Synthesis of Insoluble β-Cyclodevrin Polymer Microspheres for Removal of Organics in Aqueous Solution

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Abstract

Insoluble β-cyclodextrin-epichlorohydrin polymer microspheres can be used in many kinds of environmental applications to remove organics in aqueous solutions and air. Insoluble β-cyclodextrin-epichlorohydrin polymer (β-CD-EP) microsphere were synthesized using inverse suspension polymerization method and the influence of crosslinking agent dosage, temperature, stirring speend and emulsifier dosage on the particle size of microspheres was studied using particle size measurements. The optimal dosage of crosslinking agent occured at EP/CD=12. High EP/CD molar ratio can lead to excessive crosslinking and thus gets microspheres with larger particle size. The average particle size of the microspheres dereaced with the increasing reaction temperature, stirring speed and emulsifier dosage. The increasing stability of water in oil emulsions helps to decrease the particle size of the dispersed phase and thus helps to get microspheres with smaller particle size.

Keywords

Synthesis, insoluble, β-Cyclodextrin polymer, microspheres, particle size.

1. Introduction

The discharge of organics into water and air has become a more and more serious problem and how to cope with the organics in aqueous solutions and air has become a more and more urgent task all over the world [1].

Activated carbons (abbreviated as AC) are the most widespread adsorbent materials used to remove organic pollutants from water and air [2-3], but ACs have several deficiencies such as slow pollutant uptake and poor removal of many relatively hydrophilic micropollutants [4].

Water-insoluble β-cyclodextrin-epichlorohydrin polymers have received more and more attention in many kinds of environmental applications recent years and the polymers show good prospects for application in organic's removal, recycling and utilization from aqueous solutions or gas [1,5]. β-cyclodextrin is known to encapsulate pollutants to form well-defined host–guest complexes and can be regenerated several times using a mild washing procedure with no loss in performance [5]. Mesoporous polymer of β-cyclodextrin can rapidly sequesters a variety of organic micropollutants with adsorption rate constants 15 to 200 times greater than those of ACs and non-porous β-cyclodextrin adsorbent materials [5, 6].

In this paper, a kind of insoluble β-cyclodextrin polymer microspheres was synthesized and the influence of crosslinking agent dosage, temperature, stirring speend and emulsifier dosage on the particle size of microspheres was studied to optimize the synthesis conditions.

2. Experimental

2.1 Materials

Acrylamide (AM, AR) was twice recrystallized from acetone (AR) and then dried under vacuum. β-cyclodextrin (β-CD, AR), epichlorohydrinand (EP, AR), sodium hydroxide (NaOH, AR), sodium carbonate (Na_2CO_3, AR) and ethanol (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. All aqueous solutions were prepared using deionized water.

Diesel (0#) which is used as the oil phase was commercially available products purchased in Sinopec gas station. The emulsifiers of Span 80 and Tween 20 were obtained from Sinopharm Chemical Reagent Co., Ltd., and their HLB is 4.3 and 16.7, respectively.

2.2 Synthesis of insoluble β-cyclodevrin polymer microspheres

Preparation of β-CD-EP microsphere was achieved by the reaction of β-CD with epichlorohydrin (EP) in an alkaline medium by inverse suspension polymerization described in literature [7-10].

The procedure for preparing β-CD-EP microsphere was described as follows: firstly, β-CD was dissolved in NaOH solution (33 wt%) and stirred at a stirring speed untill β-CD was completely dissolved. Then, EP was added in dropwise while the mixture was heated gently to the predetermined temperature. The reaction mixture was polymerized under vigorous stirring for 2 h. Secondly, the reaction mixture was dripped into diesel (with Span 80 and Tween 20 (3:1) dissolved as the emulsion stabilizer) using a funnel under vigorous stirring. The polymerization was allowed to proceed for another 3 h. Finally, β-CD-EP microspheres were separated from the oil phase and were washed with ethanol and water for several times and then dried in vacuum oven at 60 °C for 12 h.

2.3 Particle size measurements of β-cyclodevrin polymer microspheres

Particle size distribution was analyzed by Rise-2008 laser particle size analyzer (Jinan Rise Science & Technology Co., Ltd., China) according to the full range Mie scattering theory at room temperature. The measurement range is 0.02~1200 μm.

3. Results and discussion

The influence of crosslinking agent dosage, temperature, stirring speend and emulsifier dosage on the particle size of microspheres was studied and the resulets are shown in Fig. 1~Fig. 4.

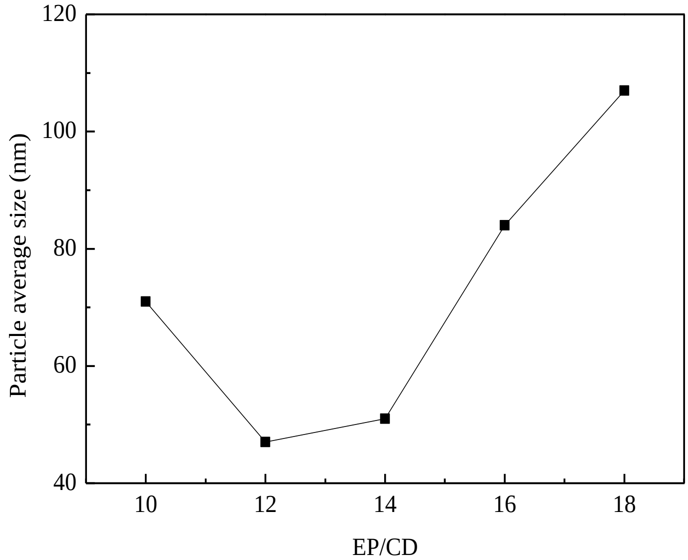

Fig.1 Influence of the dosage of crosslinking agent on microspheres size
(70℃, 600rpm, emulsifier dosage 4%)

As shown in Fig. 1, the average particle size of the microspheres dereaced firstly and then increased with the increasing crosslinking agent dosage and the optimal dosage of crosslinking agent occured at EP/CD=12. High EP/CD molar ratio can lead to excessive crosslinking and thus gets microspheres with larger particle size.

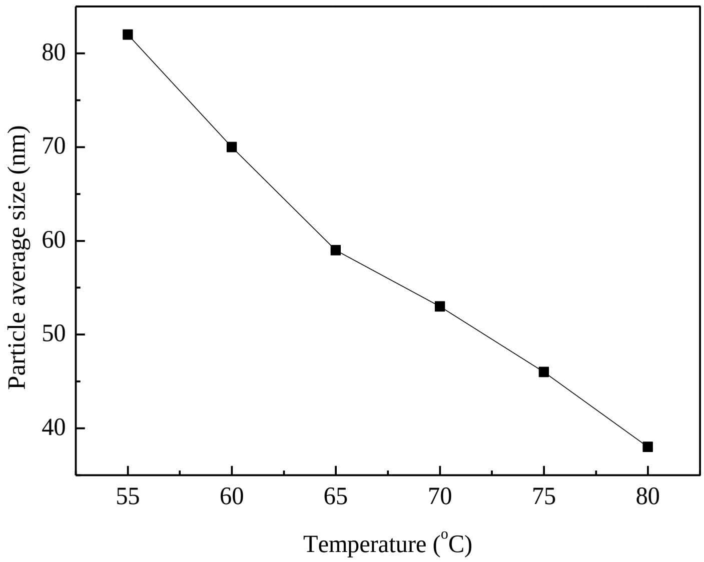

Fig.2 Influence of reaction temperature on microspheres size
(EP/CD=10, 600rpm, emulsifier dosage 4%)

Fig. 2 showed the influence of reaction temperature on microspheres size. The average particle size of the microspheres dereaced with the increasing reaction temperature. The reason is mainly because the emulsifiers are all nonionic surfactants and the HLB of the nonionic surfactants decreases with the increasing temperature. Emulsifiers with smaller HLB values tend to form more stable water in oil emulsions and thus helps to form microspheres with smaller particle size.

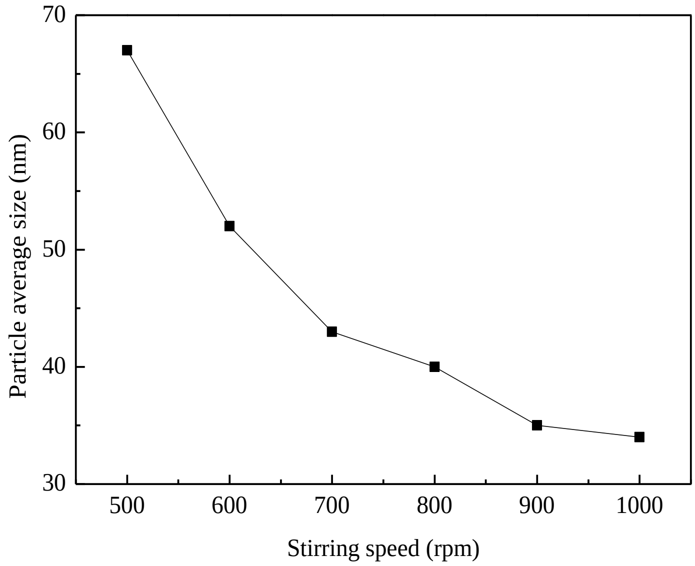

Fig. 3 Influence of stirring speed on the microspheres size
(70℃, EP/CD=10, emulsifier dosage 4%)

Fig. 3 showed the influence of stirring speed on the microspheres size of microspheres. The average particle size of the microspheres dereaced with the increasing stirring speed. Obviously, the stability of water in oil emulsions get more stable at high stirring speed and thus helps to form microspheres with smaller particle size, similar to the case as discussed above.

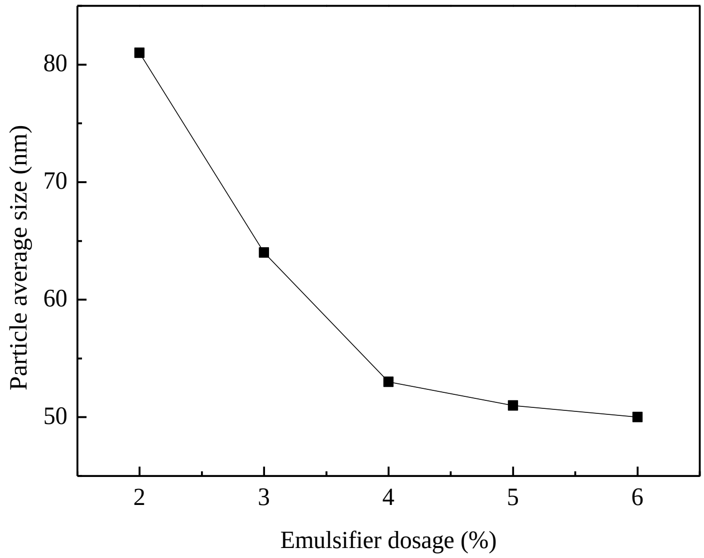

Fig. 4 Influence of emulsifier dosage on the microspheres size
(70℃, 600rpm, EP/CD=10)

Fig. 4 showed the influence of emulsifier dosage on the microspheres size of microspheres. The average particle size of the microspheres dereaced with the increasing emulsifier dosage. Obviously, the stability of water in oil emulsions get more and more stable as the emulsifier dosage increasd. The increasing stability of W/O emulsions helps to decrease the particle size of the dispersed phase and thus helps to get microspheres with smaller particle size.

4. Conclusion

Insoluble β-cyclodextrin-epichlorohydrin polymer microsphere was synthesized and the influence of crosslinking agent dosage, temperature, stirring speend and emulsifier dosage on the particle size of microspheres was studied. The average particle size of the microspheres dereaced firstly and then increased with the increasing crosslinking agent dosage and the optimal dosage of crosslinking agent occured at EP/CD=12. High EP/CD molar ratio can lead to excessive crosslinking and thus gets microspheres with larger particle size. The average particle size of the microspheres dereaced with the increasing reaction temperature, stirring speed and emulsifier dosage. The increasing stability of W/O emulsions helps to decrease the particle size of the dispersed phase and thus helps to get microspheres with smaller particle size.

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