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Synthesis of porous starch xerogels modified with mercaptosuccinic acid to remove hazardous gardenia yellow

Liping Bao[a], Xinyi Zhu[a], Hongxia Dai[b], Yongxin Tao[a], Xiaoying Zhou[c], Wenjie Liu[a], Yong Kong[a,*]

[a] Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China
[b] School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China
[c] School of Pharmaceutical Engineering and Life Science, Changzhou University, Changzhou 213164, China

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ABSTRACT

Mercaptosuccinic acid (MSA) molecules were inserted into potato starch, leading to the breaking of intrinsic H-bonds within macromolecular chains of starch and the formation of intermolecular H-bonds between MSA and starch, which could be verified by Fourier transform infrared spectroscopy (FT-TR). MSA modified porous starch xerogels (PSX/MSA) were obtained after freeze-drying the MSA modified starch, and they were characterized by field emission scanning electron microscopy (FESEM), exhibiting the intriguing porous structure due to the separation of starch chains by MSA molecules. The PSX/MSA were then used as the adsorbents to remove gardenia yellow (GY), a natural colorant with genotoxicity. Due to the porous structure of PSX and the introduced carboxyl groups from MSA, the adsorption capacity of the PSX/MSA was much higher than that of the starch xerogels alone (SX). The adsorption behaviors of GY by the PSX/MSA fitted both the Freundlich isotherm model and the pseudo-second-order kinetic model, and the efficient adsorption of GY suggested that the PSX/MSA might be potential adsorbents for the removal of dyes from contaminated aquatic systems.

1. Introduction

Natural and synthetic dyes were widely used in various industrial fields. However, it has been determined that about 10 percent of the dyes used were wasted and discharged to aquatic systems [1], leading to serious threat to environment and public health [2,3]. Thus, the removal of dyes from wastewater had great environmental importance [4]. At present, different techniques have been proposed for the removal of organic dyes from contaminated water. Among the various techniques, adsorption appeared to be an attractive and acceptable approach for the removal of dyes due to its low cost, ease of handling, high efficiency and no threat of secondary contamination [5–7]. The common adsorbents used for dyes removal primarily included oxidized multiwalled carbon nanotubes [8–10], graphene oxide (GO) [11–14], biomass sources [15–17], activated carbons [18–20], and so on. However, efforts would be still needed for the development of new potentials and effective adsorbents.

Recently, natural polysaccharides-based materials have received increasing attention as highly promising adsorbents due to their low cost, extensive sources, environmental friendliness, as well as biodegradability. More importantly, natural polysaccharides contained abundant active functionalities such as hydroxyl, carboxyl and amino groups, which enabled their further modification for effective dyes removal [1,21–23]. Starch was one of the natural polysaccharides functioning as an important energy source for humans. The native and unmodified starch had little industrial applicability [24]. Therefore, appropriate modifications seem to be an urgent task to obtain starch with extensive applications. Usually, high concentration of acid and base were used for starch modification for breaking the intrinsic H-bonds within starch chains [25], but the residual acid and base can cause secondary contamination to environment when they were discharged to aquatic systems. Recently, monolithic porous rectorite/starch composites were synthesized under moderate conditions that free from the addition of acid or base and successfully used to remove methylene blue (MB) dye [26].

In the present work, mercaptosuccinic acid (MSA) was modified into starch during the gelatinization of potato starch via breaking the intrinsic H-bonds within macromolecular chains of starch. After

* Corresponding author.
E-mail address: yzkongyong@126.com (Y. Kong).

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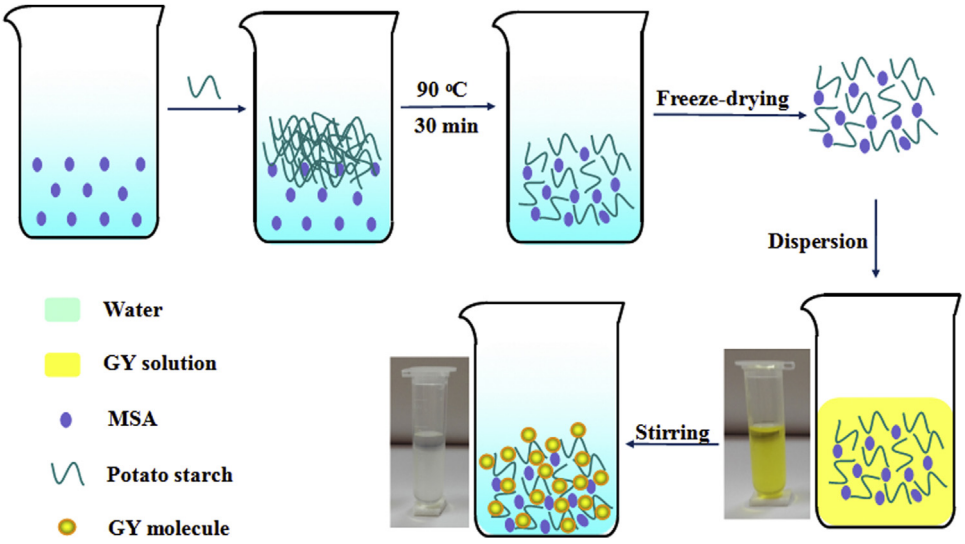

Fig. 1. Schematic illustration showing the whole process of PSX/MSA preparation and GY adsorption by the adsorbents.

freeze-drying, porous starch xerogels (PSX) were formed by inserting MSA molecules into the starch chains. The obtained PSX/MSA were used for the adsorption of gardenia yellow (GY), a natural colorant with genotoxicity [27,28]. Compared with unmodified starch xerogels (SX), the adsorption capacity was significantly enhanced at the PSX/MSA adsorbents due to the formed porous structure of PSX and the introduced —COOH groups from MSA. The adsorption behaviors of GY by the PSX/MSA were investigated, and the results indicated that the adsorption of GY fitted both the Freundlich isotherm model and the pseudo-second-order kinetic model.

2. Experimental

2.1. Reagents and apparatus

Potato starch and MSA were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). Gardenia yellow (GY) was received from Hannuo Industry Co., Ltd (Shanghai, China). Other reagents used were analytical grade and used as received. All solutions were prepared using ultrapure water with a resistivity of 18.2 MΩ. A FD-1A-50 lyophilizer (Shanghai, China) was used for freeze-drying the samples. Field emission scanning electron microscopy (FESEM) was carried out on a Supra55 field emission scanning electron microscope (Zeiss, Germany). Fourier transform infrared (FT-IR) spectra were measured on a Nicolet FTIR-8400S spectrophotometer (Shimadzu, Japan) using KBr pellets, and the UV–vis spectra of GY were measured by using a UV-2450 spectrometer (Shimadzu, Japan).

2.2. Preparation of porous starch xerogels/MSA (PSX/MSA)

First, different amounts of MSA (3, 4 and 5 g) were dissolved in 100 mL ultrapure water under stirring conditions, respectively. Next, 5 g potato starch was added to the MSA solutions, and then the mixtures were heated to 90 °C and stirred for 30 min to form gelatinized composites of starch and MSA. The three gelatinized composites were first frozen at −4 °C in a refrigerator, and then they were freeze-dried in the lyophilizer at −52 °C for 48 h with a pressure of 20 Pa to obtain the PSX/MSA. In order to describe the three samples clearly, the obtained PSX/MSA samples using 3, 4 and 5 g MSA as the reactant were labeled as PSX/MSA3, PSX/MSA4 and PSX/MSA5, respectively. The starch xerogels without addition of MSA (SX) were prepared for control group by the same procedures.

2.3. Adsorption of GY by different adsorbents

Adsorption of GY was performed in glass bottles. 0.2 g of different adsorbents (potato starch, SX, MSA, PSX/MSA3, PSX/MSA4 and PSX/MSA5) were added to 100 mL GY solution at room temperature, and the GY concentration was ranged from 100 to 400 mg L^{-1}. The glass bottles were placed on a magnetic stirrer at 100 rpm for a certain period of time during the adsorption process. Subsequently, the mixtures were centrifuged at 10000 rpm for 15 min to separate the adsorbents and the liquid phase. The GY concentration in the filtrates was determined using the UV–vis spectra of the filtrates at the wavelength of 442 nm, and was assumed to be the equilibrium concentration of GY. The equilibrium adsorption capacity and removal percentage were calculated according to the following two equations:

$$q_e = V(C_0 - C_e)/m \quad (1)$$

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where q_e and %R represent the equilibrium adsorption capacity (mg g^{-1}) and removal percentage; C_0 and C_e are the initial and equilibrium concentration of GY (mg L^{-1}), respectively; V represents the volume of GY solution (L), and m is the mass of the absorbents (g). The whole process showing PSX/MSA preparation and GY adsorption by the adsorbents is depicted in Fig. 1.

3. Results and discussion

3.1. Morphologies of PSX/MSA

FESEM images of pure potato starch, SX and PSX/MSA samples containing different MSA contents were shown in Fig. 2, that pure potato starch consisted of elliptic particles with irregular size ranging from 10 to 30 μm without any pores on its surface (Fig. 2A). However, SX exhibited a quite different wrinkle-shaped structure (Fig. 2B). The water molecules within the gelatinized starch evaporated gradually in the process of freeze-drying, resulting in the self-aggregation of the macromolecular chains of starch. Due to the insertion (during gelatinization) and evaporation (during freeze-drying) of water molecules within the starch chains, SX exhibited an apparent wrinkle-shaped morphology. Of particular interest, a porous structure was observed for all the three PSX/MSA samples, and the number of pores (*ca.* 6–7 μm in diameter) increased