The Synthesis of Porous Aminated Starch for the Adsorption of Phenol

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Summary: Starch, an affordable and biodegradable polymer, is commonly used for adsorbing chemical hazards like phenol. To enhance phenol adsorption, a porous aminated starch was developed through enzymatic and chemical modification. By optimizing enzymatic reaction time and temperature, the porous starch was successfully fabricated without granule collapse, resulting in a surface area increase from 0.33 m^2/g to 0.81 m^2/g. Amino groups were then added to the porous starch via amination, boosting phenol adsorption capability from 0.0165 g/g in native starch to 0.0198 g/g in porous aminated starch, marking over 20% improvement. Additionally, the porous aminated starch exhibited a considerably faster adsorption rate than native starch. The porous structure provided more active sites for phenol adsorption, while the additional amino group enhanced interaction with phenol through hydrogen bonding, leading to higher phenol adsorption capability and faster rate.

Keywords: Starch, Porous, Phenol Adsorption, Aminated.

Introduction

Starch is a type of carbohydrate biopolymer that can be obtained from green plants. Starch takes the advantages of abundance, low cost, good biodegradability, and biocompatibility. Thus, it is regarded as a naturally renewable material and has attracted increasing attention due to its valuable and potential applications in various food and non-food industries [1-4]. It is not only used in numerous bakery goods but also regarded as a renewable material in the coating field, adhesion, and adsorption. Starches that contain many modifiable groups on the surface can also be easily modified to tune their physical or chemical properties and exhibit more functionalities. However, starch itself exhibits poor adsorption capabilities, rendering it unsuitable for direct use as an adsorbent in the aforementioned domains.

Recently, starches have been successfully used as adsorbents, which negatively affects human health [5] According to the different mechanisms, the adsorption of phenol by using starch can be mainly divided into physical and chemical aspects. Starch and phenol molecules will interact with each other to form either an inclusion complex in the form of single amylose helices or a complex through hydrogen bonding [6-8]. In addition, the introduction of some functional groups that can form covalent bonds will also facilitate the adsorption of volatile phenol.

Researchers exert intensive efforts to modify the physical or chemical properties of the starch to enhance the phenol adsorption capability by controlling their morphology or introducing many essential functional groups. The preparation of the porous microstructure that consists of abundant pores distributed on the starch granules is an effective way to significantly improve the surface area of starch [9]. The porous starch can be obtained by physical [10, 11], chemical [12, 13] and enzymatic [14] methods. The most effective way to produce porous starch is by using ultrasonic treatment. However, high-intensity ultrasound will destroy the microstructures of starch, and it is difficult to control the pore size and pore volume in starch. The enzyme method is a facile and environmentally friendly way to promote the formation of pores by using a-amylase and glucoamylase as hydrolysis enzymes. This method can achieve more uniform pore size and pore distribution. Compared with native starch, the porous starch synthesized by enzymatic modification has shown excellent adsorption properties in different materials, such as volatile organic materials [15-17] and heavy metals [18, 19].

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In addition to tuning the morphology of native starch, researchers also aim to introduce various additional functional groups, such as carboxyl or ester groups, on the surface of starch through grafting, cross-link, and esterification to enhance the chemical adsorption capacity further [20-23] Haq et al. synthesized succinylated carboxymethyl starches (S-CMS) by reacting carboxymethyl starch with succinic anhydride and then using it for phenol adsorption. The greater number of carboxylic groups on the surface will facilitate the removal of phenol from the gaseous stream [21] They also developed carboxymethyl starch grafted poly (methacrylic acids), and the modified starch exhibits the enhanced adsorption capability of ammonia and phenol [20].

To further enhance starch's adsorption capacity for phenol, this study ventures to explore a unique strategy that combines composite enzyme treatment with chemical modification. Through this approach, a novel modified starch adsorbent material is developed. The porous starch is first synthesized by using biological enzymes, followed by optimizing the pore size and structure, which can significantly increase the surface area without compromising the integrity of the granular starch structure. The porous structure provides more active sites for phenol adsorption. Then amino groups will be introduced onto the porous starch through cross-linking, oxidation, and amination processes. The introduced amino functional group on the porous starch will effectively grab the phenol via hydrogen bonding. The porous aminated starch synthesized in this work, which takes advantage of high adsorption ability and safety, opens a new pathway to prepare the environmentally friendly adsorbent. This modified starch adsorbent material plays a significant role in various domains such as cigarette filter development, wastewater treatment, and environmental conservation. It aids in reducing the adverse impact of phenol on the environment and human health [24].

Experimental

Materials

The native starch was purchased from Shandong Linghua Group. Saccharifying enzyme, α-Amylase, sodium hydroxide (NaOH), citric acid, disodium hydrogen citrate, epoxy chloropropane (ECH), sodium sulfite (Na_2SO_3), diethylenetriamine ($C_4H_{13}N_3$), ethylenediamine (EDA), N, N-dimethylformamide (DMF), p-aminobenzenesulfonic acid, sodium periodate ($NaIO_3$), sodium chloride (NaCl) and copper sulfate ($CuSO_4$) were all purchased from Aladdin. Anhydrous ethanol, deionized water, hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2) were all purchased from Sinopharm.

The synthesis of porous aminated starch

Preparation of porous starch: The 30 g of native starch was dispersed into 100 ml of disodium hydrogen phosphate-citric acid buffer solution with a PH value of 4.5 in a three-necked flask, and stirred for 1 hour using a magnetic stirrer. α-Amylase and saccharifying enzyme with a ratio of 1:3.5 were added into the flask and the total weight of the two enzymes was 2 wt.% of starch. The mixture was placed in the water bath at 50 °C for a couple of hours before 10 ml of NaOH solution with a concentration of 1 mol/L was added to terminate the reaction. The solution was centrifuged at 4000 r/min for 5 min, followed by washing with deionized water for 3 times, and then dried in a 60 °C vacuum drying oven for 12 hours.

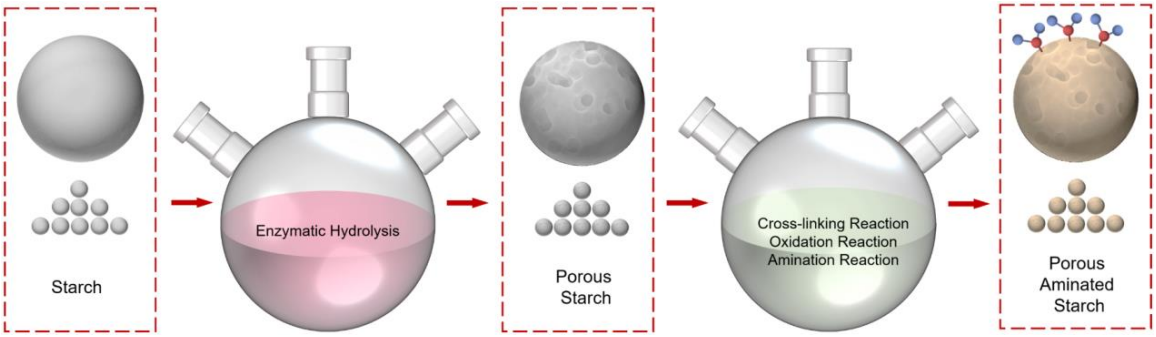

Fig. 1: Schematic diagram of the preparation of porous aminated starch

Preparation of aminated starch: The first step is the preparation of cross-linked starch. The dilute alkaline solution was prepared by adding 3.37 g of NaOH and 31.44 g NaCl into 500 ml of deionized water. 25 g of porous starch and 1 ml of epoxy chloropropane were added into 50 ml of dilute alkaline solution and then stirred for 5 hours. After the reaction, the solution was centrifuged and dried in the oven for 12 hours.

The second step is the preparation of oxidized starch. 25 g of cross-link starch was dissolved into 50 ml of deionized water. The PH value of water was adjusted to 5.0 by adding a certain amount of HCl solution. Then, 10 mL of H_2O_2 was slowly introduced and stirred at 45 °C for 3 hours before adding 10 wt.% Na_2SO_3 to terminate the reaction. The oxidized starch was washed with deionized water three times and dried in the oven at 60 °C for 12h.

The third step is the preparation of aminated starch. The oxidized starch and diethylenetriamine were mixed in the anhydrous ethanol with a weight ratio of 2:1. HCl and NaOH were used to adjust the PH value of the solution to 7.0. The prepared solution was heated at 45 °C for 3 hours. After the reaction, the solution was centrifuged and then washed with deionized water three times. The final product was dried in the oven at 60 °C for 12 hours.

Characterization of porous aminated starch

The morphological features of the modified porous starch were characterized by using the scanning electron microscope (JSM-7500VF). The Fourier-transform infrared (FTIR) spectra were recorded with a Burker ALPHA II in the range 4000–500 cm^{-1}. The X-ray diffraction (XRD) patterns of starch before and after modification were measured by using a Burker D8 Advance. An automatic specific surface and porosity analyzer was used to measure surface area of starch.

The capability of phenol adsorption was measured by using two different methods. The first method was to put 5 g of native or modified starch and 3 g of phenol in the petri-dish. The petri-dish was covered by using the parafilm and then was heated to 70 °C. The weight change of starch was recorded as a function of time. The second method is to use Mettle Toledo TGDSC3+synchronous thermal analyzer to measure the phenol adsorption capacity quantitatively. A certain number of starches were put into the synchronous thermal analyzer and then heated the temperature to 150 °C to completely remove the adsorbed gas on the surface. Since the weight of the starch was stable, the temperature was adjusted to 70 °C, and the mixed phenol/nitrogen gas was continuously introduced. The adsorption of phenol was calculated from the weight change of starch.

Results and Discussion

In this study, the porous starches are synthesized through enzymatic reaction. The morphology of native and modified porous starch are observed by using scanning electron microscopy (SEM). Two key parameters in determining the morphology of porous starch are reaction temperature and time. Fig. 2 demonstrates morphological change of starch as a function of reaction temperature. Fig. 2 (a) shows the morphology of the native starch that has the polygonal granular shape with very smooth surface. At a relatively lower temperature, both α-Amylase and saccharifying enzymes exhibit low activity, thus the hydrolysis rate is very slow. Fig. 2 (b) and (c) display that small and shallow pores distributed on the surface starch have been seen in the starch reacted at 30 °C, and both pore size and depth significantly increase as the reaction temperature increases to 50 °C. As the temperature increases to 70 °C, the pores in starch granules keep growing, and the hydrolysis degree increases. However, the granular structure is unstable and collapses severely, leading to a lower absorption capability. Therefore, it is found that 50 °C is the ideal temperature for enzymatic reaction.

In addition to temperature, time is another important factor to affect the enzymatic activity. Fig. 3 (a)-(h) demonstrate the evolution of starch as a function of time in the enzymatic reaction. It is seen that the hydrolysis degree increases as reaction time increases from 1 hour to 24 hours. In the first 2 hours, most of the pores have occurred on the surface of starch. From 2 hours, the enzyme starts to penetrate the starch's internal structure, leading to rougher surface morphology and higher porosity. It can be found that the starch granules have collapsed when the reaction time is longer than 8 hours. Therefore, the enzymatic hydrolysis duration is determined to be 6 hours which exhibits the larger surface area as well as avoids the damage of granular shape. The porous starch exhibits the same crystal structure compared to the native starch, as shown in Fig. S1.

The surface area of starch before and after

enzymatic hydrolysis was quantitatively investigated. The nitrogen adsorption and desorption isotherms of the native and porous starch samples are shown in Fig. 4. The specific surface areas and pore size are calculated by using the BET method. Compared with the native starch (0.33 m^2/g), the starch, after enzymatic hydrolysis, exhibits a much higher specific surface area (0.81 m^2/g). The pore size in modified starch is mainly distributed between 150 and 250 nm, which is larger than the native starch, showing a good agreement with the results of SEM images.

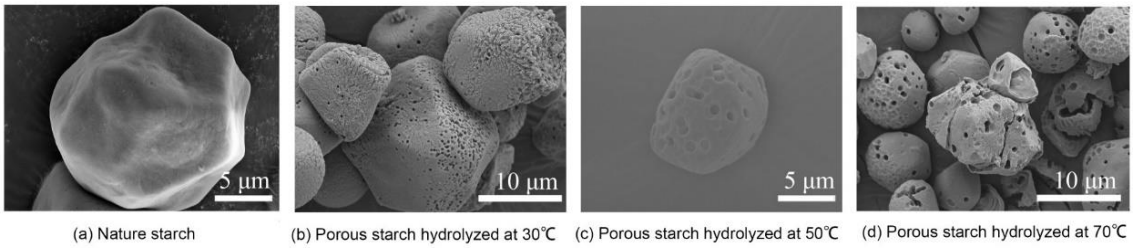

Fig. 2: SEM images of (a) nature starch and porous starch prepared at different reaction temperatures of (b) 50 °C, (c) 70 °C, and (d) 90 °C.

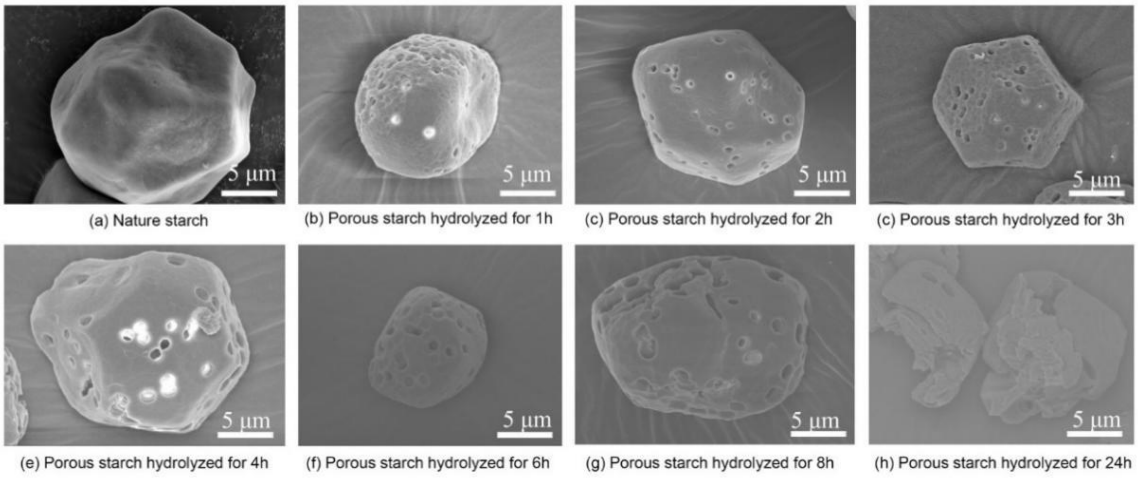

Fig. 3: SEM images of (a) nature starch and porous starch prepared at different times: (b) 1 hr, (c) 2 hr, (d) 3 hr, (e) 4 hr, (f) 6 hr, (g) 8 hr and (h) 24 hr.

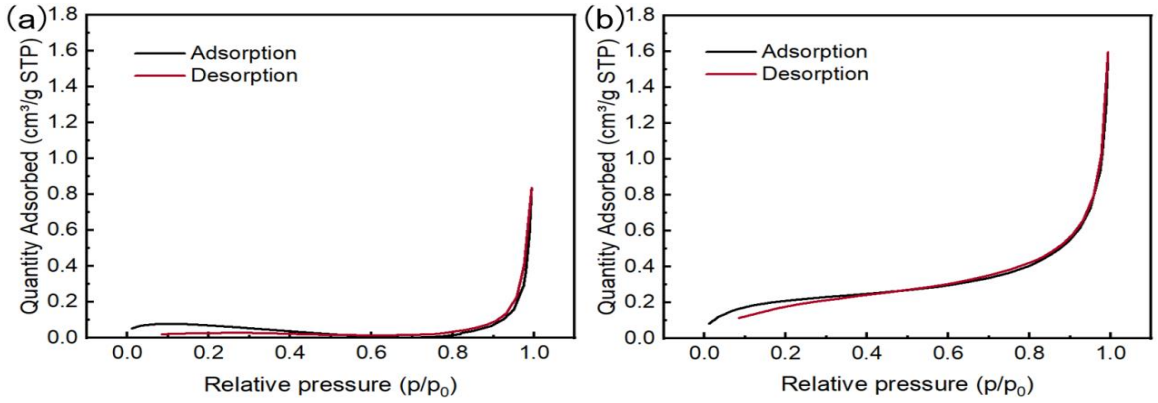

Fig. 4: (a) Nitrogen adsorption and (b) nitrogen desorption isotherms of native starch and porous starch.

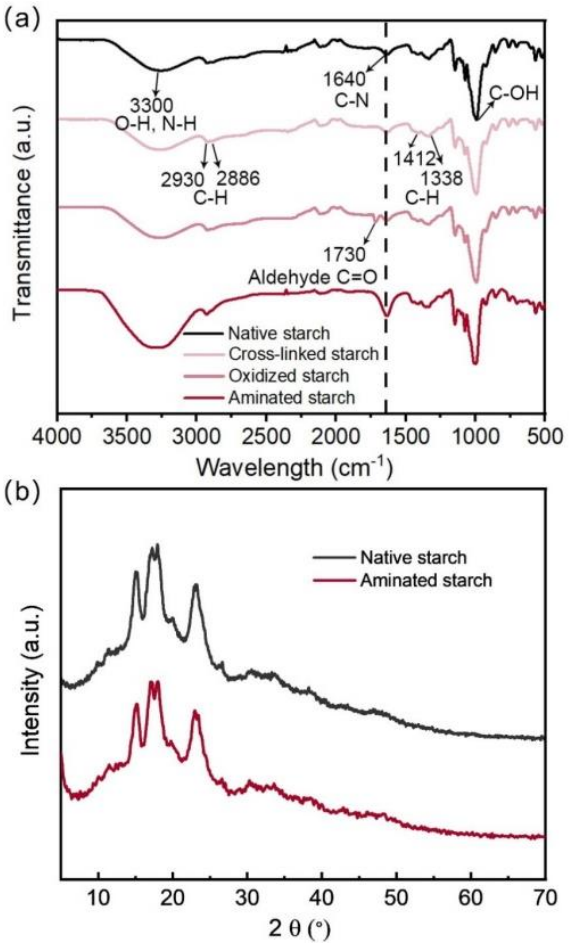

Fig. 5: (a) Fourier-transform infrared spectra (FTIR) of starch before and after chemical modification. (b) X-ray diffraction (XRD) patterns of native starch and aminated starch.

After the preparation of porous starch, the amino groups will be introduced to fabricate the porous aminated starch via cross-link, oxidation, and amination processes. The structures of nature starch and aminated starch are examined using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), as shown in Fig. 5. Fig. 5(a) displays the FTIR spectra of the modified starches. O-H and N-H bond stretching vibration peaks are located at 3300 cm^{-1}, respectively. C-H stretching vibration peaks are located at 2930 cm^{-1} and 2886 cm^{-1}. After the oxidation process, it can be seen that a new peak emerged at 1730 cm^{-1}, which corresponds to the aldehyde C=O characteristic peak. It confirms that the oxidation process successfully introduces aldehyde groups on the cross-link porous starch. After the last step of the amination process, a peak corresponding to the C-N bond at 1640 cm^{-1} is greatly increased. Meanwhile, the C=O characteristic peak at 1730 cm^{-1} vanishes, which indicates that the aldehyde groups have already been fully reacted and converted to amino groups. In addition, the peak at 3300 cm^{-1} corresponding to the N-H bond also exhibits a dramatic increase after the amination process. FTIR results indicate that the amino group has been confirmed in the chemically modified starch. Fig. 5 (b) compares the crystal structure of starches before and after amination modification examined by using X-ray diffraction. Both samples exhibit similar diffraction peaks, which are located at 15.06°, 17.14°, 17.90°, and 23.02° respectively, and these four peaks also show similar intensity. The XRD results indicate that the modification process does not change starch's crystal structure and crystallinity.

The phenol adsorption capability of native starch and porous aminated starch is investigated by putting starch and phenol in the petri-dish and measuring the weight change of starch. Fig. 6 (a) shows the weight change in starch as a function of time. Native starch and aminated starch show a similar trend of phenol adsorption behavior, that exhibit a linear increase in phenol adsorption as a function of time in the first 10 mins, and then their adsorption rates show a rapid decrease, followed by approaching a saturated value after 20 mins. However, compared with the native starch, the porous aminated starch has a faster phenol adsorption rate and larger adsorption capacity. As shown in Fig. 6 (b), phenol adsorption efficiency in the native starch is 0.0147 g/g and 0.0198 g/g at 10 mins and 60 mins respectively, while adsorption efficiency in the porous aminated starch is 0.0228 g/g and 0.0257 g/g at 10 mins and 60 mins respectively. After the modification, the adsorption efficiency in the saturated region increases by 29.7%, which is mainly due to the increased specific surface area and the introduction of the amino group.

In order to further describe the behavior of phenol adsorption in native and aminated starch, the quasi-second order kinetic equation is used to fit the adsorption kinetic curve based on the change of adsorption efficiency as a function of time. The fitting formula is as follows:

$$\frac{t}{Q_t} = \frac{Q_e^2}{K} + \frac{t}{Q_e} \quad (1)$$

In the equation:

Q_e--the fitting value of equilibrium adsorption capacity, g/g

Q_t--adsorption capacity at t time, g/g

K--quasi-second order kinetic constant, g/(g·min)

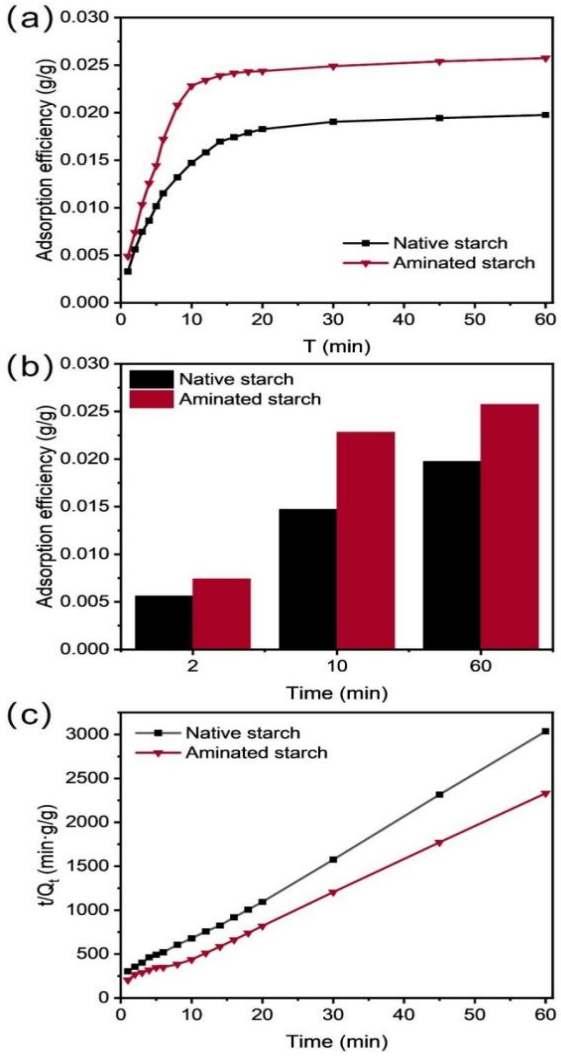

Fig. 6: (a) The capability of phenol adsorption as a function of time. (b) The capability of phenol adsorption in native starch and porous aminated starch for at 2, 10, and 60 mins. (c) The second-order dynamic fitting curve for phenol adsorption.

Fig. 7(d) shows the kinetic fitting results of the adsorption data, and the relevant parameter is shown in Table 1. The second-order kinetic model's fit to the saturated adsorption capacity yields a value that is closer to the experimental value. Therefore, the second-order kinetic model is more suitable for fitting phenol adsorption in starch. It demonstrates that there are more adsorption active sites thus a quicker adsorption rate can be observed at the beginning stage. The adsorption rate shows a rapid decrease as the adsorption sites are largely occupied. The aminated starch exhibits a faster adsorption rate than the native starch across the whole phenol adsorption test.

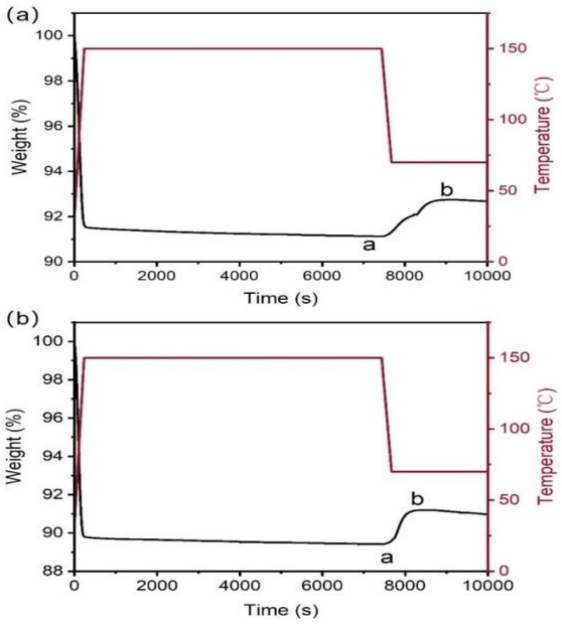

Fig. 7: The weight change of (a) native starch and (b) porous aminated starch with the introduction of phenol and nitrogen mixed gas.

Table-1: parameters fitted from quasi-second-order kinetics equation.

	Q_e (g/g)	$K \cdot 10^{-6}$ g/(g/min)
Native starch	**0.0218**	**3.63**
Aminated starch3	**0.0278**	**3.34**

In order to confirm the porous aminated starch shows the higher adsorption efficiency and faster adsorption rate than the native starch, a thermal analyzer is used to quantitatively analyze the phenol adsorption by filling the phenol and nitrogen mixed gas at 70 °C. Fig. 7 (a) depicts the weight change of

the native starch with phenol adsorption. The weight of native starch is steadily fixed at 0.911 g after heating at 150 °C over a certain period for the desorption of the residual gas. The introduction of the nitrogen-phenol mixed gas results in the weight of native starch showing a linear increase with time and then approaching a saturated value of 0.926 g after 1175 s. It indicates that the adsorption capability of native starch is 0.0165g/g. Fig. (b) demonstrates the weight change of porous aminated starch with phenol adsorption. The introduction of mixed gas leads the weight of the porous aminated starch increasing from 0.894g at the initial stage to 0.912g at the saturated stage within 652 seconds. The porous aminated starch has an adsorption capability of 0.0201g/g, 21.8% higher than the native starch. Furthermore, the slope of the adsorption curve is used for studying the phenol adsorption rate. Calculations reveal that the 1g native starch has a maximum adsorption rate of 0.0188 mg/s, while 1g porous aminated starch has a maximum adsorption rate of 0.0607 mg/s.

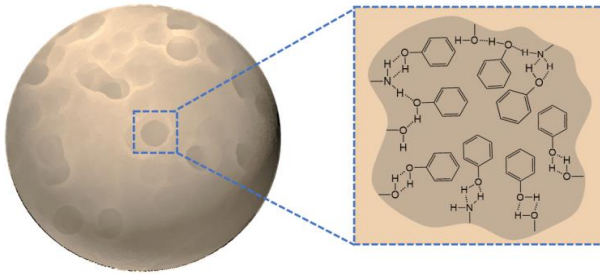

Fig. 8: Schematic diagram of the phenol adsorption mechanism in porous aminated starch.

The improvement of phenol adsorption capability and adsorption rate in the modified starch is mainly attributed to the enhanced surface area and the introduction of the amino group. Through the enzymatic reaction, the formation of a porous structure significantly increases the surface area, which will provide more active sites for phenol adsorption. At the same time, the amino group has been successfully introduced through the amination process, confirmed by FTIR spectra. The existence of amino group can further improve phenol adsorption through hydrogen bonds, as shown in Figure 8. In addition, we also design two different methods to introduce amino groups onto porous starch, see supporting information. However, the starch prepared by another two methods shows the lower phenol adsorption capability and slower adsorption rate.

Conclusions

In summary, the porous aminated porous starch is developed through enzymatic and chemical modifications. The chemical structure, morphology, and surface area have been comprehensively investigated by using a combination of SEM, FTIR and XRD. After the modification, the surface area increases from 0.33 m^2/g to 0.81 m^2/g, providing more active sites for phenol adsorption. The amino functional group has also been introduced without changing the original crystal structure of starch, which can facilitate phenol adsorption via hydrogen bonds. The phenol adsorption capability increases from 0.0165 g/g and 0.0201 g/g in native starch to 0.0198g/g and 0.0257g/g in modified starch by using two different measurements. Both methods exhibit more than 20% phenol adsorption enhancement after the modification. In addition, the porous aminated starch exhibits a significantly faster phenol adsorption rate. This strategy combined enzymatic and chemical modification is important for improving the adsorption of chemical hazards by enhancing both physical and chemical interaction.

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