Microwave synthesis and adsorption performance of a novel crosslinked starch microsphere

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HIGHLIGHTS

- CSM was synthesized in a microwave-assisted inversed emulsion system.
- The adsorption of methyl violet on CSM was exothermic and spontaneous.
- The adsorption process followed the pseudo-second-order kinetics.
- The isothermal data obeyed the Langmuir model.
- pH variations did not significantly affect the adsorption of methyl violet onto CSM.

ARTICLE INFO

ABSTRACT

A new crosslinked starch microsphere (CSM) was synthesized in a microwave-assisted inversed emulsion system with soluble starch (ST) as a raw material, MBAA as a crosslinker, and $K_2S_2O_8$–$NaHSO_3$ as an initiator. The synthesized starch microsphere was characterized and examined by scanning electron microscope (SEM), FTIR spectroscopy and adsorption isotherms of N_2 at 77 K. Adsorption performance was investigated in methyl violet solution. The results showed that the maximum adsorption capacity for MV was 99.3 mg/g at 298 K, and the adsorption fitted pseudo-second-order kinetic model well with correlation coefficients greater than 0.99. The isothermal data obeyed the Langmuir model better compared to Freundlich model and Tempkin model, and the adsorption was exothermic and spontaneous. pH variations (2.0–10.0) did not significantly affect the adsorption of MV onto CSM.

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1. Introduction

Among various starch derivatives, crosslinked starch microspheres show high stability toward swelling, high temperature, high shear and acidic conditions [1] and have been the most investigated drug carriers due to their total biodegradability, biocompatibility, non-toxicity, stability on storage, cost-effectiveness as well as simple fabrication method [2–4]. During modification, the physical and chemical properties of starch microspheres can be controlled and adjusted by regulation of the synthesis techniques or by modification of the surface of the groups [5–8], thus starch microspheres have suitable expansion, huge pore volume, high specific area and proper degree of substitution, which can enhance its ability to adsorb dyes and heavy metals, and have great prospects in the water treatment field.

Several preparation approaches of starch microspheres have been investigated, such as spray drying [9], precipitation [10], solvent evaporation [11] and emulsion-crosslinking [3] techniques, among which water-in-oil (w/o) emulsion-crosslinking technique has been extensively used and rapidly developed. In previous studies of the water-in-oil emulsion system, the synthesis reaction of starch microspheres has often been completed in the water bath heating [12]. Compared with the water bath heating synthesis, microwave radiation synthesis is becoming a standard technique applied in starch modification based on its advantages of energy saving, high conversion, and rapidity [13–16]. However, until now no work has covered the microwave radiation synthesis of starch microspheres.

In this paper, a new type of crosslinked starch microsphere (CSM) was synthesized in a microwave-assisted inversed emulsion system with soluble starch (ST) as a raw material, MBAA as a crosslinker, and $K_2S_2O_8$–$NaHSO_3$ as an initiator. The structure and morphology of starch microspheres were characterized by

Table 1
The physical characteristics and molecular structure of methyl violet dye.

Dye name	Methyl violet 2B
Abbreviation	MV
Generic name	Basic violet 1
λ_{max}	586 nm
Color index number	42535
Chemical formula	$C_{24}H_{28} \cdot N_3Cl$
Molecular structure	

scanning electron microscope (SEM), FTIR spectroscopy and adsorption isotherms of N_2 at 77 K. Methyl violet (MV) was employed as a model basic dye. Both equilibrium isotherm and adsorption kinetics were employed to research the mechanism of adsorption of MV in solution by starch microspheres. The aim of this work was to prepare the multifunctional material modified from the natural product in order to realize the efficient adsorption for dyes.

2. Materials and methods

2.1. Materials

Soluble starch was purchased from Jilin COFCO Biochemical Energy Sales Co., Ltd. (Changchun, China) with weight-average molar mass 112,000 g/mol, and the soluble starch was prepared by alcoholic–alkaline treatments with maize as a raw material. Cyclohexane, sodium hydroxide, $K_2S_2O_8$, $NaHSO_3$, anhydrous ethanol, acetone, ethyl acetate, MV were purchased from Tianjin Damao Chemical Reagent Factory, PR China, and Span60, Tween60, MBAA were purchased from Tianjin Kermel Chemical Co., Ltd., PR China. All these reagents were of analytical grade and were applied directly. All solutions were prepared by deionized water. The fundamental characteristics of MV were shown in Table 1.

2.2. Synthesis of CSM with microwave radiation

5 g ST was dissolved in 50 mL distilled water under stirring, regulating the pH to 8.0 by sodium hydroxide, and placed on the turntable of a microwave oven (Galanz P70D20TL-D4, PR China). Then, microwave irradiation was performed at 280 W for 2 min. The solution was added to 150 mL cyclohexane in which 1 g of Span60–Tween60 as dispersion agent was dissolved at 328 K water-bath under reflux. The obtained W/O emulsion was stirred at 2000 rpm for 20 min in an 500 W ultrasonic cleaner (KQ-500D, PR China). Then, 0.75 g of N,N'-methylene bisacrylamide was added and stirred for 2 min. After that, 0.61 g of $K_2S_2O_8$ and 0.14 g $NaHSO_3$ were added. The cross-linking reaction was carried out for 40 min at 333 K in a microwave chemical reactor (MCR-3, PR China). The cross-linked starch microspheres were recovered by centrifugal separation. The residuals were removed by washing the microspheres with ethyl acetate, acetone, and anhydrous ethanol. Then

they were dried in a vacuum oven (DJF-6050, Guangzhou Kangheng Instrument Co., Ltd., PR China) at 323 K for 12 h. Subsequently, they were pulverized and sieved, and a white or pale yellow CSM powder was obtained. The content of the nitrogen of CSM was 1.7%, which was determined according to the Kjeldahl method [17]. The synthetic pathway was shown in Scheme 1.

2.3. Adsorption tests

2.3.1. Adsorption isotherm

The adsorption experiments were carried out in 250 mL Erlenmeyer flasks equipped with stoppers, in which 0.20 g of the CSMs and 200 mL different concentrations of MV were added without changing pH (pH 5.3 ± 0.4). The Erlenmeyer flasks were vibrated at a speed of 150 rpm for 2 h. The temperature was controlled at 298 K, 308 K, and 318 K [18–20]. The absorbance of the solutions was determined with a UV–Vis spectrophotometer (UV–vis752, China) at $\lambda = 586$ nm (operating curve $A = 0.0748C - 0.0458$, $R^2 = 0.9967$). The equilibrium adsorption capacity was calculated according to the following equation:

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

where A, C, Q_e, C_0, C_e, V and m are the solution absorbance, the solution concentration (mg/L), the equilibrium adsorption capacity (mg/g), the initial concentration (mg/L), the equilibrium concentration (mg/L), the solution volume (L), and the mass of CSMs (g), respectively.

2.3.2. Batch kinetic studies

The procedures of kinetic experiments were basically identical to those of adsorption isotherm tests. The aqueous samples were taken at preset time intervals, and the concentrations of dye were similarly measured. All the kinetic experiments were carried out at pH 7.0 ± 0.4 and 298 K. The amount of sorption at time t, Q_t (mg/g), was calculated by [21]:

$$Q_t = \frac{V(C_0 - C_t)}{m} \tag{2}$$

where C_t (mg/L) is the liquid-phase concentrations of dye at any time.

2.3.3. Effect of pH value of the solution

200 mL of dye solution of 100 mg/L initial concentration at different pH values (2.0–10.0) was agitated with 0.20 g of CSM in a water-bath shaker at 298 K. Agitation was made for 120 min at a constant agitation speed of 150 rpm. The pH was adjusted with 0.1 M NaOH and 0.1 M HCl solutions and measured by using a pH meter (PHS-3C, China).

2.4. Characterization methods

2.4.1. Surface area and pore volume [22]

The BET-specific surface area of samples was determined by nitrogen gas adsorption–desorption at 77 K with saturation pressure of 106.65 kPa using a Surface Area and Porosity Analyzer (ASAP 2020, USA). The BET surface area was assessed within the range of relative pressures from 0.05 to 0.3. The total pore volume was calculated by measuring the amount of N_2 adsorbed at a relative pressure of 0.99.

2.4.2. Fourier Transform Infrared (FTIR) spectroscopy

A Thermo Nicolet 380 FTIR Spectrophotometer (Nicolet, USA) and the potassium bromide (KBr) pellet method were used for FTIR study. The FTIR spectra of ST, MBAA, CSM were acquired after