

## Adsorption Characteristics of Tannic Acid onto the Novel Protonated Palygorskite/Chitosan Resin Microspheres

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**ABSTRACT:** Novel protonated palygorskite/chitosan resin microspheres (p-PCRM) were prepared and applied as adsorbents for the removal of tannic acid (TA) from aqueous solution. The effects of palygorskite (PAL) content, the initial pH value of the TA solution, and contact time and temperature on adsorption capacity of the microspheres were investigated. The adsorption process was found to be pH dependant with an optimum activity at pH 8.0. In comparison with protonated chitosan microspheres ( $224 \text{ mg g}^{-1}$ ), the p-PCRM with 20 wt % PAL content exhibited higher adsorption capacity ( $455 \text{ mg g}^{-1}$ ) for TA at the same adsorption conditions. This may be attributed to the hydrogen bonding between adsorbents and adsorbates, and the porous structure formed by the introduction of PAL, which were confirmed by Fourier transform infrared and the pore parameters analysis. The study of adsorption kinetics and isotherms showed that the sorption processes were better fitted by pseudo-second-order equation and the Langmuir equation, respectively. Furthermore, the desorption study implied that the p-PCRM were recyclable when 0.1M HCl was used as eluents. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** adsorption; palygorskite; chitosan; resin microspheres; tannic acid

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### INTRODUCTION

Nature organic matter (NOM) is the main resource of the organic contaminants in surface and ground water, among which phenolics are considered as typical pollutants of NOM. As a water-soluble polyphenolic compound, tannic acid (TA, Figure 1) in the deprotonated form is a naturally occurring organic substance formed by the decomposition of organic matter. It is often used as a surrogate of NOM<sup>1</sup> for its definite structure, relatively high molecular weight (average  $1700 \text{ g mol}^{-1}$ ), and major groups including carboxylic acid, phenolic acid, alcohol acid, aldehyde acid, and methoxyl, which are similar to that of NOM. The structure of TA is shown in Figure 1. TA can create toxicity for aquatic organisms such as algae, phytoplankton, fish, and invertebrates. Moreover, it is the precursor of carcinogenic disinfection byproducts in drinking water.<sup>2</sup> Therefore, the removal of TA from effluents is of practical importance and interest.

Various techniques, such as chemical oxidation,<sup>3</sup> adsorption,<sup>4</sup> electrochemical,<sup>5</sup> ultrafiltration,<sup>6</sup> and biological methods,<sup>7</sup> have been reported to remove TA. Among them, adsorption is gaining prominence as a separation process due to its simple treatment, high efficiency, and optional adsorbents. A number of

adsorbents, such as activated carbons,<sup>8</sup> zirconium pillared clay,<sup>9</sup> cationic surfactant-modified bentonite clay,<sup>10</sup> and resin,<sup>11</sup> have been used for TA. Except for adsorption properties, cost effectiveness, operative efficacy, and regenerative availability are the main criteria for choosing an adsorbent. Taking these criteria into consideration, chitosan and clay-based hybrid adsorbents have recently attracted more and more attention. As a biodegradable and natural cationic biopolymer, chitosan is the *N*-deacetylated derivative of chitin, the second most abundant polymer in nature. Ample amino and hydroxyl functional groups on chitosan chain can endow it with many unique physical and chemical properties, of which its absorbability is a hot research topic. It has been reported that the efficient coordination or chelation of chitosan with the target molecules can be used to remove transition metals,<sup>12,13</sup> reactive dyes,<sup>14,15</sup> and phenolic compounds.<sup>16</sup> However, poor mechanical property and low specific gravity of chitosan make them rather inconvenient in practical applications. The physical nature of chitosan can be improved if it is composited with clay minerals.

Recently, studies concerned with adsorption of TA on clay, chitosan, or clay/chitosan composites have been reported in

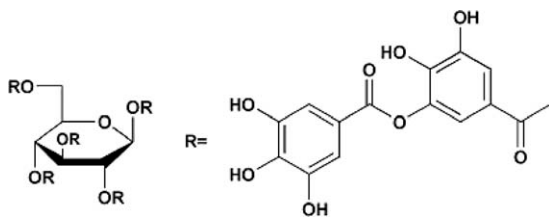


Figure 1. Structure of tannic acid.

literature. Huang et al. reported an organically modified attapulgite clay that has selective absorbability for tannin from flavonoids.<sup>17</sup> Chang and Juang prepared chitosan beads and investigated its adsorptive property for TA,<sup>18</sup> and they also studied the adsorption capacities of the activated clay/chitosan composite beads for TA, humic acid, and dyes.<sup>19</sup> An and Dultz studied TA adsorption onto chitosan-montmorillonite.<sup>20</sup> However, adsorptive properties of protonated palygorskite/chitosan resin microspheres (p-PCRM) for TA, as reported in this article, are totally original. Palygorskite (PAL) is a kind of natural hydrous clay mineral with fibrous rod-like microstructure. The nanorod crystal of PAL, about 20–40 nm in diameter and 1–5  $\mu\text{m}$  in length,<sup>21</sup> would be a reinforced material for chitosan because of its micron-filled and nano-reinforcement effect. In addition, PAL has also been used in the treatment of wastewater<sup>22</sup> and the removal of heavy metals<sup>23,24</sup> for its large specific surface area and moderate cationic exchange capacity. As an inexpensive natural nano-mineral, PAL acts as a component of hybrid materials and has wide prospects of applications in adsorbents.

In this work, a novel PCRM was prepared with emulsion cross-linking technique to obtain micron uniform-sized adsorbents which can enhance the acid resistant, improve the adsorptive capability and facilitate the separation of the adsorbents from solutions. The thus-prepared resin microspheres was further protonated to turn  $-\text{NH}_2$  on chitosan chain into  $-\text{NH}_3^+$ , which can be effectively used for TA removal. The factors influencing the adsorption capacity of the p-PCRM, such as the initial pH value of the TA solutions, contact time and temperature, and PAL content (wt %) were investigated. The nature of the adsorption process with respect to its kinetic and isotherm aspects was also evaluated, and desorption of the microspheres were investigated.

## EXPERIMENTAL

### Materials

Chitosan powder was purchased from Zhejiang Gold-Shell Biochemicals Co., China, with a deacetylation degree of about 86% and average molecular weight of  $60 \times 10^4$ . PAL (supplied by Jiangsu Jiuchuan Clay Technology Development Co., China) was activated with 37% hydrochloric acid for 24 h at room temperature, followed by washing with distilled water until pH was achieved to 6, dried at 105°C for 8 h, and then milled through a 200-mesh screen before use. Other agents used were obtained from Chinese Chemicals Company and were of analytical grade. All solutions were prepared with distilled water.

### Preparation of p-PCRM

Chitosan (2.5 g) and PAL (0.5 g) were mixed and dissolved in 1% (v/v) acetic acid solution (50 mL). The mixture was agitated

at 40°C with a disperser (IKA, Ultra-Turrax T18 basic) at 12,000 rpm for 0.5 h to obtain the homogeneously viscous composite.

PCRM was prepared according to the following procedure. The above viscous composite was emulsified by mechanical stirring (400 rpm) in 75 mL liquid paraffin containing 0.12 g span-80 at the room temperature. After 30 min stirring, the obtained microspheres were solidified by crosslinking with 5 mL formaldehyde, and the mixture was stirred at 60°C for 1 h more. Then, 4 mL glutaraldehyde was added for crosslinking for another 3 h at 70°C while the pH of the system was adjusted to 10. Finally, the microspheres were collected, extensively rinsed with petroleum ether and ethanol, respectively, and treated with 1M HCl solution for 2 h at room temperature for protonation of microspheres. The microspheres were washed with distilled water to neutral pH, dried at 60°C. A series of p-PCRM with different weight ratio of CS to PAL were obtained. Protonated chitosan resin microspheres (p-CRM) were prepared following the same protocol except for the addition of PAL. All samples were sieved through a 40 mesh before use.

### Adsorption Experiments

The adsorption experiments of sample for TA were carried out by using the batch technique. Typically, 0.10 g of adsorbent and 25.0 mL of TA solution were mixed and shaken in a thermostatic shaker bath (SHY-2A) at 100 rpm and desired temperature for a given time, and then, the adsorbent was filtrated from solution. The pH value of initial solutions was adjusted with 0.1M HCl or NaOH solution. The PAL content of the p-PCRM was fixed at 20 wt %. The effect of pH on the adsorption of TA on adsorbent was studied in the range from pH 4.0 to 9.0 at 30°C. Adsorption time of 12 h was set to allow attainment of equilibrium at constant temperatures. For kinetic and pH study, 100 mg  $\text{L}^{-1}$  was chosen as the initial concentration of TA solution. The isotherm experiments were performed at different temperatures (20°C, 30°C, and 40°C) when the initial concentrations of TA was varied from 400 to 1600 mg  $\text{L}^{-1}$  at fixed pH 8.0.

The concentration of TA was measured by an UV–vis spectrophotometer (Unico, UV-2000) at wavelength 276 nm. The adsorption capacity of the adsorbent was calculated through the following equation:

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

where  $q_e$  (mg  $\text{g}^{-1}$ ) is the adsorption capacity at equilibrium, and  $C_0$  and  $C_e$  are the initial and equilibrium concentration of TA solution (mg  $\text{mL}^{-1}$ ), respectively.  $m$  (g) is the mass of the adsorbent used and  $V$  (mL) is the volume of TA solution. All assays were carried out in triplicate and only mean values used.

### Desorption and Regeneration Studies

After the equilibrium study at an initial TA concentration of 1 mg  $\text{mL}^{-1}$ , the TA-loaded sorbents were collected by filtration and washing thoroughly with deionized water. The loaded sorbents were transferred to 0.10 mol  $\text{L}^{-1}$  HCl solution and shaken at 100 rpm for 24 h at 30°C to remove TA completely, and then

**Table I.** Effect of Palygorskite on General Properties of the p-PCRM

General parameters	Adsorbent	
	p-PCRM <sup>a</sup>	p-CRM
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	13.42	9.89
True density (g mL <sup>-1</sup> )	0.74	0.86
Porosity (%)	82.8	62.3
Degree of swelling (%)	35.1	9.1
Water content (%)	82.9	63.8

<sup>a</sup>p-PCRM: the content of PAL is 20 wt %.

filtered and washed with water. The regenerated sorbents was used in adsorption experiment again, and the process was repeated for three times. The concentration of TA solution was measured and desorption ratio of TA from the sorbents was evaluated by the following equation.

$$\text{Desorption ratio(\%)} = \frac{m_D}{m_A} \times 100 \quad (2)$$

where  $m_D$  (mg) and  $m_A$  (mg) is the amounts of desorbed and adsorbed TA, respectively.

### Characterization

The Fourier transform infrared (FTIR) spectra of PCRM, p-PCRM before, and after TA adsorption were recorded by using a Nicolet FTIR 360 spectrophotometer, and the sample and KBr were pressed to form a tablet. The surface area of the samples was obtained from the N<sub>2</sub>/77 K adsorption isotherms by applying the BET method with a Micromeritics Tristar II 3020 surface area and porosity analyzer.

## RESULTS AND DISCUSSION

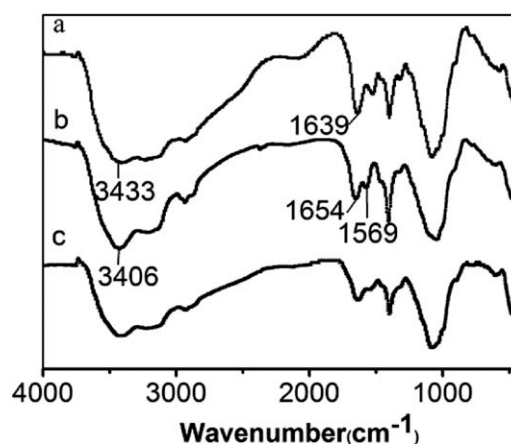
### Characteristics of p-PCRM

Pore parameters such as true density, porosity, water content, and the degree of swelling are the important index of absorbability for the resin microspheres, which were measured according to Bai and Li.<sup>25</sup> The effect of PAL on the parameters of p-PCRM were compared with that of p-CRM and shown in Table I. The porosity and the specific surface area of the composite microspheres increase evidently from 62.3, 9.89 to 82.8% and 13.42 m<sup>2</sup> g<sup>-1</sup>, respectively, which indicate that certain amounts of PAL is beneficial to the expansion of the polymer network and the generation of the porous microstructure, thus accordingly lead to the less true density of p-PCRM (0.74 g mL<sup>-1</sup>) than that of p-CRM (0.86 g mL<sup>-1</sup>). It is well known that the swelling behavior and water content of the microspheres are depended on or even proportional to the number of free active groups, such as —NH<sub>2</sub>, —OH group in the p-PCRM. The fact that higher water content and degree of swelling for p-PCRM (82.9 and 35.1%, respectively) than those of p-CRM (63.8 and 9.1%, respectively) imply the rich loading of active groups endowed by addition of PAL. It can be expected that the adsorption capacity of the p-PCRM would change in some extent due to the increased active sites and the larger specific surface area existing in the particles.

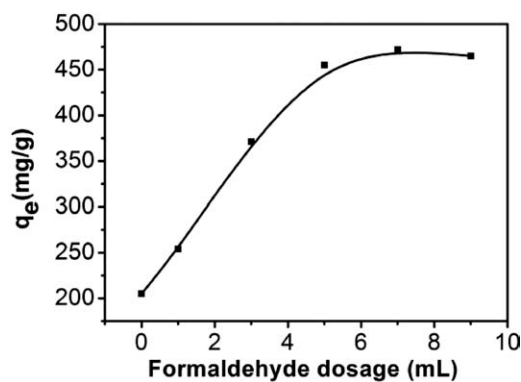
The FTIR spectra of the PCRM with 20 wt % PAL before and after protonated is shown in Figure 2(a,b), respectively. The broad band around 3433 cm<sup>-1</sup>, corresponding to the characteristic of —NH<sub>2</sub> stretching vibration in PCRM, enhanced and shifts to lower frequencies (3406 cm<sup>-1</sup>) in p-PCRM. The absorb band at 1639 cm<sup>-1</sup> attributed to C=N stretching vibration is the characteristic bond of schiff's base formed by the crosslinking reaction between —NH<sub>2</sub> of chitosan and —CHO of formaldehyde, which was covered by the —NH<sub>2</sub> bending vibration (1654 cm<sup>-1</sup>) in p-PCRM. In addition, the new bands at 1569 cm<sup>-1</sup> assigned to —NH<sub>3</sub><sup>+</sup> deformation vibration is also observed in protonated resins. The results suggested that a certain amount of free amino groups of PCRM could be obtained after being protonated. After TA adsorption, the band of —NH<sub>3</sub><sup>+</sup> at 1569 cm<sup>-1</sup> becomes weakened and the —NH<sub>2</sub> stretching band around 3406 cm<sup>-1</sup> becomes slightly broadened in Figure 2(c). These may be taken as an indication of hydrogen bonding between the amine and the negatively charged TA during the adsorption process. These results further confirm the amino groups of PCRM as potential active binding sites for adsorption of TA molecules.

### Effect of Crosslinking Agent

The dosage of crosslinking agent is the key factor, which affects the absorbability and mechanical property of the crosslinked resins. Formaldehyde, the precrosslinking agent in the reaction, can turn the chitosan droplets in acetate solution into gel microspheres. The thus-obtained microspheres in turn crosslinked with glutaraldehyde in alkaline solution, and then treated with acid to remove precrosslinking agent. Therefore, formaldehyde also acts as protective agent for amino groups from crosslinking with glutaraldehyde in some degree, for the crosslinking amino group, i.e., schiff's base, involved in chemical linkages is not available for adsorption. Figure 3 shows the relationship between the dose of formaldehyde and the adsorptive ability of the p-PCRM. It is observed that the adsorption capacity of p-PCRM increases with increasing the dosage of formaldehyde until a maximum and then decreases with an increase in formaldehyde dose. The maximum adsorption of p-PCRM for TA appears at the dosage of formaldehyde 5–7 mL. The increased



**Figure 2.** FTIR spectra of PCRM (a), p-PCRM before (b), and after (c) TA adsorption.

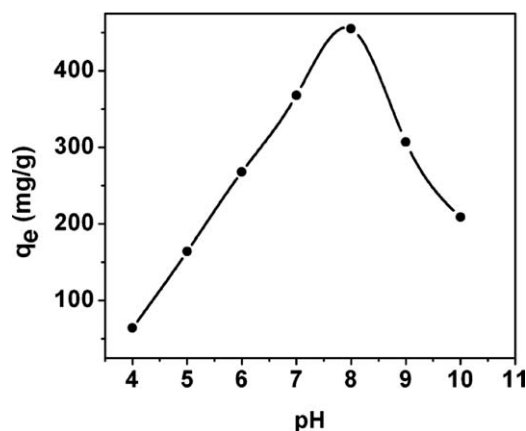


**Figure 3.** Effect of the formaldehyde dosage on the adsorbability of the p-PCRM (glutaraldehyde dosage 4 mL, pH of initial solution 8.0).

adsorbability of p-PCRM with the increasing dosage of formaldehyde may be due to the increasing free amino groups of the PCRM protected by formaldehyde. However, the further increasing dosage of precrosslinking agent will cause to the decreasing of the mechanical property and acid resistance of the microspheres for the lower crosslinking density. The crosslinking mechanism is shown in Scheme 1.

### Effect of pH

The TA removal from solution is highly dependent on the pH of the solution, which affects the dissociation degree of TA. The effect of pH value of the original solution on adsorption capacity of p-PCRM was investigated and shown in Figure 4. In the tested pH range, TA is removed more effectively by the p-PCRM at around pH 8.0 and decreases on either sides of pH

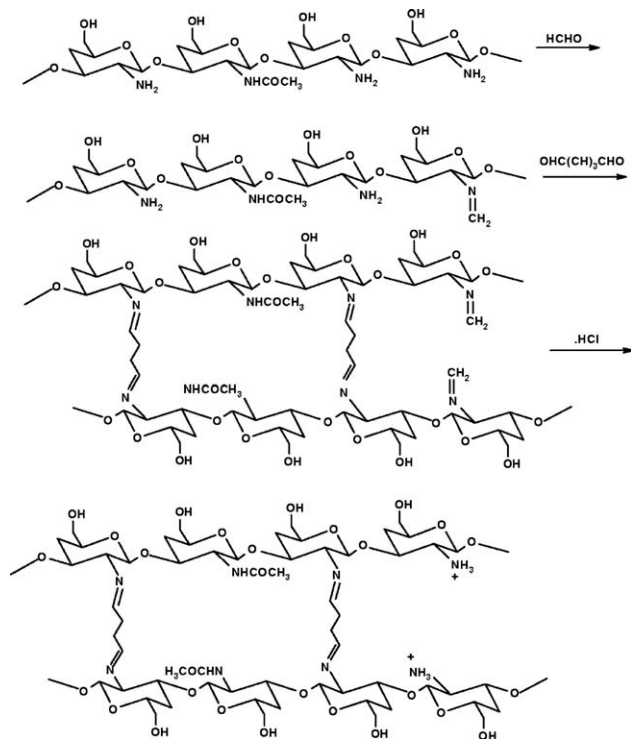


**Figure 4.** Effect of pH on adsorption capacity of p-PCRM for TA.

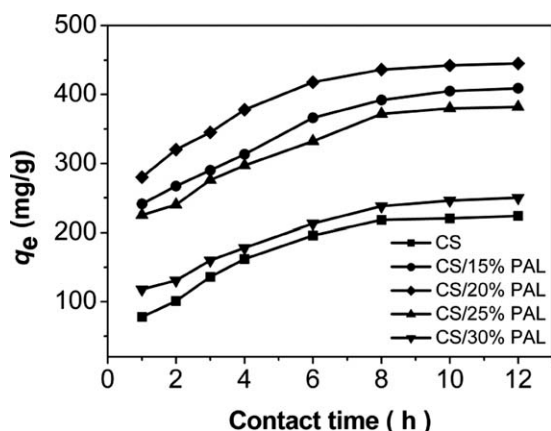
8.0. According to Ref. 18, TA occurs as a molecular form below pH 4.0, which can be assumed that the adsorbability of this unpolar organic compound is low on p-PCRM with  $-\text{NH}_3^+$  loaded. In the pH range from 4.0 to 8.0, the dissociation degree of TA increases and so does the concentration of negatively charged anions in solution. Therefore, the increased sorption ability of p-PCRM may be attributed to the enhanced hydrogen bonding of electrostatic adsorption between the negatively charged TA and positively charged p-PCRM, which is in good agreement with the results obtained from Figure 4. The maximum adsorption capacity for p-PCRM ( $455 \text{ mg g}^{-1}$ ) appears at pH 8.0 due to the completely dissociation of TA at this pH, whereas the PCRM was only  $75 \text{ mg g}^{-1}$ . This fact clearly indicates that the  $-\text{NH}_3^+$  groups of p-PCRM are responsible for the higher adsorption capacity than that of the  $-\text{NH}_2$  groups of PCRM. With the increase of pH value, the concentration of hydroxide ions in the solution accordingly increases. Thus, the competition between  $\text{OH}^-$  and TA anions for positively charged adsorption sites is the main reason for the decreased adsorption capacity. Similar findings have been reported by Viswanathan et al.<sup>26</sup> for fluoride adsorption on protonated chitosan beads.

### Effect of PAL Content

It is obvious that PAL content is an important factor influencing adsorbability of the p-PCRM. The influence of PAL content on adsorption capacity of the p-PCRM is shown in Figure 5. As it can be seen from Figure 5, the adsorption capacity of the p-PCRM increased from 224 to  $455 \text{ mg g}^{-1}$  with the increase of the PAL content from 0 to 20 wt %. According to the above investigation, the introduced PAL shows the pore-forming effect on the microspheres. This loose and porous structure may offer more adsorption sites and surface area for adsorbent and, thus, further increase the adsorbability. On the other hand, the improved network of the p-PCRM formed between  $-\text{OH}$  groups in PAL and  $-\text{NH}_2$  or  $-\text{OH}$  groups of CS is convenient for the penetration of TA molecules. The further increase of PAL ratio from 20% to 30% results in an evident decrease of the adsorption capacity. The main reason may be due to the following facts: (1) the lower hydrophilicity of PAL than that of CS; (2) the minimized network space caused by the decreased elasticity of the p-PCRM for macromolecular TA entering.



**Scheme 1.** Mechanism of crosslinking reaction.



**Figure 5.** Effect of PAL content on adsorption capacity of p-PCRM for TA (initial TA concentration, 1 mg mL<sup>-1</sup> at 30°C).

### Adsorption Isotherms

The interactive behavior between adsorbate and adsorbent can be described by different isotherm models, of which Langmuir and Freundlich isotherms are the most frequently used ones. The Langmuir isotherm model assumes monolayer coverage of adsorbate on a homogeneous adsorbent surface. It assumes that the adsorbed molecules have no interaction on the surface of the solid and the adsorption will take place only at specific site on the adsorbent. The model can be represented by the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (3)$$

where  $C_e$  is the equilibrium concentration (mg L<sup>-1</sup>),  $q_e$  is the amount adsorbed at equilibrium (mg g<sup>-1</sup>),  $q_m$  (mg g<sup>-1</sup>) and  $b$  (L mg<sup>-1</sup>) are Langmuir isotherm coefficients related to the maximum adsorption capacity of the adsorbent and the energy of adsorption, respectively.

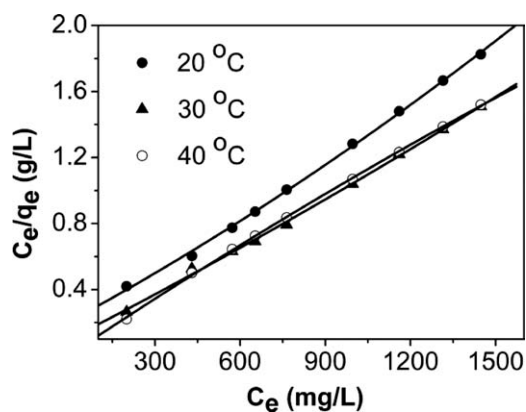
The Freundlich isotherm model is an empirical equation used to describe the multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions among adsorbed molecules.<sup>27</sup> A linear form of Freundlich equation is

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (4)$$

where  $K_f$  is the Freundlich isotherm constant (L g<sup>-1</sup>) and  $1/n$  (dimensionless) is the heterogeneity factor. The Langmuir and Freundlich parameters obtained from the  $C_e/q_e$  versus  $C_e$  (Figure 6) and  $\ln q_e$  versus  $\ln C_e$  were listed in Table II.

**Table II.** Constants for Equilibrium Isotherm Models

Temperature (°C)	Langmuir equation				Freundlich equation		
	$q_m$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )	$R_L$	$R^2$	$K_f$ (L g <sup>-1</sup> )	$1/n$	$R^2$
20	847	0.0134	0.0694	0.993	0.3568	0.8712	0.942
30	1000	0.0155	0.0606	0.998	0.4603	0.8411	0.931
40	938	0.0147	0.0637	0.996	0.2896	0.8645	0.923



**Figure 6.** Langmuir plot for the adsorption of TA onto p-PCRM at different temperatures.

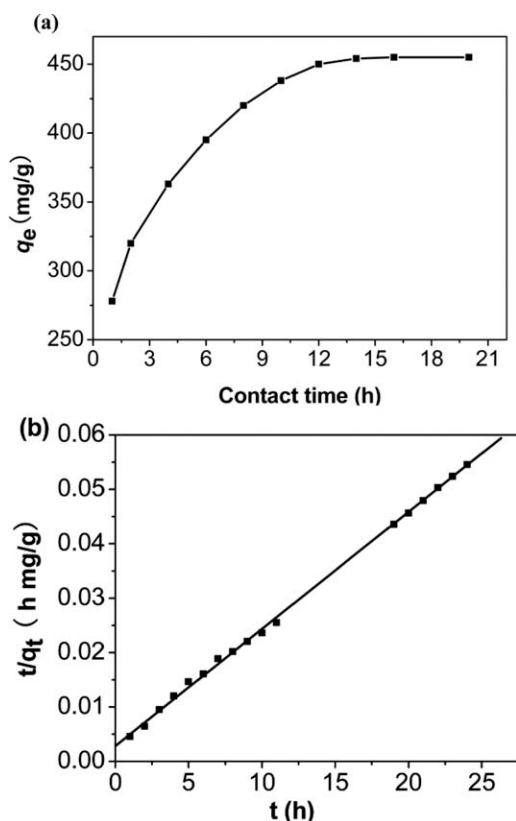
The higher correlation coefficient ( $R^2$ ) given in Table II indicates that the Langmuir isotherm fits the adsorption data better than the Freundlich isotherm. This result suggests the adsorption process takes place among the functional groups, such as  $-NH_2$  and  $-OH$  groups, on the surface of the p-PCRM, which is considered as monolayer adsorption. The maximum value of  $q_m$  at 30°C indicates that the TA adsorption process is most effective at 30°C. To find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter,  $R_L$ , which is defined by the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where  $b$  is the Langmuir isotherm constant and  $C_0$  is the initial concentration of TA (mg L<sup>-1</sup>).  $R_L$  values within the range  $0 < R_L < 1$  indicate favorable adsorption. The values of  $R_L$  between 0.0606 and 0.0694 at different temperature indicate favorable adsorption of TA on p-PCRM.

### Adsorption Kinetics

Contact time is an important parameter to reflect the adsorption kinetics of an adsorbent for a given initial concentration of the adsorbate. Figure 7(a) shows the effect of contact time on adsorption of p-PCRM for TA. It is clear that  $q_e$  continues to increase at a relatively low speed with contact time till equilibrium is reached at 12 h and then remains constant. The TA adsorption versus time curves are smooth, continuous, and leading to saturation, suggesting the possible monolayer coverage of TA on the surface of the adsorbent.<sup>10</sup>



**Figure 7.** (a) Effect of contact time on TA uptake and (b) pseudo-second-order kinetic model (adsorbent amount: 100 mg, pH: 8.0, temperature: 30°C).

To investigate the adsorption processes of TA on the adsorbents, the pseudo-first-order kinetic model [Eq. (6)] and pseudo-second-order kinetic model [Eq. (7)] were applied, which can be expressed, respectively, as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q_t$  ( $\text{mg g}^{-1}$ ) are the amounts of TA adsorbed at equilibrium and at predetermined time ( $t$ ).  $k_1$  ( $\text{h}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{h}^{-1}$ ) are the pseudo-first-order and pseudo-second-order rate constants. The parameters in these two models are determined from the linear plots of  $\log(q_e - q_t)$  versus  $t$ , and  $(t/q_t)$  versus  $t$ , respectively. The rate constants obtained from the plot of experimental data and the correlation coefficients of the two kinetic models are shown in Table III.

As shown in Table III, the correlation coefficients ( $R^2$ ) of the pseudo-first-order model and the pseudo-second-order model

are 0.958 and 0.998, respectively. It is obviously that the pseudo-second-order rate model is a better fit than the pseudo-first-order one. Moreover, the calculated  $q_{e(\text{cal})}$  value ( $454 \text{ mg g}^{-1}$ ) also agrees with the experimental data ( $455 \text{ mg g}^{-1}$ ) in the case of pseudo-second-order kinetics. These investigations indicate that the adsorptive process follows a pseudo-second-order kinetic. Figure 7(b) shows the linear plot for the pseudo-second-order kinetic of TA adsorption onto the p-PCRM. Pseudo-second-order model is based on the assumption that the rate-limiting step is a chemical sorption involving adsorption force through sharing or exchange of electrons between p-PCRM and TA.<sup>28</sup> Successful fitting of the model suggests that chemical adsorptions are the rate-controlling steps, and the adsorption rate of TA depends on the concentration of TA at the adsorbent surface and the absorbance of these adsorbed at equilibrium.<sup>29</sup>

### Desorption and Regeneration Studies

Desorption and regeneration is an indispensable criterion for microspheres to value the economics of the adsorption process, and it can also help elucidating the mechanism of an adsorption process. According to the Ref. 30, if the target molecule adsorbed onto the adsorbent can be desorbed by the strong acids, such as HCl, it can be said that the attachment of the molecular onto the adsorbent is by ion exchange or electrostatic attraction. As illustrated in Figure 3, low adsorption for TA is observed at a low and high pH range, which implies that adsorbed TA can be desorbed from adsorbent by an acid or basic medium. Therefore, 0.1M NaOH and 0.1M HCl are used as eluents to desorb TA from the loaded p-PCRM at room temperature, and the desorption ratio reach 84.6% and 93.4%, respectively. The results show that 0.1M HCl is identified as efficient eluents, which suggests that electrostatic interaction between TA and the microspheres plays a predominant role in the removal. After three cycles of adsorption–desorption process, the sorption capacity of the p-PCRM decreases from 455 to 398  $\text{mg g}^{-1}$ , whereas the desorption ratio of TA decreases from 93.4% in the first cycle to 84.0% in the third cycle. The small fraction of sorbed TA which is not recovered by regeneration presumably implies that the TA molecules are bound permanently through strong interaction with active binding sites, and caused the reduced adsorption capacity in successive cycles.<sup>10</sup> In the case of the investigation for the stability of the adsorbents, the ratio of weight loss of the p-PCRM was also tested and the value reaches 5.5% in the three repeated runs, which is much lower than that of p-CRM (12.4%). The experiment suggests that the incorporation of PAL not only increase the absorbability of the adsorbents, but also improve the acid resistance of the resin.

### Performance Evaluation

To evaluate the adsorptive ability of the p-PCRM, the maximum adsorption capacity of various adsorbents for TA are compared and listed in Table IV. It is found that the p-PCRM prepared in

**Table III.** Constants for Different Rate Models

$q_{e(\text{exp})}$ ( $\text{mg g}^{-1}$ )	Pseudo-first order			Pseudo-second order		
	$q_{e(\text{cal})}$ ( $\text{mg g}^{-1}$ )	$k_1$ ( $\text{h}^{-1}$ )	$R^2$	$q_{e(\text{cal})}$ ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g mg}^{-1} \text{h}^{-1}$ )	$R^2$
455	230	0.509	0.958	454	0.0017	0.998

**Table IV.** Tannic Acid Adsorption Capacities of Various Adsorbents

Adsorbents	Adsorption capacity (mg/g)	Reference
Organobentonite	119	10
Chitosan-montmorillonite	240	18
A new polymeric adsorbent	286	28
Activated carbon	417	8
p-PCRM	455	This work

this work shows relatively larger adsorption capacity than the other adsorbents reported in literature. Furthermore, the microscale resins facilitate the separation of the adsorbents from the solution than those of nanoscale, which is especially important for practical applications.

### CONCLUSIONS

In this study, the protonated composite microspheres for the absorption of TA were prepared by introducing 20 wt % PAL into chitosan polymeric network to improve the acid resistant and adsorptive capacity. The adsorption capacities of the p-PCRM for TA were two times more than those of p-CRM at 30°C and pH 8.0, which may be attributed to the protonated amino groups and porous structure existing in the adsorbents. The adsorption kinetics was better described by the pseudo-second-order equation, and their adsorption isotherms were better fitted for the Langmuir equation. The microspheres are recyclable when acid solution is used. As a novel microscale biosorbent, p-PCRM is a promising candidate for TA removal from wastewater.

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