JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Thermodynamics and Kinetics of *p*-Aminophenol Adsorption on Poly(aryl ether ketone) Containing Pendant Carboxyl Groups

Xiqian Li,[†] Xiao Zhou,*[,†] Jun Mu,[‡] Lijun Lu,[‡] Dachuan Han,[‡] Chunmei Lu,[‡] and Mingtai Wang[‡]

[†]Obstetrics & Gynecology, China-Japan Union Hospital, Jilin University, Changchun, 130033, P. R. China

[‡]Jilin Entry & Exit Inspection and Quarantine Bureau of China, Changchun, 130062, P. R. China

ABSTRACT: We have studied the adsorption of *p*-aminophenol on poly(aryl ether ketone) containing pendant carboxyl groups (PEK-L). The pH effect, adsorption kinetics, isotherms, and thermodynamics are investigated in batch experiments. The kinetics of the adsorption follows a pseudosecond-order model. Langmuir and Freundlich isotherms are employed to describe the adsorption process, indicating that the former fits the data better. The thermodynamic functions, $\Delta G°$, $\Delta H°$, and $\Delta S°$ are calculated. The method is applied to the determination of *p*-aminophenol in drug tablet samples, and the accuracy is assessed through recovery experiments.

INTRODUCTION

Phenols are common pollutants released into the environment during many processes. As a kind of phenol, *p*-aminophenol (PAP) is widely applied in many fields, such as medicine, sulfur and azo dyes, rubber, feeding-stuff, petroleum, and photography, etc. For instance, PAP is used for the production of paracetamol,[1] which is one of the most produced pharmaceuticals worldwide. PAP is recognized to be toxic and irritable to the eyes, skin, and respiratory system. It may increase the core body temperature in humans, and its biological half-life is long.

Much attention has been paid to explore effective methods to the analysis of PAP. During the past decades, different kinds of methods have been applied to the determination of PAP, including spectrophotometry,[1−8] liquid chromatography,[1,9,10] chemiluminescence,[11] capillary electrophoresis,[12] and various electrochemical strategies.[13−16] Among these methods, spectrophotometry is most commonly used because of its advantages of simple, rapid, and low cost of operation. However, spectrophotometric methods often suffer from the drawbacks of low sensitivity. To enhance the sensitivity, different kinds of preconcentration methods have been introduced, such as extraction,[2,3] aqueous two-phase system liquid−liquid extraction,[4] and adsorption.[5,6]

Adsorption is a popular separation/preconcentration method because it has several advantages of cost effectiveness, simple operation, and environmental friendliness.[17] Various adsorbents have been developed for the separation/preconcentration of PAP including impregnated Amberlite resin,[5] metal ferrocyanides,[6] and imprinted polymer.[14] It is of interest to develop novel effective materials for the adsorption of PAP. As an alternative, aromatic poly(ether ketone)s (PEKs) have attracted considerable attention because of their excellent chemical, physical, and mechanical properties.[18,19] Zhao et al.[19] have prepared poly(aryl ether ketone)s containing pendent carboxyl groups (PEK-L) and applied PEK-L to the adsorption of Cu, Pb, Co, Ni, and Cd. The adsorption kinetics, isotherms, and thermodynamics are examined in batch experiments in detail. PEK-L has shown significant potential for removal of the metal ions from aqueous solutions. The carboxylic groups contained in PEK-L make ion-exchange interactions possible and can be used as a preconcentration material based on this mechanism. However, our thorough survey of the literature has not found many studies applied to PEK-L as the adsorbent in other fields except Zhao et al.'s work.[19]

In the present study, PEK-L has been applied to the adsorption of PAP from aqueous solutions. Effects of various experimental parameters are investigated such as adsorbent dosage, sample pH, contact time, and experimental temperature. Adsorption−desorption studies have often been carried out to evaluate the reusability of PEK-L.

EXPERIMENTAL SECTION

Reagents. All the chemicals were of analytical grade and used as received without any purification. *p*-Aminophenol (PAP) was supplied by Aladdin Reagent (Shanghai, China). The stock solution of PAP (100 $\mu g \cdot mL^{-1}$) was prepared daily by dissolving an appropriate amount of PAP in a small volume of HCl (0.05 $mol \cdot L^{-1}$) and diluting with water to the mark. The standard stock solution was stored in a 4 °C refrigerator. PEK-L was prepared according to previous work.[19] Distilled−deionized water was used throughout the experiments.

Apparatus. A TU 1810 ultraviolet−visible spectrophotometer (Beijing Purkinje General Instruments Co., Ltd., China) was used for spectrophotometric determinations. A pHS-3C digital pH meter (Shanghai Rex Instruments Factory, China) was used for pH measurements. Deionized water was prepared by the Milli-Q SP system (Millipore, Milford, MA, USA).

Adsorption Procedures. In a typical adsorption procedure, 0.02 g of PEK-L mixed with 10 mL of PAP solution in special glass-stoppered tubes was shaken under a controlled temperature of (293 ± 1) K. After reaching the sorption equilibrium, the suspension was filtered through 0.45 μm filters, and PAP

Received: August 22, 2011
Accepted: September 29, 2011
Published: October 13, 2011

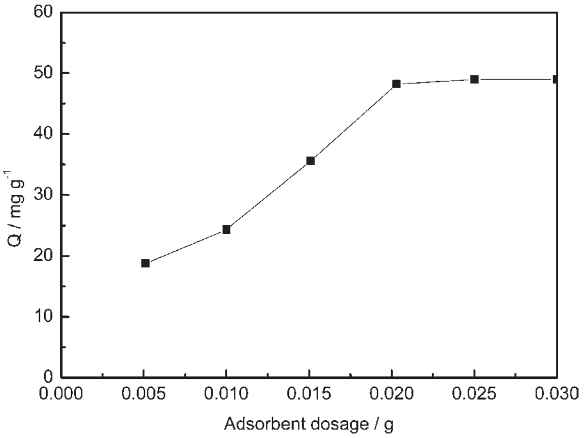

Figure 1. Effect of PEK-L dosage on the adsorption of PAP with PEK-L. Contact time = 2 h, [PAP] = 0.5 μg·mL^{-1}, pH = 2.0.

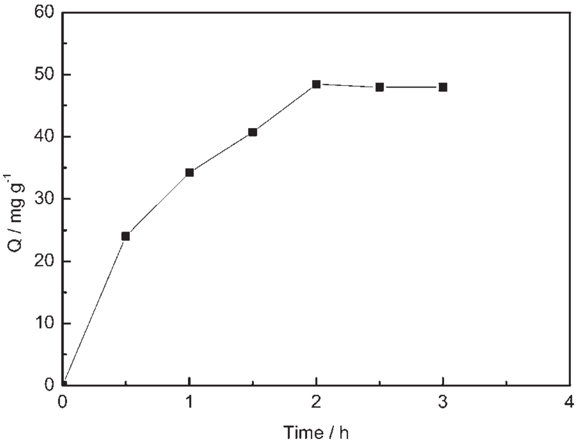

Figure 2. Effect of contact time on the adsorption of PAP with PEK-L. PEK-L dosage = 0.02 g, [PAP] = 0.5 μg·mL^{-1}, pH = 2.0.

concentration in the liquid phase was determined with spectrophotometry. The adsorption capacity of PAP was calculated as follows.

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e represent the initial and equilibrium metal ion concentrations (μg·mL^{-1}), respectively; V is the volume of the metal ion solution (mL); and m is the amount of adsorbent (mg).

Determination Procedures. Three solutions were prepared, i.e., S_1 (0.1064 mol·L^{-1} phenol solution), S_2 (1.758·10^{-4} mol·L^{-1} $FeCl_3$ solution), and S_3 (1000 mL of solution containing 5.0024 g of NaOH and 0.36 mL of NaOCl). Some amount of PAP was mixed with 1 mL of S_1, 1 mL of S_2, and 10 mL of S_3 and diluted to 50 mL with deionized water. After settled for 20 min, the concentration of PAP was determined at 632 nm.[8]

RESULTS AND DISCUSSION

Influence of PEK-L Dosage. Figure 1 shows the influence of PEK-L dosage on the adsorption of PAP in the range of (0.005 to 0.03) g when the concentration and pH of PAP are fixed. It can be seen that the adsorption capacity increases first and then keeps constant when the mass of PEK-L is higher than 0.02 g. Therefore, 0.02 g is selected in subsequent experiments.

Table 1. Kinetic Parameters for the Adsorption of PAP with PEK-L

$q_{e,exp}$	pseudofirst-order			pseudosecond-order		
mg·g^{-1}	k_1	$q_{e,cal}$	R^2	k_2	$q_{e,cal}$	R^2
0.15	0.0007	1.15	0.8458	0.35	0.06	0.9867

Influence of pH. As an amphoteric compound, PAP has a Lewis acid group (—OH) and a Lewis base group (—NH_2). The pK_{a1} and pK_{a2} values are 8.50 and 10.30, respectively.[20] The initial pH of PAP is thus a major parameter affecting the adsorption capacity. In the present study, the adsorption of PAP as a function of pH has been studied over pH range of 1.0 to 12.0. The desired pH was maintained by dilute HCl or NaOH solution. The adsorption capacity decreases with increasing pH values. A possible reason may be as follows. Pendent carboxyl groups are contained in PEK-L, implying that the interactions between PEK-L and PAP occur at —NH_2 functional groups of PAP.[2] When the sample pH of PAP decreases, the amount of —COOH groups increases, leading to high adsorption capacities. In the present work, a sample pH of 2.0 of PAP is chosen.

Adsorption Kinetics. Figure 2 shows the effect of contact time on the adsorption. The adsorption capacity increases significantly until the contact time reaches 2 h. Further increase of contact time cannot lead to stronger adsorption capacity. Therefore, 2 h is selected as the contact time in subsequent experiments.

Adsorption kinetics has been investigated to examine the controlling mechanism for the adsorption process. The pseudofirst-order and pseudosecond-order kinetic models are employed to fit the kinetic adsorption data. The two models can be expressed as follows

$$\text{Pseudo first-order}: \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

$$\text{Pseudo second-order}: \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{3}$$

where q_t and q_e are the amounts of PAP adsorbed at time t and at equilibrium (mg·g^{-1}), respectively. k_1 (min^{-1}) and k_2 (g·mg^{-1}·min^{-1}) are the rate constant of the pseudofirst-order and pseudosecond-order sorption process.

Kinetics parameters with the pseudofirst-order and pseudosecond-order have been investigated for the adsorption of PAP on PEK-L. Results are summarized in Table 1. Obviously, the calculated adsorption capacity (q_{cal}) is close to the experimental adsorption capacity (q_{exp}) when expressed with the pseudosecond-order model. The correlation coefficient value of the pseudosecond-order model is higher than that of the pseudofirst-order model. Therefore, the pseudosecond-order model is suitable to model the adsorption curve of PAP on PEK-L. It is interesting to note that in Zhao et al.'s work[19] the adsorption of transitional metal ions on PEK-L can also be well described by the pseudosencond-order kinetic model. This implies that the rate-limiting step of the adsorption process on PEK-L is chemical sorption.

Adsorption Isotherms. The equilibrium adsorption isotherm is fundamental for describing the interactive behavior between the

Table 2. Parameters of Langmuir and Freundlich Isotherms

Langmuir			Freundlich		
$q_{\max}$/ mg·g^{-1}	b/ L·mg^{-1}	R^2	n	k	R^2
0.30	0.43	0.5186	0.78	0.19	0.9730

solution and the adsorbent. To achieve this goal, the adsorption data are analyzed with Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes that the adsorption occurs at specific homogeneous adsorption sites within the adsorbent. Monolayer adsorption and maximum adsorption occur when adsorbed molecules on the surface of the adsorbent form a saturated layer. The expression for the Langmuir isotherm is as follows.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{4}$$

where $q_{\max}$ represents the maximum adsorption capacity of adsorbents (mg·g^{-1}) and b is the Langmuir constant (L·mg^{-1}) related to the affinity of binding sites and is a measure of the energy of adsorption.

The Freundlich isotherm expresses adsorption at multilayer and on an energetically heterogeneous surface. This isotherm can be expressed as

$$\log q_e = \frac{1}{n} \log C_e + \log K \tag{5}$$

where k and n are empirical constants that indicate the relative sorption capacity and sorption intensity, respectively.

Table 2 shows the parameters of the Langmuir and Freundlich isotherms. The correlation coefficient values with the Langmuir model (0.5186) are lower than that with the Freundlich model (0.9730). This indicates that the latter fits the adsorption data better than the former. The reason may be because the Langmuir model assumes that the surface of the sorbent can accommodate only a monolayer of the sorbate ions and no interaction between the sorbed species. The freundlich isotherm model does not have any restriction on the sorption capacity of the sorbent and is more appropriate in situations where the sorption sites possess a heterogeneous nature.

Adsorption Thermodynamics. Thermodynamic parameters are evaluated since they provide in-depth information on inherent energetic changes that is associated with adsorption. The Gibbs energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes are calculated with the following equations.

$$K_d = \frac{q_e}{C_e} \tag{6}$$

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{7}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

where K_d denotes the distribution coefficient. At 293 K, $\Delta G°$, $\Delta H°$, and $\Delta S°$ are determined as −5.144 kJ·mol^{-1}, 11.872 kJ·mol^{-1}, and 0.0226 kJ·mol^{-1}·K^{-1}, respectively.

$\Delta H°$ is positive, indicating that the adsorption procedure of PAP with PEK-L is endothermically driven. When $\Delta H°$ is in the range of (5 to 10) kJ·mol^{-1}, the adsorption mechanism is physiosorption; i.e., the bond between adsorbent and adsorbate is van der Waals interactions. When $\Delta H°$ is in the range of (30 to 70) kJ·mol^{-1}, the adsorption belongs to chemisorption; i.e., a chemical bond is formed between the adsorbate and the surface. In the present system, the $\Delta H°$ value demonstrates that neither fully physical nor fully chemical and some complex mechanism dictates the adsorption process.

Table 3. Thermodynamic Parameters

T	$\Delta G°$	$\Delta H°$	$\Delta S°$
K	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}·K^{-1}
293	−5.144	11.872	0.0226
303	−5.165		
313	−4.756		
323	−4.612		
333	−4.272		
343	−4.112		

Table 4. Determination of PAP in Paracetamol Tablets (n = 5)

		0.5 μg·mL^{-1} spiked		1.0 μg·mL^{-1} spiked	
sample	measured (μg·mL^{-1})	found (μg·mL^{-1})	recovery	found (μg·mL^{-1})	recovery
1	0.05	0.52	93.9	1.00	95.2
2	0.04	0.51	93.9	0.99	95.2
3	0.04	0.49	91.3	0.98	93.9
4	0.02	0.48	91.3	0.98	95.2
5	0.02	0.49	93.9	0.96	93.9
6	0.01	0.47	91.3	0.95	93.9
7	0.01	0.49	96.5	0.99	97.8

$\Delta S°$ is also positive, which implies that the degree of freedom increases at the solid−liquid interface during the adsorption process. It also suggests that there are some structural changes in both the adsorbate and adsorbent. The negative value of $\Delta G°$ indicates the sorption process is spontaneous. In addition, it can be concluded from Table 3 that the $\Delta G°$ increases with increasing experimental temperature. As is well-known, a more negative $\Delta G°$ implies a greater driving force of adsorption, resulting in higher adsorption capacity.

Reusability of PEK-L for the Adsorption of PAP. It is important for an effective adsorbent to be easily desorbed without destroying the adsorbent. Methanol is employed as the desorption agent. Results of the adsorption−desorption processes for three cycles indicate that the adsorption of PAP on PEK-L is not significantly changed and that the elution ratios are above 80 %. Therefore, PEK-L is regenerable and can be used several times.

Sample Analysis. PEK-L has been employed for the adsorption and desorption of PAP in several commercial paracetamol tablets. All samples are spiked with standard stock solution of PAP at two concentration levels and then analyzed five times (n = 5). Results are shown in Table 4. Recovery values within the range of 91.3 % to 97.8 % have been obtained, indicating that the present method is free from interferences when used for the determination of PAP in tablets containing paracetamol.

CONCLUSIONS

In this study, poly(aryl ether ketone) containing pendant carboxyl groups (PEK-L) has been applied to the adsorption of *p*-aminophenol. Experimental parameters affecting the adsorption capacity have been studied in detail, including adsorbent dosage and pH. The adsorption kinetics follows the pseudosecond-order rate model very well. The Freundlich isotherm fits the adsorption data better than the Langmuir isotherm. The adsorption process is spontaneous and endothermic in nature. It is probably because the adsorption process is neither a fully physical nor fully chemical mechanism but some complex mechanism. No significant variation on the adsorption capacity is verified after three cycles of adsorption−desorption processes. PEK-L is a promising material when used for the adsorption and determination of *p*-aminophenol in practice.

AUTHOR INFORMATION

Corresponding Author

*Tel./Fax: 86 431 87607208. E-mail: zhouxiao100@hotmail.com (X. Zhou).

REFERENCES

(1) Peng, D. M.; Huang, K. L.; Liu, Y. F.; Liu, A. X. Determination of *p*-aminophenol in compound tramadol hydrochloride tablets by colorimetry and HPLC. *Chin. J. Pharm.* **2006**, *37*, 488–489.

(2) Yang, Y. Y.; Liu, Z. Y.; Dai, Y. Y. Extraction of *p*-aminophenol based on chemical complexation. *J. Chem. Eng. Chin. Univ.* **1997**, *11*, 355–360.

(3) Wei, F. Y.; Wei, H. Y.; Cui, P.; Qing, W. X. Studies on complexation extraction mechanism of *p*-aminophenol with tributyl phosphate. *Chem. Eng. (China)* **2006**, *34*, 8–11.

(4) Rodrigues, G. D.; Lemos, L. R.; Patrício, P. R.; Silva, L. H. M.; Silva, M. C. H. Aqueous two-phase systems: A new approach for the determination of *p*-aminophenol. *J. Hazard. Mater.* **2011**, *192*, 292–298.

(5) Filik, H.; Hayvali, M.; Kilic, E.; Apak, R.; Aksu, D.; Yanaz, Z.; Cengel, T. Development of an optical fibre reflectance sensor for *p*-aminophenol detection based on immobilised bis-8-hydroxyquinoline. *Talanta* **2008**, *77*, 103–109.

(6) Tewari, B. B.; Boodhoo, M. Removal of *p*-aminophenol and *p*-nitrophenol from aqueous solution through adsorption on antimony, cadmium, and zirconium ferrocyanides. *J. Colloid Interface Sci.* **2005**, *289*, 328–332.

(7) Bloomfield, M. S. A sensitive and rapid assay for 4-aminophenol in paracetamol drug and tablet formulation, by flow injection analysis with spectrophotometric detection. *Talanta* **2002**, *58*, 1301–1310.

(8) Xue, G. R.; Jia, W. P.; Zhang, D. S.; Zhang, X. L. Determination of *p*-aminophenol with spectrophotometry. *J. Shanxi Teacher's Univ.* **1994**, *8*, 33–35.

(9) Crevar, M.; Ivkovic, B.; Vladimirov, S.; Kuntic, V.; Vujic, Z. Statistical optimization of reverse phase high performance liquid chromatography for the analysis of caffeine paracetamol and its degradation product *p*-aminophenol. *Acta Chim. Slov.* **2008**, *55*, 665–670.

(10) Wyszecka-Kaszuba, E.; Warowna-Grzeskiewicz, M.; Fijalek, Z. Determination of 4-aminophenol impurities in multicomponent analgesic preparations by HPLC with amperometric detection. *J. Pharm. Biomed. Anal.* **2003**, *32*, 1081–1086.

(11) Bosch, M. E.; Sánchez, A. J. R.; Rojas, F. S.; Ojeda, C. B. Determination of paracetamol: Historical evolution. *J. Pharm. Biomed. Anal.* **2006**, *42*, 291–321.

(12) Chu, Q.; Jiang, L.; Tian, X.; Ye, J. Rapid determination of acetaminophen and *p*-aminophenol in pharmaceutical formulations using miniaturized capillary electrophoresis with amperometric detection. *Anal. Chim. Acta* **2008**, *606*, 246–251.

(13) Safavi, A.; Maleki, N.; Moradlou, O. A selective and sensitive method for simultaneous determination of traces of paracetamol and *p*-aminophenol in pharmaceuticals using carbon ionic liquid electrode. *Electroanalysis* **2008**, *20*, 2158–2162.

(14) Santos, W. J. R.; Lima, P. R.; Tarley, C. R. T.; Kubota, L. T. A catalytically active molecularly imprinted polymer that mimics peroxidase based on hemin: application to the determination of *p*-aminophenol. *Anal. Bioanal. Chem.* **2007**, *389*, 1919–1929.

(15) Lamas-Ardisana, P. J.; Queipo, P.; Fanjul-Bolado, P.; Costa-Garcia, A. Multiwalled carbon nanotube modified screen-printed electrodes for the detection of *p*-aminophenol: Optimisation and application in alkaline phosphatase-based assays. *Anal. Chim. Acta* **2008**, *615*, 30–38.

(16) Ensafi, A. A.; Dadkhah-Tehrani, S.; Karimi-Maleh, H. A voltammetric sensor for the simultaneous determination of L-cysteine and tryptophan using a *p*-aminophenol-multiwall carbon nanotube paste electrode. *Anal. Sci.* **2011**, *27*, 409–414.

(17) Zhao, X. W.; Jia, Q.; Song, N. Z.; Zhou, W. H.; Li, Y. S. Adsorption of Pb(II) from an aqueous solution by titanium dioxide/carbon nanotube nanocomposites: kinetics, thermodynamics, and isotherms. *J. Chem. Eng. Data* **2010**, *55*, 4428–4433.

(18) Cai, M.; Zhu, M.; Xiao, F.; Ding, N.; Song, C. Synthesis of copolymers of poly(ether sulfone ether ketone ketone) and poly(ether ketone diphenyl ketone ether ketone ketone) by electrophilic Friedel-Crafts solution polycondensation. *Polym. Adv. Technol.* **2011**, *22*, 254–261.

(19) Zhao, X. W.; Zhang, G.; Jia, Q.; Zhao, C. J.; Zhou, W. H.; Li, W. J. Adsorption of Cu(II), Pb(II), Co(II), Ni(II), and Cd(II) from aqueous solution by poly(aryl ether ketone) containing pendant carboxyl groups (PEK-L): Equilibrium, kinetics, and thermodynamics. *Chem. Eng. J.* **2011**, *171*, 152–158.

(20) Dean, J. A. *Lange's Handbook of Chemistry*; Science Press: Australia, 1991; pp 5−49.