# Original Research Adsorption Behaviors of Acetaminophen onto the Colloid in Sediment

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# Abstract

The main aim of this study was to describe the adsorption behaviours of acetaminophen (APAP) onto colloid and solid particle in sediment in terms of their impact on the factors of the processes (e.g., contact time, temperature, kinetic, thermodynamic characteristics) that were analyzed systematically. Sediment was collected from a typical tributary in the mid-Weihe River and a separation device was employed to separate sediment into colloid and solid particle. Results show that the adsorption of APAP onto colloid and solid particle reached equilibrium after about 12 hours and 48 hours, respectively. The adsorption capacity of APAP onto colloid was at least 28-fold larger than that onto solid particle with an initial APAP concentration of 10.0 mg·L<sup>-1</sup> at 25°C. The Langmuir isotherm model was more suitable for describing the adsorption behaviours of APAP onto both colloid and solid particle in sediment. The adsorption processes were feasible, spontaneous, entropy-increasing, and endothermic in nature, the adsorption capacity increased with increasing temperature. The mechanisms controlling APAP adsorption onto colloid and solid particle were mainly physisorption, but physisorption less on APAP pollution to the groundwater system in the Weihe River basin.

Keywords: adsorption, acetaminophen, sediment, colloid, thermodynamics

#### Introduction

Acetaminophen (or paracetamol, abbreviated as APAP) is an analgesic and antipyretic drug heavily used all over the world. APAP is ranked as one of the top three drugs prescribed in England [1], and is one of the top 200 prescriptions in the US [2]. Clinical research shows that overdoses of APAP may be toxic and result in severe side effects, such as kidney injury and liver failure [3, 4]. According to preliminary statistics, the output of APAP is  $2\times10^5$  tons per year globally, China is the second largest APAP manufacturing country and many kinds of cold medicine used in China contain APAP [5]. Muir et al. [6] found that during

therapeutic use of APAP, about 58-68% of the dose could not be used by the body. Thus it is directly released into the environment as its primary form or metabolin through urine or excrement. As a result it brings potential risks to the environment, which turns APAP into an important environmental research object.

When polluted surface water (mainly river water) infiltrates to the subsurface system, river sediment is an important medium that influences the water movement and solute transport to the groundwater system. The adsorption characteristics of pollutants onto river sediment directly influence their mobility from the sediment-water interface to sediments beneath the channel surface. In a certain time, sediments adsorb and detain pollutants in sediment layers so that water can move through, preventing the groundwa-

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Organic carbon (weight %)	Moisture content	Volume weight (g·(cm <sup>3</sup> ) <sup>-1</sup> )		Mechanical composition (weight %)				
			Porosity %	Silt Fine sand		Medium sand	Coarse sand	
				<0.25         0.25-0.35         0.35-0.5           mm         mm         mm	0.25-0.35	0.35-0.5	>0.5	
					mm	mm		
0.46	5.90	1.53	42.42	1.85	52.20	41.03	4.92	

Table 1. Physicochemical properties of the sediment sample.

Table 2. Kinetics rate constants for APAP adsorption onto colloid and solid particle in sediment.

Adsorbent	Q <sub>e,exp</sub> (mg·kg <sup>-1</sup> )	Pseudo-first-order model			Pseudo-second-order model		
		R <sup>2</sup>	$k_{1}$ (h <sup>-1</sup> )	$Q_{e,cal} (\mathrm{mg}\cdot\mathrm{kg}^{-1})$	R <sup>2</sup>	$k_2 (\text{kg} \cdot (\text{mg} \cdot \text{h})^{-1})$	$Q_{e,cal} (\mathrm{mg}\cdot\mathrm{kg}^{-1})$
Colloid	167.95	0.9333	0.1261	181.31	0.8850	0.0006	222.05
Solid Particle	6.4911	0.9573	0.0672	7.2933	0.9391	0.0053	10.059

ter from becoming polluted [7, 8]. Researchers have reported the adsorption characteristics of florfenicol [9], polycyclic aromatic hydrocarbon [10], organochlorine pesticides [11], etc. onto different sediments. Moreover, Lorphensri et al. [12, 13] investigated adsorption and transport of APAP with low organic content aquifer medium. Alumina, silica, and porapak P were selected to represent positively charged, negatively charged, and hydrophobic organic content of an aquifer medium, respectively. Results indicate that APAP showed no significant adsorption to any of the media at initial concentrations from 1.0 mg·L<sup>-1</sup> to 10.0 mg·L<sup>-1</sup>. Column transport experiments further indicate that APAP exhibited virtually no retardation to low organic content aquifer medium. Yamamoto et al. [14] investigated adsorption of APAP onto sediments collected from the Akui, Tamiy and Tatara rivers in Japan. Results indicate that adsorption capacities of APAP onto these sediments exhibited obvious differences at the same aqueous-phase concentrations, which could even reach about 800 µg·kg-1. Lin et al. [15] collected river water and sediment samples from the Ji-Lung River in Taiwan and conducted adsorption and combined adsorption-biodegradation experiments in laboratory batch studies. Results indicate that although biodegradation was found to be a primary mechanism for degradation, adsorption onto sediments was also responsible for a 30% loss of aqueous-phase APAP, which could not be neglected. Thus it can be seen that adsorption behaviors of APAP onto sediments from different locations, structures, and properties exhibit obvious differences. However, sediment has complex components, such as coarse and fine particles of inorganic state, more subtle colloid particles, and organic matter of trace amounts. The differences in the adsorption abilities of pollutants among these components are still unknown.

Colloid particles play an important role in the groundwater system, and they have a strong affinity with pollutants due to their large specific surface area [16]. Johson and Amy [17] investigated adsorption of polycyclic aromatic hydrocarbon with humic acid colloid. Results indicate that polycyclic aromatic hydrocarbon showed significant adsorption to humic acid, which further improved the solubility of polycyclic aromatic hydrocarbon in true solution phase. Stotzky [18] collected colloid from soil samples and conducted adsorption-biodegradation experiments in laboratory batch studies. Results indicated that colloid adsorbed and fixed the DNA released from microorganisms, and avoided DNA degradation by the nuclease. Heidmann et al. [19] investigated adsorption of heavy metal ions onto colloid, which was collected from soil samples. Results indicated that heavy metal ions showed low concentrations and biological activities due to the adsorption onto colloid. Many recent investigations [20, 21] further indicated that colloid in soils and sediment not only adsorbs pollutants but also carries pollutants that can migrate in a true solution phase, which increases the risk of groundwater pollution. To our knowledge, however, most previous studies focused on the adsorption of heavy metal ions, radioactive substances, and polycyclic aromatic hydrocarbons onto colloid in soils and sediment, but the adsorption behaviours of APAP onto colloid are less abundantly reported.

The Weihe River is the biggest tributary of the Yellow River, and a large population resides in the Weihe River basin. A large quantity of APAP enters the Weihe River through a sewage system of municipal works. This study collected sediment from a typical tributary in the mid-Weihe River and a separation device was employed to separate sediment into colloid and solid particles. Compared with APAP adsorption onto solid particles, the impact factors in the processes of APAP adsorption onto colloid such as contact time, temperature, and kinetic and thermodynamic characteristics were analyzed systematically.

# **Materials and Methods**

# Sediment Sampling

The sampling site of sediment was chosen at the confluence of the Bahe and Weihe rivers in early May 2013 (Fig. 1). Sampling was conducted using a PVC pipe to collect the top 5 cm of the sediment for laboratory analysis [22]; a total mass of 2-3 kg was collected, including a replicate sample for standby application. The sediment was not polluted by APAP, and it was air-dried and sterilized for lab analysis. Some basic physicochemical properties of the sediment are listed in Table 1.

#### Chemical Reagent

APAP was purchased from Boston Biomedical Inc. (Boston, USA) with United States Patent (USP) grade. The molecular formula of APAP is C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub> and its molecular weight is 151.17. Methyl alcohol in flowing phase was purchased from Waters Company (New York, USA) with high performance liquid chromatography (HPLC) grade. Ultrapure water in flowing phase was purchased from Wahaha Company (Hangzhou, China) with HPLC grade. Kaolin was purchased from Xideli Chemical and New Material Inc. (Zhengzhou, China) with analytical grade.

#### Detection Method of APAP in Solution

A Waters (New York, USA) ACQUITY ultra performance liquid chromatography (UPLC) H-Class with ultraviolet/visible spectrophotometry detector and BEH Shield RP18 1.7  $\mu$ m 2.1×150 mm column was used for the quantification of APAP in solution, under the optimized conditions as follows: methanol/water=50:50 as mobile phase, 0.2 mL·min<sup>-1</sup> of flow rate, 20°C±0.1°C column temperature, 5  $\mu$ L of injection volume, 249 nm detected wavelength, and 2.220 min of retention time.

# Adsorption Procedure

Adsorption experiments were conducted by the Organization for Economic Co-operation and Development (OECD) batch equilibrium method [23]. Each time 4.0 g of sediments and 20 mL APAP solution were mixed in a 25 mL centrifuge tube (HMBT, Xihua Instrument Technological Inc., (Beijing, China), which was then shaken in a thermostat shaker (THZ-82, Guohua Electrical Appliance Inc., (Changzhou, China) at 150 rpm.

#### Separation Method of Colloid in Sediment

Colloid and solid particle in the sediment were separated by a separation device that was previously designed by the authors [24]. The schematic of the separation device is shown in Fig. 2. 10 mL supernatant fluid was taken after the adsorption experiment, and was then injected, under pressure into the separation device through fluid inlet 1. The concentrations of APAP and colloid were determined from the sample taken through sampling hole 8. The concentration of APAP in the true solution phase was determined from the sample taken through fluid outlet 6. The uptake of APAP onto colloid and solid particle were calculated by deducting the latter from the former concentrations.

# Detection Method of Colloid

The concentration of colloid was determined by testing turbidity of solution using spectrophotometric method (ultraviolet/visible spectrophotometry detector, Waters Company (New York, USA)), due to the certain relationship between turbidity and colloid concentration in solution [25]. Kaolin was employed to make standards of colloid solution with known concentrations, a standard curve of colloid concentration and turbidity was established through measurement of turbidity. The colloid concentration of the actual sample was calculated according to the standard curve through the measurement of turbidity.



Fig. 1. Location of the sampling site.

Adsorbent		Langmuir isoth	Freundlich isotherm				
	$Q_{max}$ (mg·kg <sup>-1</sup> )	$\frac{K_L}{(L \cdot mg^{-1})}$	$\mathbb{R}^2$	$R_L$	$K_F ({ m mg  kg^{-1}}) \ ({ m L  mg^{-1}})^{1/n}$	1/ <i>n</i>	R <sup>2</sup>
Colloid	436.11	0.0680	0.9851	0.7164	35.358	0.6668	0.9530
Solid Particle	44.438	0.0188	0.9949	0.8856	0.9157	0.8708	0.9903

Table 3. Isotherm parameters for APAP adsorption onto colloid and solid particles in sediment.

#### Adsorption Kinetics

The kinetic studies were performed following a similar procedure at 25°C (298 K, pH 7.0). The initial concentration was set to 10.0 mg L-1 for each APAP in a series of reactors with the same specification. The aqueous samples were separated at predetermined time intervals by following the separation method. The concentrations of APAP were analyzed by the UPLC. Each experiment was duplicated under identical conditions with two replicate samples for each time interval. Blanks containing no APAP were done and the loss (generally quite low) was compensated for calculation. The uptake of APAP at time t,  $Q_t$  (mg·kg<sup>-1</sup>), was calculated by the following equation:

$$Q_t = \frac{V(C_0 - C_t)}{m} \tag{1}$$

...where  $C_0$  and  $C_t$  are the initial concentration and concentration at time t of the APAP (mg·L-1) in the solution, respectively, V is the volume of the solution (L), and m is the weight of the adsorbent (g).

#### Adsorption Isotherm

In adsorption isotherm studies, solutions with different initial concentrations were added, which ranged from 1.0 to 20.0 mg L<sup>-1</sup> (1.0, 2.0, 5.0, 10.0 and 20.0 mg L<sup>-1</sup>, pH 7.0). The equilibrium time of colloid was set as 12 hours, and equilibrium time of solid particle was set as 48 hours, and these times were considered sufficiently long according to the kinetic studies. The aqueous samples were separated by following the separation method. The concentrations of APAP were analyzed by the UPLC. Each initial concentration had two replicate samples. Blanks containing no APAP were done and the loss (generally quite low) was compensated for calculation. The uptake of APAP at equilibrium,  $Q_e$  (mg·kg<sup>-1</sup>), was calculated by the following equation:

$$Q_e = \frac{V(C_0 - C_e)}{m} \tag{2}$$

...where  $C_e$  is the equilibrium concentration of the APAP  $(mg \cdot L^{-1})$  in the solution.



- 3 Cover gasket for the right side
- 4 Separation chamber
- 7 Cover gasket for the left side
- 8 Sampling hole (with stopper)

- 11 Filter membrane (0.22 μm)
- 13 Filter membrane (0.001 µm)

Fig. 2. The schematic of separation device: (a) the main structure diagram, and (b) the assembly structure diagram.

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Adsorbent	Temperature	298K	308K	318K	
	$Q_{max}(mg kg^1)$	436.11	489.15	508.81	
Colloid	$K_L$ (L mg <sup>-1</sup> )	0.0680	0.0821	0.1193	
Conoid	$K_L$ (L mol <sup>-1</sup> )	10274	12414	18039	
	R <sup>2</sup>	0.9851	0.9924	0.9782	
	$Q_{max}$ (mg kg <sup>1</sup> )	44.438	49.053	50.479	
Solid Particle	$K_L$ (L mg <sup>-1</sup> )	0.0188	0.0204	0.0289	
Solid I atticle	$K_L$ (L mol <sup>-1</sup> )	2837.5	3089.9	4370.3	
	R <sup>2</sup>	0.9949	0.9973	0.9986	

Table 4. Langmuir isotherm parameters for APAP adsorption onto colloid and solid particle in sediment with different temperatures.

#### Thermodynamics

In the thermodynamic study, the initial concentration ranged from 1.0 to 20.0 mg L<sup>-1</sup> (1.0, 2.0, 5.0, 10.0, and 20.0 mg L<sup>-1</sup>, pH 7.0) at 25°C (298 K), 35°C (308 K), 45°C (318 K). The equilibrium time of colloid was set as 12 hours, and equilibrium time of solid particle was set as 48 hours, which were considered sufficiently long according to the kinetic studies. The aqueous samples were separated by following the separation method. The concentrations of APAP were analyzed by the UPLC. Blanks containing no APAP were done and the loss (generally quite low) was compensated for the calculation.

#### **Results and Discussion**

#### Adsorption Kinetics

The adsorption of APAP onto colloid and solid particle in sediment as a function of contact time at solution pH 7.0 are shown in Fig. 3. Two widely used kinetic models, pseudo-first-order and pseudo-second-order kinetic models, were employed to interpret the kinetics results (Fig. 3). The linearized form of the pseudo-first-order kinetic model is given as follows [26, 27]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{3}$$

...where  $Q_e$  (mg·kg<sup>-1</sup>) and  $Q_t$  (mg·kg<sup>-1</sup>) are the APAP adsorption capacities for the adsorbent at the equilibrium and at any time *t* (h), respectively.  $k_1$  (h<sup>-1</sup>) is the rate constant of pseudo-first-order kinetic model. The rate constant  $k_1$ , the equilibrium adsorption capacity  $Q_e$ , and the determination coefficient R<sup>2</sup> are given in Table 2.

The linearized form of pseudo-second-order kinetic model is given as follows [26, 27]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{4}$$

...where  $k_2$  (kg·(mg h)<sup>-1</sup>) is the rate constant of pseudo-secondorder kinetic model. The values of equilibrium adsorption capacity  $Q_e$  and rate constant  $k_2$ , calculated from the intercept and the slope of the linear plot of  $t/Q_t$  versus t, along with the value of determination coefficient R<sup>2</sup>, are listed in Table 2.

It can be observed in Fig. 3 that the equilibrium time of APAP adsorption onto colloid and solid particle existed 4fold differences, which were 12 hours and 48 hours, respectively. In addition, it can also be observed that the adsorption capacity of APAP onto colloid and solid particle at equilibrium time existed differences about two orders of magnitude. For the colloid specifically, the adsorption capacity reached above 160 mg·kg<sup>-1</sup>. This might be attributed to the existence of more adsorption sites on the surface of colloid. Fig. 4 showed the scanning electron microscope images of sediment before and after the separation of colloid. The surface of solid particle in sediment seemed to be smooth, implying the lack of potential adsorption sites. It is well known that the colloid has a large specific surface area. Thus, it shows a strong affinity with organic pollutants, which is the same with experimental data.

As seen in Table 2, R<sup>2</sup> values obtained by the pseudofirst-order kinetic model for APAP adsorption onto colloid and solid particle were 0.9333 and 0.9573, and the calculated  $Q_e$  values ( $Q_{e,cal}$ ) were 181.31 and 7.2933 mg·kg<sup>-1</sup>, respectively. Meanwhile, R<sup>2</sup> values obtained by the pseudo second-order kinetic model for APAP adsorption onto colloid and solid particle were 0.8850 and 0.9391, and the calculated  $Q_e$  values ( $Q_{e,cal}$ ) were 222.05 and 10.059 mg·kg<sup>-1</sup>, respectively. However,  $Q_e$  values ( $Q_{e,exp}$ ) for APAP adsorption onto colloid and solid particle obtained by experiments were 167.95 and 6.4911 mg·kg<sup>-1</sup>, respectively. Thus it should be noted that the R<sup>2</sup> values obtained by the pseudo first-order kinetic model were higher, and the calculated  $Q_e$ values  $(Q_{e,cal})$  were in good agreement with the experimental results compared with the pseudo second-order kinetic model, suggesting the applicability of the pseudo first-order kinetic model to describe the adsorption kinetics data of APAP onto both colloid and solid particles.

#### Adsorption Isotherm

The adsorption isotherms of APAP onto colloid and solid particle in sediment were studied at 25°C (298 K) and with a solution of pH 7.0. Results showed that APAP adsorption capacity increased with the increasing equilibrium of APAP concentration for both colloid and solid particle. For the same initial concentration, the adsorption capacity of APAP onto colloid and solid particle at equilibrium time exhibited significant differences. Two-parameter isotherm models (Langmuir and Freundlich) were used to fit the experimental data, which are shown in Fig. 5.

Adsorbent	Adsorbant	$AU^{(1,1)}$ ( $[1,1,m,0,1^{-1})$ )	400 (1,1 (mol V)-1)		$\mathbf{D}^2$		
		23 (KJ (IIIOFK))	298K	308K	318K	K	
	Colloid	22.091	0.1507	-22.886	-24.139	-25.911	0.9166
	Solid Particle	16.898	0.1224	-19.698	-20.578	-22.162	0.9084

Table 5. Thermodynamic parameters for APAP adsorption onto colloid and solid particle in sediment.

The linearized form of Langmuir isotherm model can be written as [28]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max}K_L} + \frac{C_e}{Q_{\max}}$$
(5)

...where  $C_e$  (mg·L<sup>-1</sup>) is the equilibrium concentration of APAP in solution,  $Q_e$  (mg·kg<sup>-1</sup>) is the APAP adsorption capacity onto the adsorbent,  $Q_{max}$  (mg·kg<sup>-1</sup>) is the maximum APAP adsorption capacity onto the adsorbent, and  $K_L$  (L·mg<sup>-1</sup>) is the Langmuir isotherm constant related to the free energy of adsorption. The values of  $Q_{max}$  and  $K_L$  can be calculated from the intercept and the slope of the straight line of the linearized form of the Langmuir isotherm.

The linearized form of the Freundlich isotherm model can be written as [28]:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

...where  $K_F$  ((mg·kg<sup>-1</sup>)·(L·mg<sup>-1</sup>)<sup>1/n</sup>) and 1/n are the Freundlich constants which are related to adsorption capacity and adsorption intensity, respectively. The values of  $K_F$  and 1/n can be calculated from the intercept and the slope of the straight line of the linearized form of the Freundlich isotherm.

The parameters of Langmuir and Freundlich isotherm models for APAP adsorption onto colloid and solid particle in sediment, along with the values of determination coefficient ( $\mathbb{R}^2$ ), are given in Table 3. As shown in Table 3, the values of  $\mathbb{R}^2$  obtained by the Langmuir isotherm model for APAP adsorption onto both colloid and solid particles were higher than the Freundlich isotherm model.

Although the values of  $R^2$  obtained by Freundlich isotherm model were comparatively lower, they were still larger than 0.9. The  $K_F$  value of colloid was about 39-fold larger than that of solid particles, indicating that colloid had a larger adsorption capacity. In addition, the adsorption is considered easy when 1/n<0.5 and difficult when 1/n>2[26, 27]. The 1/n values of colloid and solid particle in this study were 0.6668 and 0.8708, respectively, which further proved that colloid had a comparatively stronger affinity with APAP than solid particle.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor,  $R_L$ , which is defined as follows [28]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

...where  $C_0$  (mg·L<sup>-1</sup>) is the initial concentration of APAP in solution. The adsorption is considered favourable when  $0 < R_L < 1$  and linear when  $R_L = 1$  [29]. The values of  $R_L$ obtained in this study were between 0.7164 and 0.8856 (Table 3), which were close to 1, indicating that the adsorption of APAP onto colloid and solid particle in sediment were favorable. The Langmuir isotherm model represents linearity at low equilibrium concentration, which fits the data.



Fig. 3. Effect of contact time on APAP adsorption onto colloid and solid particle in sediment.

#### Thermodynamics

The adsorption of APAP onto colloid and solid particle in sediment were studied as a function of temperature (298 K, 308 K, 318 K) at solution pH 7.0. The above experimental data were evaluated by the Langmuir isotherm model (Fig. 6) as it is more suitable to describe the adsorption behaviours of APAP onto colloid and solid particle in sediment. The obtained results are listed in Table 4.

The values of  $K_L$  for the Langmuir isotherm at 298 K, 308 K, and 318 K were used to calculate thermodynamic parameters such as Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) using the following equations [30]:

$$\Delta G^{\rm O} = -RT \ln K_{\rm r} \tag{8}$$

$$\ln K_{L} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(9)

...where  $K_L$  (L·mol<sup>-1</sup>) is the Langmuir constant, R (8.314 J·(mol·K)<sup>-1</sup>) is the gas constant, and T (K) is absolute temperature. The values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  can be calculated from the intercept and the slope of the linear plot of  $\ln K_L$  versus 1/T. The obtained values of thermodynamic parameters for APAP adsorption onto colloid and solid particle in sediment are given in Table 5.

As shown in Fig. 6, the adsorption capacity of APAP onto colloid and solid particles increased with the increasing temperature, which indicated that the adsorption of APAP onto both colloid and solid particle favored higher temperatures. The negative values of  $\Delta G^{\circ}$  suggested the feasibility of the APAP adsorption onto colloid and solid particles, and the spontaneous nature of the adsorption process also can be





b)

Fig. 4. The scanning electron microscope (SEM) images of sediment before and after the separation of colloid: (a) the original sediment, (b) solid particle.



Fig. 5. Two-parameter isotherm models (Langmuir and Freundlich) fit of adsorption isotherm.

a)

18 350 298K 298K 16 308K 308K 0 0 300 318K 14 318K Δ Δ 250 12 10 Q<sub>e</sub> (mg kg<sup>-1</sup>) Q<sub>e</sub> (mg kg<sup>-1</sup>) 200 8 150 6 100 4 50 2 Solid Particle Colloid 0 0 ò 5 10 15 20 0 10 12 14 16 18 20 C<sub>e</sub> (mg L<sup>-1</sup>) C<sub>e</sub> (mg L<sup>-1</sup>)

Fig. 6. Langmuir model fit of APAP adsorption onto colloid and solid particles in sediment with different temperatures.

observed from data in Table 5. In general, the value of  $\Delta G^{\circ}$ for physisorption is between -20 and 0 kJ·mol<sup>-1</sup>, and that for chemisorption is between -400 and -80 kJ·mol<sup>-1</sup> [31]. The values of  $\Delta G^{\circ}$  obtained for APAP adsorption onto solid particle in this study were between -19.698 and -22.162 kJ·mol<sup>-1</sup>, and that onto colloid were between -22.886 and -25.911 kJ·mol<sup>-1</sup>, indicating that the adsorption of APAP onto both solid particle and colloid were neither pure physisorption nor pure chemisorption, but were mainly physisorption. In addition, physisorption took less proportion in the APAP adsorption process onto colloid. The positive values of  $\Delta H^{\circ}$  further indicated that the APAP adsorption onto colloid and solid particle were endothermic in nature. The value of  $\Delta H^{\circ}$  for physisorption is between 2.1 and 20.9 kJ·mol<sup>-1</sup>, and that for chemisorption is between 80 and 200 kJ·mol<sup>-1</sup> [32]. The values of  $\Delta H^{\circ}$  obtained for APAP adsorption onto colloid and solid particle in this study were 22.091 and 16.898 kJ·mol<sup>-1</sup>, respectively, which further proves that the adsorption of APAP onto both colloid and solid particle were mainly physisorption. The positive values of  $\Delta S^{\circ}$  showed an increase in randomness at the solid/liquid interface during the APAP adsorption process onto both colloid and solid particles [33].

# Conclusions

In this study, sediment samples from a typical tributary in the mid-Weihe River were collected and a separation device was employed to separate sediment into colloid and solid particles. The acetaminophen (APAP) adsorption onto solid particle was compared with APAP adsorption onto colloid in terms of their impact on the factors of the processes (e.g., contact time, temperature, kinetic, thermodynamic characteristics), which were analyzed systematically. The following conclusions can be drawn:

1. The equilibrium time of APAP adsorption onto colloid and solid particle existed 4-fold differences, which were 12 hours and 48 hours, respectively.

- For the same initial concentration, the adsorption capacity of APAP onto colloid and solid particle at equilibrium time exhibited significant differences. The adsorption capacity of APAP onto colloid was about 28 times that of the solid particle with an initial concentration of 10.0 mg L<sup>-1</sup> at 25°C.
- The Langmuir isotherm model was more suitable for describing the adsorption behaviours of APAP onto both colloid and solid particles in sediment.
- 4. The adsorption of APAP onto colloid and solid particle in sediment were feasible and spontaneous, with entropy increasing and endothermic in nature and the adsorption capacity increasing with temperature. The mechanisms controlling APAP adsorption onto colloid and solid particle were neither pure physisorption nor pure chemisorption, but were mainly physisorption. In addition, physisorption had a lesser effect on the APAP adsorption process onto colloid.

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