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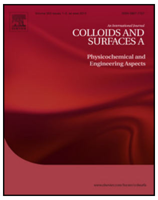

Cross-linkable chitosan-based hydrogel microbeads with pH-responsive adsorption properties for organic dyes prepared using size-tunable microchannel emulsification technique

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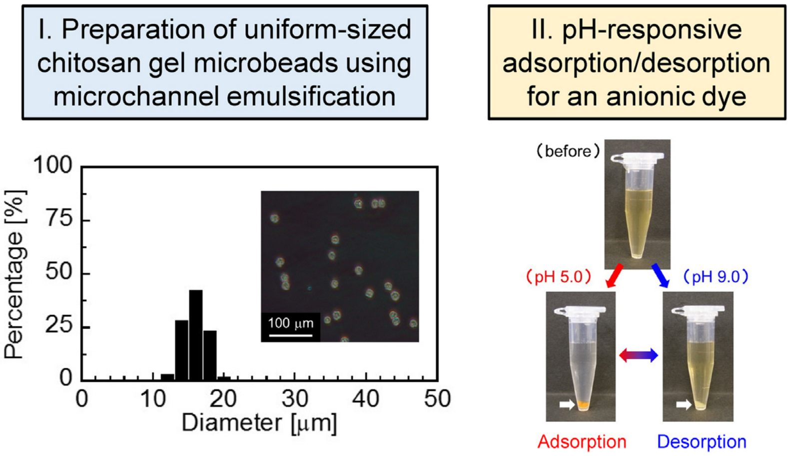
HIGHLIGHTS

- Novel method for preparing highly-uniform chitosan hydrogel beads is proposed.
- Particle formation process by microchannel emulsification was characterized.
- Adsorption properties for an anionic dye were evaluated based on the Langmuir model.
- The chitosan hydrogel beads showed very good stability for long-term use.

GRAPHICAL ABSTRACT



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ABSTRACT

Cross-linked chitosan hydrogel microbeads were prepared from monodisperse water-in-oil (W/O) emulsions and their adsorption properties for an anionic organic dye, Acid Orange 7 (AO7), were investigated. Preparation of monodisperse W/O emulsions with a mean diameter of 22–28 μm and coefficient of variation below 10% were achieved by microchannel (MC) emulsification. The mean diameter and diameter distribution were affected by the viscosity and flow rate of the chitosan solution pressed into MCs. Chitosan gel microbeads were formed by gelation of chitosan-containing water droplets by alkali treatment followed by cross-linking treatment. The resulting microbeads still had a narrow diameter distribution. The pH-responsive adsorption property of chitosan gel microbeads was studied using AO7. The experiment results indicated that negatively charged AO7 molecules adsorbed onto positively charged chitosan gel microbeads via electrostatic interaction. The chitosan gel microbeads were stable for more than 100 days and could be reused in repetitive adsorption-desorption cycles.

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1. Introduction

Chitosan is a polysaccharide consisting of D-glucosamine linked linearly by β-1,4 glycosidic bonds, and it is derived from chitin via deacetylation reaction. Recently, chitin and chitosan have attracted much attention because they exist abundantly on the earth and are expected to be utilized as renewable materials from naturally occurring polysaccharide bioresources. In particular, chitosan has unique physicochemical properties derived from the large number of primary amino groups in its molecule; these are protonated in acidic solutions. Thus, functionalization and application of chitosan-based materials have been widely investigated in various fields [1].

One of the most important and promising applications of chitosan is utilization as an adsorption material. The primary amino groups of chitosan are protonated (deprotonated) under acidic (alkaline) pH conditions because the pKa value of amino groups in chitosan is reportedly 6.3–7.0 [2,3]. Based on this characteristic, chitosan can act as a pH-responsive adsorbent. To date, various adsorptive properties have been demonstrated for treating waste water containing dyes [4–6] and heavy metal ions [7,8], solid phase extraction and chromatographic separation in biotechnological fields [9], and controlled release in drug delivery systems [10–13]. These have been achieved mainly via electrostatic interaction between protonated chitosan and negatively charged adsorbates or formation of chelates. For these usages, the biodegradability, biocompatibility, and low toxicity of chitosan are more advantageous than those of synthetic adsorption materials.

There are various requirements for a chitosan-based adsorption material. (1) Size controllability: the diameter of adsorbent particles and their distribution are important factors that affect the adsorption performance of materials because their separation properties are dominated by mass transfer near and/or inside particles [14] and because broad size distribution often causes the difficulty in the practical operation. (2) Particle stability: repetitive and long-term usage under various conditions is required. (3) Adsorption capacity: a high adsorption capacity is advantageous for a separation material. To satisfy these requirements, novel precise preparation techniques and qualitative/quantitative characterization of fine chitosan particles are desired.

The simplest method for preparing particulate chitosan is direct usage of dry powders of native and chemically modified chitosans. This method can be applied for mass production with low cost, although it is difficult to obtain small, uniform-size particles. Utilization of template droplets consisting of chitosan solution is a promising way to obtain size-controlled chitosan beads. Membrane emulsification [15] is a technique for preparing emulsion droplets with a narrow size distribution, and monodisperse and quasi-monodisperse chitosan gel beads have been prepared via physical or chemical gelation of chitosan-containing droplets prepared by membrane emulsification [10–13,16–20]. The effects of various process parameters such as the chitosan concentration and flow rate of chitosan solution on the characteristics of chitosan beads have been investigated. In addition, Mark et al. reported another droplet-based method for preparing relatively larger chitosan beads (ranging from 148 to 257 μm) using a polymeric micronozzle [21].

In the last two decades, a microchannel (MC) emulsification technique for preparing very uniform emulsion droplets has been developed and investigated to extend its application field [22–24]. In this method, monodisperse (coefficient of variation: CV < 5%) emulsion droplets can be obtained by mixing dispersed phase and continuous phase via MCs fabricated on single-crystal silicon, polymer, or stainless-steel plates. In MC emulsification, droplets are generated spontaneously via an interfacial tension-driven process [25] without generating severe shear force and heat. Recently, a remarkable improvement in droplet productivity has been achieved using high-density integration of MCs on a plate (>10^4–10^5 MCs per plate) [23,26,27]. Since the individual droplet generation process can be directly observed under a microscope, an analysis of the MC emulsification behavior provides valuable information about emulsification performance based on the visualization of the effect of various process parameters such as the viscosity of both phases and the interfacial tensions. The usefulness of an analysis based on computational fluid dynamics has been also demonstrated [28–30]. Therefore, the MC emulsification technique has attracted attention as not only a production process alternative but also as a unique and powerful tool for scientific study.

This study investigated the preparation of uniform-sized chitosan gel microbeads using MC emulsification followed by physical and chemical gelation of chitosan-containing emulsion droplets. This is the first report of the preparation of chitosan-containing emulsion and chitosan gel microbeads using the MC emulsification technique. To clarify the effect of various process parameters such as chitosan concentration and flow rate of chitosan solution on the emulsification, MC emulsification was performed under various conditions. Using the obtained chitosan-containing emulsions, chitosan gel microbeads were then prepared by a two-step gelation process: physical gelation with alkali treatment to deprotonate the amino groups of chitosan followed by a chemical cross-linking reaction using ethylene glycol diglycidyl ether (EGDE). Since chitosan is soluble in acidic solutions, stabilization by chemical cross-linking improves the stability of the chitosan gel microbeads. With this treatment, the microbeads can be applied under widely varying pH conditions. In addition, the adsorption properties of chitosan gel microbeads were evaluated using an anionic dye, Acid Orange 7 (AO7), to clarify the adsorption ability of the obtained microbeads. The amino group-based pH responsive adsorption behavior, an analysis of adsorption capacity based on the Langmuir model, long-term stability, and reusability were all examined. We believe that this paper contains a set of useful findings about chitosan gel microbeads from preparation to application.

2. Materials and methods

2.1. Materials

Chitosan (chitosan 100D) was kindly donated by Dainichi Seika Inc. Ltd (Tokyo, Japan). The degree of deacetylation of this chitosan was 97%, and the average molecular weight determined from a viscometric method according to Wang et al. [31] was 360 kDa. Span 85 (sorbitan trioleate) and Tween 85 (polyoxyethylene (20) sorbitan trioleate) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Isooctane was purchased from Kanto Chemical Co., Inc. (Tokyo Japan). Ethylene glycol diglycidyl ether (EGDE) and Acid Orange 7 (AO7) were obtained from Tokyo Chemical Industry, Co., Ltd. (Tokyo, Japan). The water used in all experiments was prepared with a Direct-Q water purified system (Merck Millipore Corporation, Billerica, USA) and had a resistivity of 18.2 MΩ cm. All other chemicals were from Wako Pure Chemical Industries and were of extra pure grade.

2.2. Microchannel emulsification for producing monodisperse W/O emulsions containing chitosan

Isooctane containing 5 wt% of Span 85 was used as a continuous phase for preparing W/O emulsions. The continuous phase was saturated with water before use to prevent solubilization of prepared water droplets into the continuous isooctane phase. Chitosan solution buffered with 100 mM acetic acid/sodium acetate (pH 5.0) was used as a to-be-dispersed phase. A laboratory-scale

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