



# Kinetic Study and Effect of Coexisting Ions on the Adsorption of Polyvinyl Alcohol (PVA) by Activated Carbon Fibres

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## ABSTRACT

A synthetic polymer pollutant, polyvinyl alcohol (PVA), is widely detected in wastewaters and natural waters. In this study, commercial activated carbon fibres (ACF) were tentatively used for adsorptive removal of PVA. Adsorption kinetics and the effect of coexisting ions on the adsorption of PVA were investigated. Kinetic models including pseudo-first-order, pseudo-second-order and Elovich models were used to simulate the kinetic data. The correlation coefficients of nonlinear pseudo-second-order and Elovich models are all above 0.969. The correlation coefficient of linear pseudo-second-order kinetic model is above 0.999, which is especially higher than those of linear pseudo-first-order model. The kinetic study indicates that both pseudo-second-order and Elovich kinetic models could describe the adsorption kinetics better. It can be inferred that chemisorption occurred between the PVA molecules and ACF while rate-determining step might be diffusive in nature. It is worthy to mention that most of the uptake occurred within the initial 120 min. Nitrate anions have no significant influence on PVA adsorption. For the common inorganic anions such as bicarbonate, phosphite and sulphate, the inhibition was observed with increasing concentrations. The presence of humic acid inhibited the PVA uptake as well.

## INTRODUCTION

Polyvinyl alcohol (PVA), a recalcitrant and water soluble polymer, has received much attention in recent years. PVA is a synthetic polymer obtained from the hydrolysis of polyvinyl acetate. It possesses interesting properties such as good surface alignment effects, low cost and inexpensive processing (Veres et al. 2004). As a result, PVA is commonly used in a wide range of industrial, medical and food applications, including resins, lacquer, surgical threads and food-contact applications (DeMerlis & Schoneker 2003). However, critical evaluation supported the safety of PVA as a coating agent for pharmaceutical and dietary supplement products, and the acute oral toxicity of PVA was found to be as low as 20 g/kg (DeMerlis & Schoneker 2003). The improper discharge of PVA-containing wastewater from industrial effluents can pose a threat to human health. In addition, PVA affects the environment adversely and accumulates in human body through food chain. For example, PVA has the potential to prevent the sedimentation of heavy metals in natural waters and leads to other serious environmental issues (Schönberger et al. 1997). Therefore, it can be a great need if PVA was removed before the PVA containing wastewaters are discharged into the environment.

Several methods have been used to remove polyvinyl alcohol from wastewaters such as physical method, chemical method and biological method. Javad Tavakoli and coworkers found that about 90% destruction of PVA occurred in 90 min at 200°C and 0.7 MPa oxygen partial pressure (Tavakoli et al. 2001). Although these methods and technologies have significant removal capability, the investment cost and operation cost of these technologies are particularly high. Meanwhile, the related operation procedures are complicated, and there are still many difficulties concerning industrial application. As a low-energy solid extraction technology, the adsorption method has an unparalleled advantage in the treatment of dissolved organic pollutants.

Accordingly, screening an optimal adsorbent emerges to be a fundamental approach to achieve efficient PVA removal. Hung-Suck Park and coworkers have employed powdered activated carbon as an adsorbent to remove PVA. They found that the maximum PVA 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 (Park et al. 2008). Meanwhile, fibrous adsorbents have advantages such as fast adsorption rate and ease of handling in comparison with granular adsorbents

and powdered adsorbents. Recently, activated carbon fibres (ACF) have attracted wide attention due to their especially high removal efficiency and adsorption capacity. Nishith Verma and co-workers used ACF to remove volatile organic compound. The experimental results revealed that ACF is a prominent adsorbent for capturing VOCs at ppm levels under dynamic adsorption/desorption conditions (Verma et al. 2004). As a result, it demonstrates that ACF is an ideal adsorbent to achieve high-efficiency adsorptive removal of PVA. Accordingly, ACF was employed for PVA adsorption in this study. The adsorption kinetics, and the effect of coexisting anions and humic acid on PVA adsorption were investigated. The results would provide a better reference for actual water treatment.

## MATERIALS AND METHODS

**Chemicals:** Polyvinyl alcohol (PVA, 95.5%) and other chemicals were procured from Tianjin Kermel Chemical Reagents Co., Ltd., Tianjin. Other chemicals including nitrate, bicarbonate, phosphate and sulphate were of analytical-reagent grade. 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 m<sup>2</sup>/g. Deionized (DI) water was used throughout this study.

**Batch adsorption studies:** All working solutions were prepared by diluting the stock solution with DI water to the desired concentration. Kinetic experiments were carried out in a 500 mL beaker. A desired amount of ACF (200 mg) was added to a conical flask containing 500 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<sup>-1</sup> of HCl or NaOH. The suspension was mixed with a magnetic stirrer at 160 rpm. Samples of 5 mL were taken from the suspension at predetermined times. Finally, samples were collected at desired time intervals and filtered through a 0.45 μm pore-size membrane before measurement.

The effects of humic acid and coexisting anions such as HCO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and SiO<sub>3</sub><sup>2-</sup> on the PVA adsorption was investigated in a series of conical flasks. A dose of 10 mg of ACF was added into the vessels containing 50 mL of PVA solution at 20 mg L<sup>-1</sup>. The anion concentrations ranged from 0.01 to 10 mg L<sup>-1</sup>. The solution pH was adjusted to neutral solution pH. The solutions were mixed at 160 rpm for 24 h. After filtration by a 0.45 μm membrane filter, the residual concentration of PVA in the filtrates was analysed. The reaction temperature was controlled at a constant of 298 K unless otherwise stated.

**Analysis of PVA:** According to the procedures described by Finley (Finley 1961), boric acid and iodine solutions were added into the samples, and then the PVA concentra-

tion was determined by measuring the absorbance at a fixed wavelength of 690 nm using an UVmini-1240 spectrophotometer (Shimadzu, Japan). The adsorption capacity was calculated using the following equation:

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

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

Where,  $q_e$  and  $q_t$  (mg/g) are the adsorption capacity at equilibrium and time  $t$  (min),  $C_0$  is the initial concentration of PVA in solution, while  $C_e$  and  $C_t$  (mg/L) are the concentrations of PVA at equilibrium and  $t$  (min), respectively,  $V$  (L) is the volume of solution, and  $W$  (g) is the mass of the adsorbent used.

## RESULTS AND DISCUSSION

**Adsorption kinetics:** Adsorption kinetics of PVA onto ACF was investigated at neutral solution pH. Typical kinetic models, including pseudo-first-order, pseudo-second-order and Elovich models were used to fit the experimental data. The nonlinear pseudo-first-order model is expressed as (Lagergren 1898):

$$q_t = q_e(1 - e^{-k_1 t}) \quad \dots(3)$$

The nonlinear pseudo-second-order model can be expressed as (Ho & McKay 1999):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad \dots(4)$$

The mathematical representations of the linear models of pseudo-first-order and pseudo-second-order kinetics are given in the following equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(6)$$

Where  $q_e$  and  $q_t$  are the adsorption capacities (mg/g) of the adsorbent at equilibrium and at time  $t$  (min), respectively;  $k_1$  (1/min) and  $k_2$  (g/(mg min)) are the related adsorption rate constants for the pseudo-first-order and pseudo-second-order models, respectively.

The Elovich model can be expressed as (Kithome et al. 1988):

$$q_t = a + k \ln t \quad \dots(7)$$

Where,  $a$  (g mg/min) and  $k$  (mg/g) are constants.

Non-linear kinetic models were used to fit the experimental kinetic data, and the simulated curves are presented in Fig. 1. It can be observed that the adsorption was very fast and approximate 90% of the PVA molecules were absorbed within 120 min. The result shows that all of three nonlinear

Table 1: Nonlinear kinetics parameters of PVA adsorption.

Nonlinear model		Parameters	
Pseudo-first-order model	$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g)	$R^2$
	0.0894	26.27	0.901
Pseudo-second-order model	$k_2$ (g·mg/min)	$q_e$ (mg/g)	$R^2$
	0.00513	27.50	0.969
Elovich model	a	k	$R^2$
	10.67	2.74	0.983

Table 2: Linear kinetics for simulation parameters of PVA adsorption.

Models	Linear pseudo-first-order model			Linear pseudo-second-order model		
	$q_e$ (mg/g)	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_e$ (mg/g)	$k_2$ (g·mg/min)	$R^2$
Parameters	10.15	0.0052	0.960	28.88	0.0025	0.999

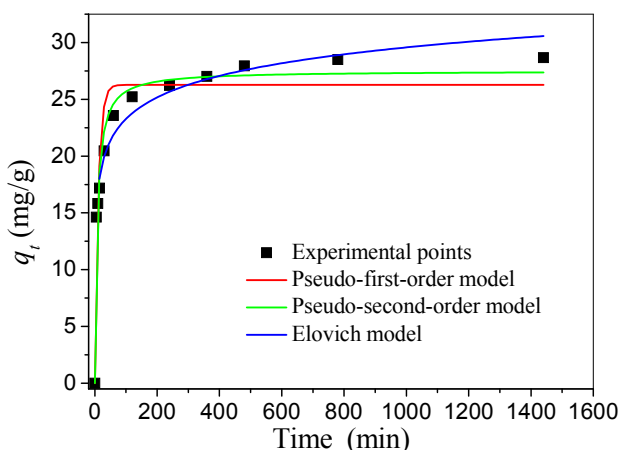


Fig.1: Nonlinear kinetic simulations of PVA adsorbed onto ACF.

kinetic models could describe the adsorption kinetics, while only pseudo-second-order and Elovich models fitted the experimental data better. As given in Table 1, the correlation coefficients ( $R^2$ ) of pseudo-second-order and Elovich models are all above 0.968. Accordingly, the rate determining step might be diffusive in nature for the uptake of PVA in this case (Aharoni et al. 1991).

Meanwhile, as demonstrated in Fig. 2, the experimental data were also comparatively simulated by linear kinetic models including pseudo-first-order and pseudo-second-order models. The kinetic parameters, simulated using the two models, are listed in Table 2. The  $R^2$  value of pseudo-second-order kinetic model is above 0.999, which is still higher than that of pseudo-first-order model ( $R^2=0.960$ ). The calculated  $q_e$  value is much close to the experimental value using pseudo-second-order kinetic model as well. Accordingly, pseudo-second-order kinetic model fitted the experimental

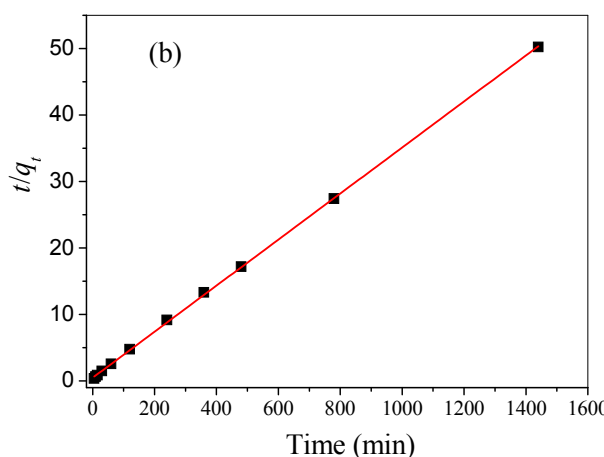
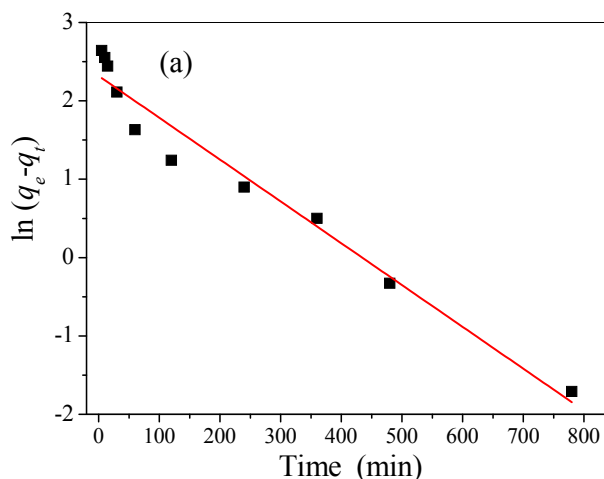


Fig. 2: Linear kinetic simulation for pseudo-first-order and pseudo-second-order kinetic models for the uptake of PVA onto ACF.

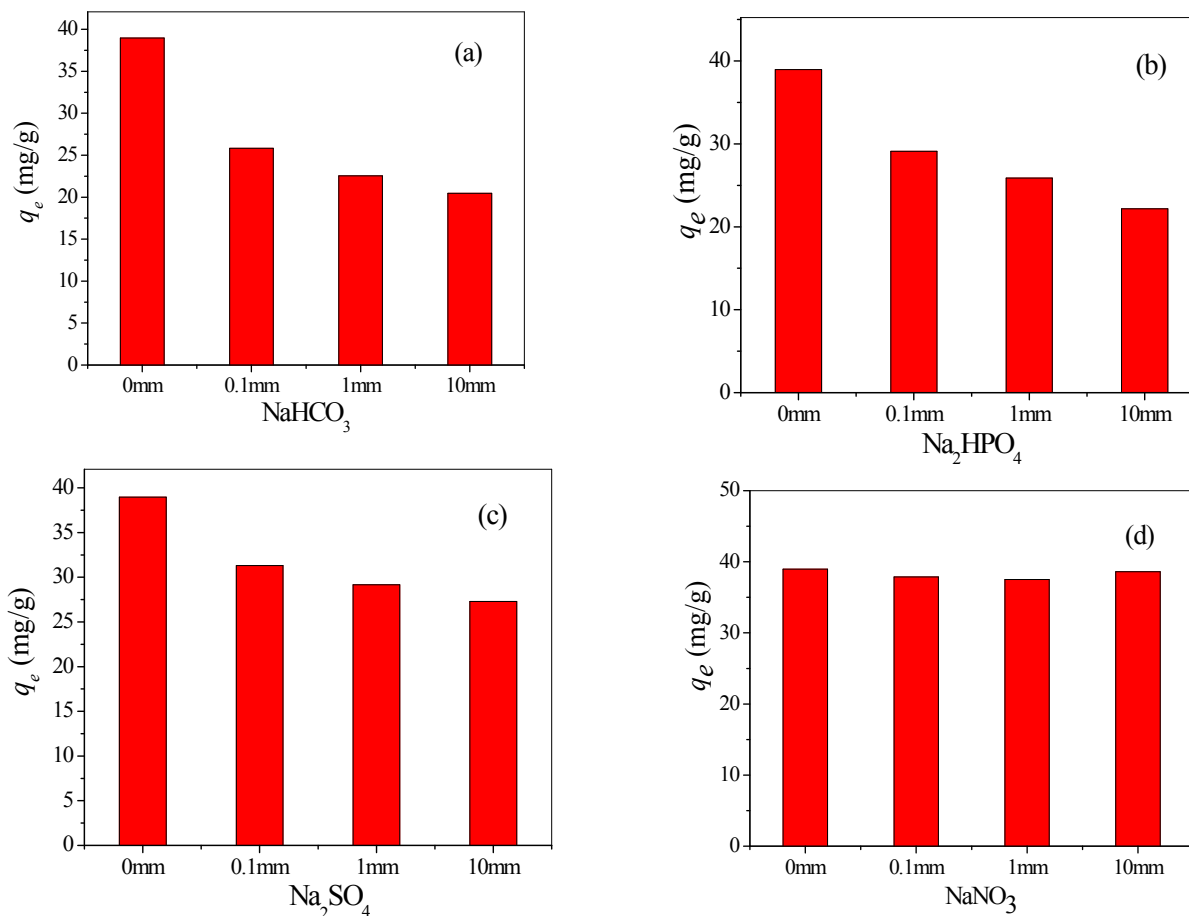


Fig. 3: Effect of natural coexisting ions on adsorption of PVA.

data better. As such, it can be inferred that chemisorption occurred between the PVA molecules and the ACF surface.

**Effect of the coexisting inorganic anions:** There is also a great need to investigate the effect of the coexisting inorganic anions on PVA removal. PVA usually coexists with several salts in natural waters and wastewaters. The presence of these inorganic anions might accelerate or retard PVA adsorption. These inorganic anions exert their influence through two approaches. On one hand, they can screen the electrostatic interaction of opposite charges in adsorbents and PVA molecules, in which an increase in salt concentration could decrease the amount of PVA adsorbed. On the other hand, these anions may enhance the dissociation degree of PVA molecules and facilitate the uptake of PVA (Crini & Badot 2008).

As illustrated in Fig. 3, the decrease of PVA uptake was observed with increasing concentration of bicarbonate, phosphate and sulphate. In the presence of bicarbonate, phos-

phate and sulphate, when the concentration of these three anions increased from 0 to 10 mM, the PVA adsorption capacity reduced from 39.0 mg/g to 20.5 mg/g, 22.2 mg/g and 27.3 mg/g, respectively. These inorganic anions might have stronger electrostatic interaction. For nitrate, no obvious increase or decrease for PVA adsorption was observed when its concentration increased from 0.1 to 10 mM. Nitrate might not screen the electrostatic interaction or enhance the dissociation degree of the PVA molecules.

**Effect of natural organic matter:** Natural organic matter humic acid is a kind of macromolecule widely existing in natural water bodies. Humic acid has an important influence on the adsorption and removal of pollutants from water. As shown in Fig. 4, a decrease in PVA uptake was observed with increasing humic acid concentrations. The PVA adsorption capacity reduced from 39.0 mg/g to 26.9 mg/g with an increase of humic acid concentration from 0 to 10 mM. As a result, the presence of humic acid could evidently inhibit the PVA uptake.

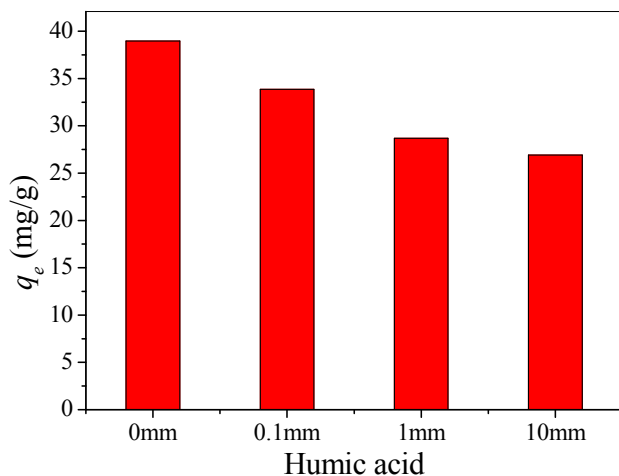


Fig. 4: Effect of natural organic matter humic acid on adsorption of PVA.

**CONCLUSION**

ACF were tentatively used for adsorptive removal of PVA. Adsorption kinetics and effect of coexisting anions on the adsorption of PVA were emphatically investigated. The kinetics experiments indicate that both pseudo-second-order and Elovich kinetic models could describe the adsorption kinetics better. It indicates that chemisorption occurred between the PVA molecules and ACF surface while rate-determining step might be diffusive in nature. Nitrate anions had no evident influence in PVA adsorption. The presence of bicarbonate, phosphate and sulphate decreased the PVA uptake dramatically. Natural organic matter humic acid could inhibit PVA uptake as well.

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