution pH, and adsorption isotherm were emphatically studied. By the study of pH effect, it was observed that near-neutral solution pH conditions were more favourable for the adsorptive removal of PVA. For the isotherm study, Langmuir model described the adsorption isotherm better than Freundlich model, with a maximum PVA adsorption capacity of 6287.4 mg/g at 288 K. The changes of enthalpy and entropy of the adsorption processes are 12.38 KJ mol⁻¹ and 43.7 J mol⁻¹ k⁻¹, respectively. The negative value of Gibbs free energy change and the positive value of enthalpy also demonstrated that the adsorption process is spontaneous and endothermic. All these results indicated that the ACF is a suitable adsorbent for the removal of PVA from water.

INTRODUCTION

Polyvinyl alcohol (PVA) is a well-known recalcitrant and water-soluble polymer (Giroto et al. 2006, Tokiwa et al. 2001). Due to its unique physical and chemical properties such as strong adhesion, oil resistance and wear-resistance, PVA has been used extensively in a wide range of industrial, commercial, medical and food products, including paint, textile, medicine, construction, printing and other industries. However, the value of BOD/COD for PVA is only 0.064. The PVA wastewater has a certain viscosity, complex composition and is very difficult for biodegradation. If PVA was discharged into a water body, its high surface activity will lead the receiving water to produce a large amount of foam. PVA not only affects the water sense and self-purification cycle performance, but also accelerates the speed of migration of heavy metals and destructs the water environment (Li et al. 2015a, Moulay 2015, Chai et al. 2015). China is a large country of PVA production and consumption. A huge amount of PVA is used as an additive in textile, papermaking and chemical industry annually. Due to the difficulty for bio-treatment, most of the PVA is actually discharged into the water body along with wastewater. Therefore, before PVA wastewater is discharged into the environment, it must be removed efficiently.

At present, the treatment of PVA wastewater can be divided into three categories, including physical, biological and chemical methods. Adsorption is an important physicochemical method, which can simply transfer various pollutants from one phase to another effectively and efficiently. Adsorption process is regarded as one of the most powerful, efficient and cost-effective water treatment technologies due to ease of operation, universal nature and high efficiency (Qu 2008, Ali et al. 2012). As a solid extraction technology with low energy consumption, it has an incomparable advantage in the treatment of dissolved organic matters from aqueous solution.

A number of adsorbents can be used for the adsorptive removal of PVA. Compared to activated carbon, activated carbon fibre (ACF) possesses more extensive surface area, abundant micropores, small pore size, narrow distribution, large adsorption capacity and high adsorption speed. ACF is the third generation of activated carbon after powdered activated carbon (PAC) and granular activated carbon (GAC) (Li et al. 2007). Due to its narrow pore size distribution, abundant micropores, large specific surface area, unique surface chemical properties and the capacity of fast adsorption and desorption, it has been developing rapidly in recent years. It is widely used in waste gas treatment, water treatment and other fields. Wei and coworkers studied the

kinetics and thermodynamics of adsorption of methylene blue on activated carbon fibres (Bao et al. 2015). The results showed that Langmuir isotherm model well described the adsorption process, and the removal rate of methylene blue can be as much as 99.3%. Many studies have demonstrated the application potential of ACF. Therefore, ACF has a wider application prospect in wastewater treatment as well. In this research, the efficient removal of PVA by ACF was investigated. Effect of solution pH was explored as the solution pH is one of the key parameters for the uptake of PVA. Adsorption isotherm was investigated and thermodynamics analysis was conducted to better understand the adsorption mechanism.

MATERIALS AND METHODS

Chemicals: Polyvinyl alcohol (PVA) was purchased from Tianjin Kernel Chemical Reagents Co., Ltd. (Tianjin, China) and used without further purification. The activated carbon fibre (ACF) was provided by Liaoning Anshan Senxin Activated Carbon Environmental Materials Co., Ltd. (China). Its thickness is 2 mm and the average surface area is 1500 m²/g. Deionized (DI) water was used throughout this study.

Batch adsorption studies: A stock PVA solution of 2000 mg/L was prepared by dissolving PVA in DI water. It was stored in a brown volumetric flask and kept at room temperature. The stock solution was diluted with DI water to prepare the desired PVA solutions for the subsequent batch experiments. Adsorptive removal of PVA was determined by batch experiments in conical flasks. For the pH effect study, a desired amount of ACF (20 mg) was added to a conical flask containing 50 mL of PVA solution with a concentration of 20 mg/L. The solution pH was maintained at 7.0 by adding 0.1 mol L⁻¹ of HCl or NaOH. For isotherm study, a dose of 10 mg ACF was added into conical flasks at 50 mL with the PVA solution of 20, 50, 80, 100, 150, 300, 600, 1000, 2000 mg/L, respectively. These mixtures were shaken at 120 rpm for 24 h to achieve equilibrium at 298 K. The adsorption isotherm study was also determined at 288 and 308 K.

Analysis of PVA: The concentration of PVA was analysed using a UVmini-1240 spectrophotometer (Shimadzu) by monitoring the wavelength of maximum absorption (690 nm), according to the procedures described by Finley (Finley 1961, Xu et al. 2015). The adsorption capacity (q_e) of PVA was calculated using the following equation:

$$q_e = \frac{V \times (C_0 - C_t)}{m} \quad \dots(1)$$

Where, q_e (mg/g) is the adsorption capacity at equilibrium and t min, respectively; C_0 is the initial concentration of PVA in solution, while C and C_t (mg/L) are the concentra-

tions of PVA at equilibrium and t min, respectively; V (L) is the volume of solution, and m (g) is the mass of the ACF.

RESULTS AND DISCUSSION

Effect of ACF dose on PVA adsorption: The effect of ACF dosage on PVA adsorption was investigated first, as presented in Fig. 1. The dosages of ACF vary from 5 to 100 mg in 50 mL solution. From Fig. 1, the uptake of PVA decreased with an increase of ACF dosage. The maximum adsorption capacity of PVA occurred at 5 mg of ACF dosage. Obviously, a very limited amount of adsorbent could significantly remove most PVA molecules. Considering all the factors, the dosage of ACF was selected as 20 mg in 50 mL solution in the following experiments.

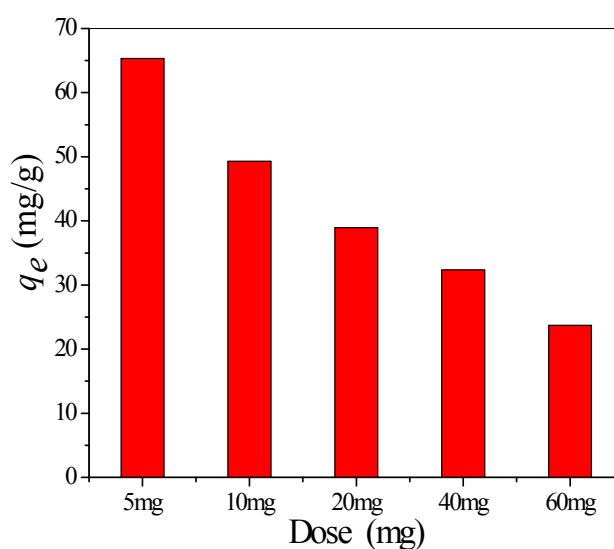


Fig. 1: Effect of ACF dosage on PVA adsorption.

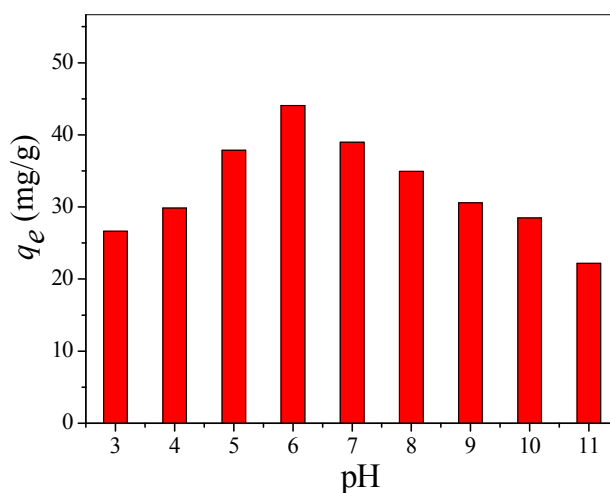


Fig. 2: Effect of solution pH on PVA adsorption.

Effect of solution pH on PVA adsorption: Solution pH is an important factor affecting the adsorption process, as both the surface properties of an adsorbent and the species of an adsorbate can be influenced profoundly. The effect of solution pH for PVA adsorption on ACF was investigated from pH 3.0 to 11.0, as presented in Fig. 2. It demonstrates that the uptake of PVA is highly pH dependent. Acidic and alkaline conditions are not beneficial to the PVA removal. The highest uptake of PVA was achieved at about pH 6.0, at which the PVA uptake was 44.1 mg/g. As such, neutral solution pH is especially favourable for the PVA removal.

Adsorption isotherms: Adsorption isotherm is the basis for the analysis of adsorption capability and the related adsorption mechanism. Two classical isotherm models including Langmuir and Freundlich models were used to fit the experimental data. The two isotherm models can be expressed as follows (Langmuir 1916, Freundlich 1906):

$$\text{Langmuir model: } q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad \dots(2)$$

$$\text{Freundlich model: } q_e = k_F C_e^{\frac{1}{n}} \quad \dots(3)$$

Where, q_e and q_m represent the amount of equilibrium adsorption capacity and the maximum adsorption capacity (mg/g), respectively; k_L (L/mg) is the Langmuir coefficient; C_e is the equilibrium concentration (mg/L); k_F is roughly an indicator of the adsorption capacity; n is the heterogeneity factor.

The fitting curves of Langmuir and Freundlich models at three temperatures are illustrated in Fig. 3. Meanwhile, the adsorption parameters obtained from the simulated isotherm models are listed in Table 1. As can be seen from Fig. 3, both Langmuir and Freundlich models well fitted the experimental data. Even though, the experimental data are closer to the simulated curve by Langmuir model than that by Freundlich model. Langmuir model can predict equilibrium adsorption behaviour better at different reaction temperatures, and the correlation coefficients (R^2) of Langmuir model are quite higher than those of Freundlich model. It demonstrates that ACF surface is more homogeneous to some extent. By Langmuir model, the calculated maximum adsorption capacities at 288, 298 and 308 K were 6287.4 mg/g, 6980.9 mg/g, 7039.3 mg/g, respectively. It indicates that the adsorption capacity of PVA on the ACF increases with the temperature rising. As a result, with the temperature increasing, the thermal motion of molecules in solution is accelerated and adsorption activation energy decreases. The adsorption process is deduced to be an endothermic process in nature.

Thermodynamic parameters: Thermodynamic analysis

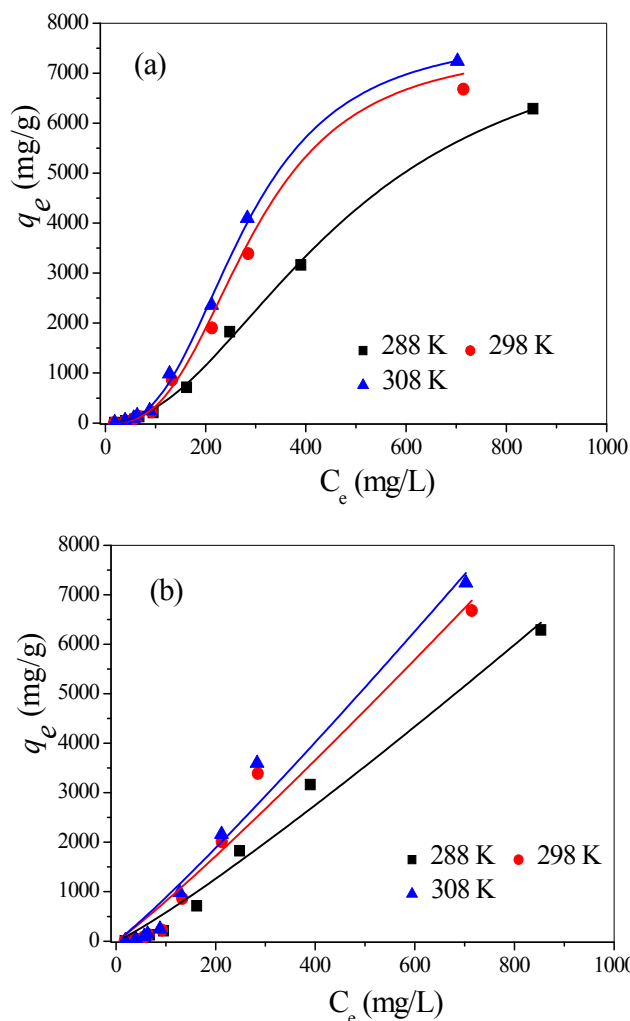


Fig. 3: Isotherms simulated by Langmuir (a) and Freundlich (b) models for PVA adsorption on ACF.

could provide more information about adsorption mechanism. Thermodynamic parameters associated with the adsorption process such as standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated using the following equations:

$$\Delta G^0 = -RT \ln K_0 \quad \dots(4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \dots(5)$$

$$\ln k_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \dots(6)$$

In these equations, T is in Kelvin; ΔH^0 is the entropy of adsorption and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). As presented in Fig. 4, the thermodynamic equilibrium constant K_0 for the adsorption process was determined by plotting $\ln q_e/C_e$ versus q_e and extrapolating to zero q_e using a graphical method (Yuan et al. 2009, Li et al. 2015b). The

Table 1: Simulated isotherm parameters for the adsorption of PVA on ACF.

	Langmuir isotherm			Freundlich		
	q_m (mg/g)	k_L (L/mg)	R^2	k_F (mg/g)	n	R^2
288K	8166.4	2.81×10^{-6}	0.998	3.29	1.123	0.979
298K	7547.7	9.63×10^{-7}	0.988	5.36	1.089	0.959
308K	7761.6	2.2×10^{-7}	0.998	5.75	1.093	0.965

Table 2: Thermodynamic parameters for PVA adsorption on ACF.

T/K	$\ln K^0$	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J·mol ⁻¹ ·K ⁻¹)
288 K	0.101	-0.242	12.38	43.7
298 K	0.229	-0.567	12.38	43.7
308 K	0.436	-1.116	12.38	43.7

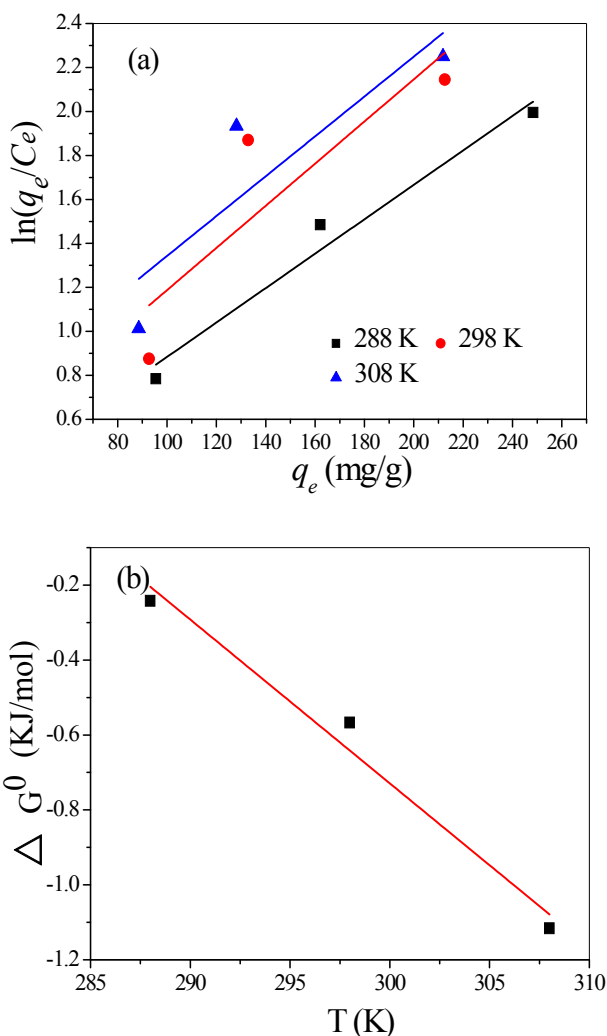


Fig. 4: (a) Plots of $\ln q_e/C_e$ versus q_e for PVA adsorption on ACF; (b) changes of free energy (thermodynamic calculations).

intersection with the vertical axis gives the value of $\ln K_0$ at the three different temperatures. The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of a plot $\ln K_0$ versus the reciprocal of absolute temperature ($1/T$) (Fig. 4).

As presented in Table 2, the enthalpy and entropy of the adsorption process were found to be 12.38 KJ mol⁻¹ and 43.7 J mol⁻¹ k⁻¹, respectively. The positive value of the reaction enthalpy indicates that the adsorption process is endothermic and the uptake of PVA increases with a rise in the reaction temperature. This is consistent with the aforementioned adsorption performance. The positive value of the entropy indicated that the adsorption process is entropy production. The negative values of ΔG^0 at the three temperatures suggest the spontaneous nature of PVA adsorption. The ΔG^0 decreases with the increasing temperature, indicating that high temperature is beneficial to the adsorption of PVA by ACF.

CONCLUSION

Activated carbon fibre (ACF) could efficiently remove polyvinyl alcohol (PVA) in a batch adsorption system. It was observed that a very limited amount of ACF removed the PVA efficiently. Near-neutral solution pH conditions were more favourable for the adsorptive removal of PVA. Langmuir model described the adsorption isotherm quite better than Freundlich model and the ACF surface is deduced to be more homogeneous to some extent. The changes of enthalpy and entropy of the adsorption processes are 12.38 KJ mol⁻¹ and 43.7 J mol⁻¹ k⁻¹, respectively. The negative value of Gibbs free energy change and the positive value of enthalpy indicate that the adsorption process is spontaneous and endothermic.

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