Preparation of cationic starch microspheres and study on their absorption to anionic-type substance

Jie Zheng, YaNan Wang, ZuoShan Feng, ZeMin Kuang, DeZhou Zhao and XueMin Jiao

ABSTRACT

Cationic starch microspheres (CSMs) were prepared from lab-made neutral starch-based microspheres using a cationic adsorbent, namely 3-chloro-2-hydroxypropyltrimethyl ammonium chloride, as the cationic etherifying agent. Detection by scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR), and laser diffraction techniques revealed that CSMs had coarse surfaces with good sphericity and dispersibility. Differential thermal analysis showed the lower thermostability of the CSMs’ main chains. Furthermore, scores of experiments confirmed that CSMs are capable of absorption to \(N\)-(phosphonomethyl) iminodiacetic acid (PMIDA), a type of anionic substance, which is the intermediate to the preparation of glyphosate, maximally up to 95.24 mg/g. Compared with the Freundlich isotherm model, the Langmuir isotherm model can better describe the absorption process. The kinetic study showed that the pseudo-second-order model demonstrated a better correlation of the experimental data in contrast with the pseudo-first-order model. It can be therefore concluded that the rate-limiting step was the chemical absorption rather than the mass transport.

Key words | absorption, cationic starch microspheres, PMIDA, preparation

INTRODUCTION

Starch is a common, linear copolymer, which is composed of \(\alpha\)-D-starch linked via \(\alpha\)-D-1,4 glycosidic bond (Tuovinen et al. 2004; Björses et al. 2011). It is often used as a disintegrant (Elfstrand et al. 2007; Elfstrand et al. 2009), adhesive (Zhao et al. 2008; Gregory et al. 2010), or flocculant (Kuo & Lai 2009) due to properties such as biodegradability, easy supply, non-toxicity, easy storage, and high biocompatibility (Delval et al. 2003; Delval et al. 2005; Fang et al. 2008). The great number of hydrogen bonds in the starch structure, however, are a major constraint that seriously limits development as starch-based materials.

The \(N\)-(phosphonomethyl) iminodiacetic acid (PMIDA) is intermediate during the preparation of glyphosate herbicide (Chen et al. 2010); it is a type of anionic substance in water solution (Shi et al. 2005; Paz et al. 2005; Shi et al. 2006). PMIDA pollution often exists in industrial wastewater from producing glyphosate herbicide (Chen 2003), rubber, medicine, and electroplating industries. The concentration of the industrial mother liquor for producing glyphosate herbicide is about 8.3 g/L. The water-solved PMIDA constitutes a pollutant to the environment, posing a threat to human health through natural water circulation. Conventional treatment methods include membrane separation, evaporation and crystallization, and electrolysis. To date, there are very few studies providing solutions on removing PMIDA from water. Generally, absorption is an effective way to treat harmful substances dissolved in water (Bhatnagar & Sillanpää 2010; Yang et al. 2011a, 2011b). The key is to find an efficient and inexpensive adsorbent. Therefore, natural polymer adsorptive materials with both biocompatibility and biodegradability (Bhatnagar & Sillanpää 2010) are undoubtedly ideal options for a universal adsorbent.

Methods of using starch-based microspheres to remove contaminants from water are effective in water treatment processing. So far, little research has been carried out on how cationic starch microspheres (CSMs) absorb anionic pollutants, and their absorption applications have been seriously confined. These anionic pollutants are widely present in our daily environment and hard to eliminate (Yang et al. 2010). The mechanism of cationic absorbents absorbing anionic pollutants could involve physical absorption and ion exchange, both of which contribute to a high absorption capacity,
which is why anionic pollutants can be blocked or absorbed onto the cationic sites of the surfaces (Ferrero 2010).

In this study, the new type of CSMs were modified and prepared by referring to Hamdi et al. (1998) and Miao et al. (2009) for use as an adsorbent in the adsorbent process of removing PMIDA from water. The synthesis of CSMs included two main steps: prepare neutral starch-based microspheres (NSMs) and NSMs’ etherification reaction with 5-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTA). NSMs were prepared from soluble starch using the w/w emulsification cross-linking method, in which polyethylene glycol solution was employed instead of commonly used organic solvent. That way, the oil-phase residuals generated during the application of organic solvent (Benoit et al. 1999) were excluded. Meanwhile, the w/w emulsification cross-linking method included no use of any surfactant in the whole process, ensuring the safety performance of NSMs. The N,N'-methylenebisacrylamide (MBAA) was chosen as an efficient cross-linking agent, and K2S2O8 and Na2SO3 as initiating agents. The free radical, SO4^− (SO3^− ·), was generated while being mechanically agitated in a regulated manner. These SO4^− · (SO3^− ·) caused the fracturing of C2 and C3 bonds on amylose to form starch radicals, which were then combined with MBAA functional groups into a double amide compound. The CSMs were prepared from the NSMs at a specific temperature in alkaline conditions, with CHPTA being the cationic etherifying agent.

The aim of this study was to discuss the properties of absorption of PMIDA by CSMs in the experiment, where the adsorption rate could reach up to 60%. The Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The results concerning the absorption capacities were presented and discussed. It is expected that these results may be applied to the removal of anionic contaminants from wastewater.

**MATERIALS AND METHODS**

**Materials**

Water soluble starch, which is soluble in hot water (Katoa et al. 2003), and PEG 10,000 were purchased from Chengdu Kelong Chemical Company (Chengdu, China). The MBAA, triethanolamine, and NaHSO3 were obtained from Shanghai Qiangshun Chemical Company (Shanghai, China). The CHPTA and PMIDA were kindly provided by YanZhou Tiancheng Chemical Company (Shandong, China) and Chongqing Jianfeng Chemical Ltd (Chongqing, China), respectively. Absolute alcohol, Pb(NO3)2, NaOH, HCl, and BH3O3 were supplied by Chongqing ChuanDong Chemical Ltd (Chongqing, China). Arsenazo (III) was purchased from East China Normal University Chemical Factory, Shanghai, China. Deionized water was homemade using an SZ-96 automatic water distiller (Shanghai Yarong Biochemical Instrument Co., Shanghai, China). All the reagents, except CHPTA, were of analytical grade and used without further purification.

**Preparation of CSMs**

**Preparation of NSMs**

The procedure introduced by Hamdi et al. (1998) and Miao et al. (2009) was employed with some modifications, namely a proportional increase in the amount of reactants and with MBAA as cross-linking agent, in order to obtain mechanically stable polymers. A definite cross-linking reaction was conducted as follows, and as shown in Figure 1. Six grams of starch-enriched flour, 0.4 g K2S2O8, and 1.6 g MBAA were added to a beaker with 30 mL of NaOH solution (15 g/L), which were homogenized as dispersed phase (w1). A total of 120 mL of PEG (10,000) solution (40 g/L in water PEG) performed as continuous phase (w2). The w1 was slowly added dropwise into the w2 with constant stirring at the rate of 400 rpm at 30 °C for 30 minutes to obtain w1/w2 emulsion. After that, 0.2 g of NaHSO3, dissolved in 3 mL of NaOH solution (15 g/L), was slowly added dropwise to w1/w2 emulsion. The mixture was stirred for 2 hours, and the rate of mechanical agitation and reaction temperature were kept consistent. Then, the mixture was cooled to room temperature. The emulsion was precipitated by absolute alcohol and purified sequentially with absolute alcohol and distilled water twice. After vacuum drying of the centrifuged emulsion at 40 °C for 8 hours, NSMs particles of 50 μm diameter were obtained and kept in desiccators for further use.

![Optical microphotograph of soluble starch (a) and CSMs (b) (×500).](https://iwaponline.com/wst/article-pdf/71/10/1545/468107/wst071101545.pdf)
Synthesis of CSMs

The CSMs were prepared by a modified etherification reaction according to Kuo & Lai (2007). A total of 5.3 g of liquid, CHPTA ($\omega = 65\%$), distilled water and NaOH ($\omega = 10\%$), which were in accordance with the 1:3:3 ratio, and 3 g NSMs were poured into a 100 mL beaker and stirred vigorously with an artificial stirrer until fully mixed. Then, the mixture was heated to 50 °C and maintained for 5 hours. Thus, the $\text{CH}_2\text{CHCH}_2\text{N}^+(\text{CH}_3)_3$ group was introduced into NSMs to obtain the CSMs. The obtained CSMs were collected and washed twice, with absolute alcohol and deionized water, respectively.

Characterization

SEM

Morphology of the samples was examined at a magnification of 500× using a scanning electron microscope (SEM) (TESCAN VEGAIII SEM, Jike TESCAN company, Brno, Czech Republic), which operated at an accelerating voltage of 20 kV. Microparticles for SEM studies were mounted on metal stubs with single-side adhesive (KYKYSBC-12, scientific instruments plant of the Chinese Academy of Sciences, Beijing, China) before morphology measurement.

Fourier transform infrared (FTIR) spectroscopy

Infrared spectra of the polymeric adsorbents were obtained from a Nicolet-5DXC FTIR spectrometer (Nicolet Magna 550 series II Fourier transform infrared spectrometer; Thermo Nicolet Corporation, Waltham, MA, USA). The spectra were transformed against a KBr background before recording. The amino groups on samples were measured in the range between 4,000 and 250 cm$^{-1}$.

Particle size analysis

A Mastersizer RISE-2008 laser particle analyzer (Jinan Runzhi Technology Company, China) was used to analyze the particle size distributions of CSMs. The dry CSMs were poured into absolute alcohol and dispersed by ultrasound prior to measurement. The size distribution of CSMs was plotted using a computer program supplied by the manufacturer and the average particle size was expressed as mean diameter in micrometers.

Differential thermal analysis

Differential thermal analysis (DTA) is a method that is used for observing the change of energy and recording the difference between reference and sample substance (Murat 2010). The samples of DTA were analyzed by the instrument DTG-60H (Daojin Company, Japan) in this experiment. The experimental results were acquired through the related software rendering curve.

Absorption tests

The concentration decay curves and equilibrium sorption capacities were determined in batch experiments. In a typical experiment, 0.5 g of the adsorbent was placed in a 250 mL triangle flask containing 30 mL of PMIDA. And the mixture was shaken by ultrasound from KQ3200DE (Kunshan Ultrasonic Instruments Company, Kunshan, China) for 10 minutes to ensure CSMs were scattered completely in the PMIDA solution. All tests were carried out at different temperatures and were kept static for some time. Subsequently, the solution was then separated from the CSMs by reduced pressure suction filter and subjected to PMIDA determination. CSMs were measured in triplicate and the average value used in the subsequent analysis. The kinetic data of the adsorbed amount of PMIDA at time $t$, $q_t$ (mg/g of adsorbent), were obtained by Equation (1):

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where $C_0$ (mg/L) is the initial PMIDA concentration, $C_t$ (mg/L) is the concentration of the solution at time $t$, $V$ (L) is the volume of treated solution, and $m$ (g) is the mass of adsorbent. All experiments were performed with three concentrations of PMIDA (5, 10, and 15 g/L) in the absorption solution.

PMIDA concentrations were measured by titration experiments. Take a certain volume of PMIDA solution accurately in a 250 mL conical flask, then adding 3 mL 50% triethanolamine as masking agent. At the same time, we added boric acid buffer, 10 mL, and 0.1% arsenazo (III), 2–3 drops, as an indicator. Then, titration was carried out with standard nitrate solution. As the color of the solution became pure blue, the experiment ended.

The amount (mg) of PMIDA used is as follows:

$$m = c \times V \times 0.2271$$
where $m$ is the amount of PMIDA within the sample solution (mg); $V$ is the volume of the consumed standard nitrate solution (mL); $c$ is the concentration of the standard nitrate solution (0.05 mol/L); 0.2271 is the amount of PMIDA that 1.00 mL 1.000 mol/L standard nitrate solution could consume.

RESULTS AND DISCUSSION

Physical characterization

Morphology of CSMs

The morphology of starch and CSMs is shown in Figure 1. SEM micrographs demonstrated that the soluble starch particles were irregular and of different sizes, and that the CSMs were spherical with a rough surface and some cracks were blocked up during the cross-linking reaction. Furthermore, the CSMs had a high polydispersity in size; it is considered that the aggregation was mainly due to the emulsification method involved. When emulsified by mechanical stirring, microspheres were formed in the emulsion systems. The systems were thermally stable, as the emulsifier reduced the internal tension.

Structural organization by FTIR

The structural organization of the CSMs was further investigated using FTIR. The FTIR spectra of the soluble starch particles and the CSMs are shown in Figure 2(a) and 2(b), respectively. The spectrum of soluble starch and CSMs both showed broad and strong bands in the region between 3,400 and 2,920 cm$^{-1}$. This explains why the hydroxyl groups were not damaged by the cross-linking reaction except that, the soluble starch band is broader than that of the CSMs. This is possible because the hydrogen bond connections were decreased by cross-linking and carboxylation. There were six major bands located clearly at 1,647, 1,463, 1,383, 1,162, 1,082, and 986 cm$^{-1}$. Within the same range, the spectrum of CSMs showed significant changes in comparison with that of soluble starch. Among them, the bands at 1,637 cm$^{-1}$ became less sharp, suggesting that the peak of C=O and C-O were decreased by the cross-linking reaction. The band at 1,458.4 cm$^{-1}$ became weak, which was the characteristic peak of $-$CH$_2$CHCH$_2$$-$ N + (CH$_3$)$_3$. The bands from 1,156.1 to 1,020.8 cm$^{-1}$ were the features of ether bands (C – O), indicating that there were more ether bands (C – O) after cross-linking of soluble starch. Furthermore, the spectrum of CSMs in this study appeared as a large number of bands from approximately 250 to 750 cm$^{-1}$, which was caused by the difference between CSMs and ether bands (C – O).

Particle size analysis

Size distributions of the CSMs are shown in Figure 3. The average diameter of the CSMs was 87.66 μm. Furthermore, over 90% of the microspheres were smaller than 122.55 μm. The size distribution of the CSMs was wide in range because the droplets generated in the emulsion were of a wide range. The coalescence and breakup of droplets occurred frequently during the emulsification and cross-linking process. Consequently, the wide distribution of sizes could not be avoided.
Differential thermal analysis

The DTA results are shown in Figure 4. The peaks of 1, 2, and 3 in Figure 4(a) represent the three reaction stages of soluble starch: the loss of absorbed water, the fracturing of the CSM molecular main chain, and the carbonization decomposition reaction, respectively (Zhang et al. 2009; Athawale et al. 2000). From Figure 4(a), we found that the three reaction stages of soluble starch were an absorption process. There were only two peaks in Figure 4(b) to express the absorption reactions. Furthermore, two values, the peak of 1 in the two curves, were almost the same, suggesting the loss of absorbed water at the same temperature. The abscissa value of the 2 peak in Figure 4(b) was less than that in Figure 4(a), suggesting that the main chain of the CSM has lower stability than soluble starch. There was no peak of carbonization decomposition reaction found in Figure 4(b) until 700 °C, signifying that the temperature of carbonization decomposition for CSMs was higher than 700 °C.

The absorption isotherm and kinetic characteristics of PMIDA absorption on CSMs

Effect of absorption time

To obtain simple and explicit relationships between CSMs and PMIDA in aqueous solution, time was used as a measurement parameter. The kinetic results of absorption of PMIDA onto CSMs from aqueous solutions are shown in Figure 5, at different temperatures: 298, 308, and 318 K. PMIDA’s initial concentrations were 5, 10, and 15 g/L, respectively. It was slowly adsorbed by CSMs and the absorption process reached equilibrium in about 2 hours.

As shown in Figure 5, although the experiment temperatures and initial concentration of PMIDA solution were different, the equilibrium time was almost the same. To understand the mechanism of absorption, a pseudo-first-order equation (Saeid 2004) and a pseudo-second-order kinetic model (Özcan & Özc 2005) were used to study the experimental data of temperatures in the absorption process.

The pseudo-first-order equation was derived from the widely used Lagergren equation, which can be described as follows:

$$q_t = q_e [1 - \exp(-k_1 t)]$$

where $k_1$ is the rate constant for pseudo-first-order (minute$^{-1}$), $q_t$ is the amount of organic molecules adsorbed at time $t$ (minute) (mg/g), and $q_e$ the equilibrium absorption capacity (mg/g).

The pseudo-second-order kinetic model can be analyzed by the following Equation (4):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$
where \( k_2 \) (g/mg/minute) is the rate constant of pseudo-second-order absorption; the meanings of \( q_t \) and \( q_e \) in the pseudo-second-order kinetic model are the same in comparison with the pseudo-first-order equation. Absorption kinetic parameters at three different temperatures and three different initial concentrations are shown in Table 1. The values of correlation coefficient \( (R^2) \) suggest a better fit of the pseudo-second-order model with the experimental data compared with the pseudo-first-order model. Furthermore, the equilibrium absorption capacity calculated from the pseudo-second-order kinetic model fitting is nearer the equilibrium absorption amount \( q_e \)-exp than the pseudo-first-order kinetic model fitting, according to the experiments. This means that chemical absorption is the determining step of the absorption process rather than mass transfer in solution (Li et al. 2009a, b). The CSMs in this study have a relatively high equilibrium absorption amount \( q_e \) and the equilibrium time was short. There have been more conclusions similar to this one. One example is the biosorption of RB2, MB, Cu\(^{2+}\), and Pb\(^{2+}\) (Chiou and Li 2002; Yang et al. 2010; Yang et al. 2011a, b).

### Effect of equilibrium PMIDA concentration

As the same gradient, equilibrium of PMIDA concentration was difficult to control; a different initial concentration was determined. Figure 6 shows the effect of the initial PMIDA concentration, which has positive correlation with the equilibrium concentration of absorption. All the data were determined after about 2 hours, when the absorption equilibrium was achieved. The absorption equilibrium is shown based on the well-known Freundlich and Langmuir isotherms (Delval et al. 2002; Vinod et al. 2001; Gil et al. 2011). The results concerning the influence of equilibrium concentrations on absorption are presented in Table 2. The Langmuir and Freundlich absorption isotherm can express the experiment process in which PMIDA adhered to CSMs. The Langmuir isotherm is expressed as follows:

\[
q_e = \frac{abq_e}{1 + bce}\tag{5}
\]

where \( q_e \) is the equilibrium absorption capacity (mg/g), ‘a’ signifies the maximum amount of PMIDA adsorbed onto monolayer coverage. Furthermore, ‘b’ is the Langmuir constant; \( c_e \) is the equilibrium concentration of PMIDA in the bulk solution \( C_e \) (mg/L). To simplify the calculation, it can be written as Equation (6).

\[
\frac{c_e}{q_e} = \frac{1}{a}c_e + \frac{1}{ab}\tag{6}
\]

The Freundlich isotherm is expressed as follows:

\[
q_e = K_fC_e^{1/n}\tag{7}
\]

where the meaning of \( q_e \) and \( c_e \) are the same compared with Langmuir. The \( K_f \) (mg/L) absorption coefficient representing the rate of absorption; \( n \) (\( n > 1 \)) is the Freundlich constant representing the degree of heterogeneity in the distribution of the energetic center and is related to the magnitude of the absorption driving force (Gupta et al. 2010). The logarithm on both sides of Equation (7) can be taken to reach another form of expression as follows:

\[
\ln q_e = \ln K_f + \left(\frac{1}{n}\right)\ln C_e\tag{8}
\]

### Table 1 | Absorption kinetics parameters of PMIDA on CSMs at different temperatures and different initial concentrations

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( q_e \text{-exp (mg/g)} )</th>
<th>( k_1 )</th>
<th>( q_e \text{-cal (mg/g)} )</th>
<th>( \text{R}^2 )</th>
<th>( k_2 )</th>
<th>( q_e \text{-cal (mg/g)} )</th>
<th>( \text{R}^2 )</th>
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<tbody>
<tr>
<td>298</td>
<td>81.31</td>
<td>0.0398</td>
<td>262.57</td>
<td>0.8266</td>
<td>0.0100</td>
<td>83.76</td>
<td>0.9825</td>
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<tr>
<td>308</td>
<td>65.45</td>
<td>0.0400</td>
<td>228.63</td>
<td>0.7982</td>
<td>0.0112</td>
<td>65.95</td>
<td>0.9945</td>
</tr>
<tr>
<td>318</td>
<td>44.55</td>
<td>0.0317</td>
<td>106.82</td>
<td>0.8267</td>
<td>0.0107</td>
<td>44.71</td>
<td>0.9949</td>
</tr>
</tbody>
</table>

**Figure 6** | Effect of initial concentration on PMIDA absorption by CSMs.
For the absorption on the first layer of solid surface, the Gibbs energy of absorption can be estimated on the basis of absorption equilibrium data measured at different temperatures. The relational expression is given as follows:

\[ \Delta_{\text{ads}}G_1 = -RT\ln(q_s b_1) \]  

(9)

where \( R \) and \( T \) have their usual meanings, namely the gas constant (J/mol/K) and the thermodynamics temperature (K), respectively; \( q_s \) is the molecular mass of PMIDA (mg/mol); \( b \) indicates the Langmuir constant concerning the affinity of binding sites (L/mg); and the subscript 1 in \( b_1 \) pertains to the first layer adsorbed.

The results from Table 2 demonstrate that the Langmuir and Freundlich models can be used to explain the absorption isotherm in this study. The model of Langmuir was found to be more satisfactory in that its correlation coefficient \( R^2 \) was higher than Freundlich’s. Thermodynamically, free enthalpy change \( \Delta G^\Theta \) during the spontaneous absorption process is always of a negative value at constant temperature and pressure. In Table 2, negative \( \Delta G^\Theta \) values show that the absorption of PMIDA onto CSMs is spontaneous.

### Effect of absorption temperature

The influence of temperature on the adsorbed amounts is shown in Figure 7, descriptive of how variations in temperature affected PMIDA absorption by CSMs. When the temperature was 301 K, the amount of absorption was more than that at all other temperatures. The results showed that the adsorbed amount increased with the increase of temperature when the temperature was less than 301 K, suggesting that the absorption is endothermic. The temperature rise, however, leads to the decrease of absorption when the temperature was more than 301 K, suggesting that the absorption process was controlled by an exothermic process. All the test results indicated that the absorption of PMIDA declined mainly owing to the presence of oppositely charged ions that give high affinity between PMIDA and CSMs.

### CONCLUSIONS

The batch experiments studied the absorption property of PMIDA in aqueous solution on CSMs. The results indicate that CSMs are an effective adsorbent for PMIDA. The absorption process can be well described by a Langmuir isotherm with a maximum absorption capacity of 95.24 mg/g. The effect of temperature on the absorption was significant: when it was below 301 K, the amount of absorption increased with the rise in the temperature; but when above 301 K, the absorption decreased with the temperature rise. Moreover, it can be concluded that 301 K may be the suitable adsorption temperature for PMIDA absorption by CSMs. The kinetic study showed that a pseudo-second-order kinetic model provided a better correlation of the experimental data in comparison with the pseudo-first-order model. This indicates that the rate-limiting step may be the chemical absorption rather than the mass transport.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( b ) (L/mg)</th>
<th>( A ) (mg/g)</th>
<th>( R^2 )</th>
<th>( \Delta G^\Theta ) (K/mol)</th>
<th>( K_f )</th>
<th>( n )</th>
<th>( R^2 )</th>
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<tr>
<td>298</td>
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<td>0.9513</td>
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</table>

Table 2 | Langmuir and Freundlich isotherm parameters at different temperatures
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