

# Preparation of Cellulose–Tungsten Carbide Composite Beads with Ionic Liquid for Expanded Bed Application

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**ABSTRACT:** Expanded bed adsorption (EBA) is an integrated technology for capturing target biomolecules directly from unclarified feedstock. The adsorbents should be designed specially to ensure the perfect performance of the expanded bed. In this study, an ionic liquid (IL), 1-butyl-3-methylimidazolium chloride, was used to dissolve cellulose directly to prepare cellulose–tungsten carbide composite beads with water-in-oil suspension and cooling/ethanol regeneration. The preparation conditions were optimized, especially for four key factors, the cellulose concentration, ratio of the oil phase to the cellulose solution, stirring speed, and addition of tungsten carbide powder. The results showed that the tungsten carbide powder

emerged well in the cellulose matrix as an inert densifier. The composite beads had a spherical appearance, a suitable size and size distribution, an appropriate wet density of 1.32–1.68 g/mL, a porosity of 90–96%, a pore radius of 45–65 nm, and a specific surface area of 30–42 m<sup>2</sup>/mL. These results show the potential application for this EBA process. Compared to the traditional technology with cellulose xanthate viscose, the new method with the IL as the nonderivatizing dissolution solvent is technically feasible, has concise processing, and is environmentally friendly. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3453–3461, 2011

**Key words:** adsorption; composites; matrix

## INTRODUCTION

Expanded bed adsorption (EBA) is one of the most promising and practical purification operations of the past 20 years; it allows the adsorption of target proteins directly from unclarified feedstock, such as fermentation broth, cell homogenate, or crude extract. EBA technology integrates solid–liquid separation, concentration, and primary purification into a single-unit operation, which certainly increases the overall yield and reduces the operational time and the cost for capital investment and consumables.<sup>1–3</sup> An improvement in the efficiency of EBA has been proven in many bioprocess cases.<sup>4</sup> Unlike packed beds, EBA adsorbents are expanded in the column at an expansion range of 2–3, which can prevent the blocking of particle-containing feedstock. To ensure the unique performance of the expanded bed, the adsorbents should be designed specially. Generally, the adsorbents have high densities to increase the operation velocity of the fluid phase and relatively wide size distributions to form perfectly classified

fluidization of the adsorbent particles in the column. Normally, the ratio of the largest particle diameter to the smallest one should be higher than 2.2.<sup>5</sup>

During the past 20 years, several kinds of EBA adsorbents have been developed.<sup>6</sup> In the early 1990s, a series of Streamline adsorbents were developed and marketed by Amersham Biosciences (now GE Healthcare, Uppsala, Sweden) as first-generation adsorbents for expanded beds. Streamline adsorbents are based on 6% crosslinked agarose containing a crystalline quartz core as the densifier and have particle sizes in the range 100–300 μm and a mean density of about 1.2 g/mL. Recently, GE Healthcare developed new generation of EBA adsorbents (named Streamline Direct) with a higher density of 1.8 g/mL and sizes in the range 80–165 μm.<sup>7</sup> Meanwhile, the Fastline<sup>8</sup> and HyperZ<sup>9</sup> series adsorbents were developed by UpFront Chromatography A/S (Copenhagen, Denmark) and Pall BioSeptra (Christophe, France), respectively. In addition, some new materials, such as agarose–Nd–Fe–B alloy,<sup>10</sup> agarose–glass beads,<sup>11</sup> cellulose–titanium oxide,<sup>12</sup> cellulose–stainless steel,<sup>13</sup> cellulose–nickel powder,<sup>14</sup> cellulose–tungsten carbide,<sup>15</sup> dextran–silica,<sup>16</sup> and polyvinyl alcohol–perfluorocarbon,<sup>17</sup> have been studied in laboratories.

Polysaccharides, include agarose, dextran, and cellulose, are the most important resource for preparing chromatographic matrixes because of their excellent hydrophilicity, chemical modification, mechanical strength, and low nonspecific adsorption. As we

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know, cellulose is one of most abundant and low-cost natural polymers. In the 1970s, Peska et al.<sup>18</sup> developed a method for preparing cellulose beads on the basis of the thermal sol-gel transition process of cellulose xanthate viscose.<sup>18</sup> From then on, porous cellulose beads have been widely used for chromatographic separation. To prepare cellulose beads, the first step is to dissolve cellulose to obtain a viscous solution. However, the processing and derivatization of cellulose are quite difficult because of the strong hydrogen bonds and partially crystalline structure of the natural cellulose resource. Traditional methods based on cellulose xanthate viscose are technologically complex and brings some environmental burdens, which involve the use of hazardous chemicals and the exhaust of some toxic gases. Over the past decades, several new solvents have been developed to dissolve cellulose, including lithium chloride (LiCl)/*N,N*-dimethylacetamide, LiCl/*N*-methyl-2-pyrrolidone, LiCl/1,3-dimethyl-2-imidazolidinone, dimethyl sulfoxide/paraformaldehyde, *N*-methyl-morpholine-*N*-oxide, aqueous solutions of NaOH, some molten salt hydrates, and aqueous solutions of metal complexes.<sup>19</sup> However, these solvents are still limited by their dissolution capability, environmental problems, solvent recovery, and uncontrollable side reactions.

In 2002, Swatloski et al.<sup>20</sup> reported the use of an ionic liquid (IL) as a solvent for cellulose, both for the regeneration of cellulose and for the chemical modification of the polysaccharide. After that, great attentions has been paid to this new field.<sup>21–23</sup> As we know, ILs are a group of salts that exist as liquids at relatively low temperatures (<100°C); these are considered a new generation solvents for cellulose with many attractive properties, including chemical and thermal stability, nonflammability, and an immeasurably low vapor pressure. The dissolution of cellulose in ILs is a nonderivatizing process, which has been used successfully to prepare regenerated cellulose films and fibers.<sup>24,25</sup> Among the different ILs used, 1-butyl-3-methylimidazolium chloride (BmimCl) is one of the most appropriate dissolving solvents for cellulose resources. BmimCl has the ability to dissolve cellulose with degrees of polymerization in the range 290–1200 and can obtain a high cellulose concentration of 10 wt % when it is heated to 100°C.<sup>20</sup>

In our previous study, a series of cellulose-densifier composite beads were prepared with cellulose xanthate viscose for EBA applications.<sup>12–15</sup> However, as mentioned previously, the preparation of cellulose xanthate viscose is time consuming and restricted by operational complexity and environmental problems. In this study, IL of BmimCl was used as a nonderivatizing green solvent to dissolve cellulose and to prepare cellulose-tungsten carbide composite beads.

Here, tungsten carbide powder was used as an inert densifier with a high density. Water-in-oil suspension was applied to prepare beads with a relatively wide size distribution, which is essential for EBA application, as mentioned previously. The regeneration of cellulose beads from IL was explored, and some important factors, such as the cellulose concentration, densifier addition, stirring speed, and ratio of the oil to the cellulose solution, were optimized. The properties, including wet density, size distribution, water content, porosity, pore volume, pore radius, and specific surface area, of the composite beads were studied for potential applications as EBA matrices. Some comparison of the cellulose beads made by IL dissolution and the technology of cellulose xanthate viscose are discussed, too.

## EXPERIMENTAL

### Materials

Refined cotton with a polymerization degree of 1070 was purchased from Haiyan Refined Cotton Co., Ltd. (Zhejiang, China). BmimCl was purchased from Tianxudong Technology Co., Ltd. (Shenzhen, China). Tungsten carbide powder with a density of 15.0 g/cm<sup>3</sup> and a mean particle diameter of 2–5 μm was ordered from Huagong Wearable Material Co. (Sichuan, China). Vacuum-pump oil was purchased from Sifang Special Oil Factory (Beijing, China). All other reagents were analytical reagent grade and were purchased commercially.

### Preparation of the composite beads

The cellulose-tungsten carbide composite beads were prepared with water-in-oil suspension and cooling/solvent regeneration. Typically, 2 g of refined cotton was dissolved in 50 mL of BmimCl at 95°C under an agitation of 150 rpm to obtain a 4% cellulose solution. Then, an appropriate amount of tungsten carbide powder (12.5–30 g) was added to the cellulose solution and homogenized by continuous agitation for 20 min. The cellulose solution/tungsten carbide mixture was dispersed in the oil phase (vacuum oil with 2% Tween 80 added) in a 500-mL flask with agitation at high speed (750–800 rpm) for 20 min at 90°C. With continuous stirring, the temperature was dropped to 40°C by a decrease of 5°C every 15 min. Then, ethanol was slowly added to the suspension to further regenerate the cellulose beads from IL. After 5 min, the temperature was decreased to room temperature. Then, the resulting beads were filtered out and washed five times with ethanol. Finally, the beads were washed with water and stored in 20% ethanol. By screening with standard sieves, the cellulose-tungsten carbide

composite beads with a particle size range of 75–300  $\mu\text{m}$  were obtained.

### Measurement of the physical properties

The shapes and structures of the composite beads were observed by a TM-1000 scanning electron microscope (Hitachi Instruments, Tokyo, Japan) and a Nikon E200 microscope (Nikon Jiangnan Optical Instruments, Nanjing, China). The particle size distribution and mean particle diameter ( $D$ ) was determined with a laser particle size analyzer (Mastersizer 2000, Malvern Instruments, Worcestershire, United Kingdom).

The wet density ( $\rho_p$ ; g/mL of wet particles) was measured by water replacement in a 5-mL gravity bottle. The water content ( $\omega$ ) was obtained by dehydration at 120°C to a constant mass. With the presumption that all pores in the beads were full of water, the porosity ( $P$ ; %), which expresses the pore volume per volume of wet particles, and the pore volume ( $V$ ; mL/g of dry particle), which expresses the volume per gram of dried particles, were roughly estimated as follows, in which  $\rho_w$  represents the density of water<sup>26</sup>:

$$P = \frac{\rho_p \omega}{\rho_w} \times 100\% \quad (1)$$

$$V = \frac{\omega}{(1 - \omega)\rho_w} \quad (2)$$

The specific surface area ( $S$ ;  $\text{m}^2/\text{mL}$ ) was measured by the adsorption of methylene blue solution and was calculated as follows<sup>27</sup>:

$$S = \frac{(c_0 - c)G\rho_p}{m_p} \times 2.45 \quad (3)$$

where  $C_0$  and  $C$  represent the initial and equilibrium concentrations of methylene blue solution,  $G$  represents the volume of added methylene blue solution, and  $m_p$  represents the mass of the sample particles, respectively. The constant 2.45 ( $\text{m}^2/\text{mg}$  of methylene blue) indicated that 1 mg of methylene blue could cover an area of 2.45  $\text{m}^2$  with the assumption of monomolecular-layer adsorption.

According to the cylindrical pore structural model, the mean pore radius ( $R$ ; nm) was estimated as follows<sup>28</sup>:

$$R = 2 \times 1000 \times \frac{V(1 - \omega)\rho_p}{S} \quad (4)$$

## RESULTS AND DISCUSSION

To obtain spherical cellulose–tungsten carbide composite beads with the method of IL dissolution,

some important preparation conditions, such as the dissolution temperature with IL, cellulose content, dispersion system, cooling control, and ethanol addition, were investigated first. After that, four key factors, the cellulose concentration, ratio of the oil phase to the cellulose solution, stirring speed, and addition of tungsten carbide powder, were studied in detail to optimize the bead size, wet particle density, and porous properties for potential application for EBA.

### Preparation of the spherical cellulose composite beads

The preparation of cellulose composite beads with water-in-oil suspension mainly included three procedures, cellulose dissolution, the dispersion of the cellulose solution in the oil phase, and the regeneration of cellulose beads, as shown in Figure 1.

First, cellulose was dissolved in IL of BmimCl to obtain a homogeneous viscous solution. Some factors, such as the dissolution temperature, dissolution time, and cellulose content, were studied. The dissolution rate was improved with increasing dissolution temperature. At a dissolution temperature of 95°C, a 4 wt % cellulose solution was prepared in 40 min. An increase in the cellulose content caused a longer time to dissolve, and the composite beads were hard to form when the cellulose solution was too viscous. On the contrary, a too-low viscosity of cellulose solution led to the conglutination of beads. In this study, the appropriate cellulose content was chosen as 2–5%, and the cellulose solution could be prepared in 40 min at 95°C. For the preparation of cellulose xanthate viscose as in the previous study,<sup>12</sup> some additional chemicals (e.g., alkali and carbon disulfide) were needed, and the procedures lasted about 60 h and included alkalization, aging, etiolation, and dissolution. Moreover, the complicated procedure led to some instability of viscose quality for different batches. Therefore, compared to the traditional method of cellulose xanthate viscose, the nonderivatizing dissolution of cellulose with IL reduced the preparation time and improved the quality of the cellulose viscous solution and prevented the use of hazardous chemicals.

During the dispersion of the cellulose solution in the oil phase, the important factors were the ratio of the oil phase to the cellulose solution and the stirring speed. When the stirring speed was too fast or the ratio of the oil phase to the cellulose solution was lower than 2, some bead conglutination was observed because of droplet collision. On the contrary, when the stirring speed was below 300 rpm, it was difficult to disperse the cellulose viscous solution in the oil phase. The results indicate that the appropriate stirring speed was in the range 500–900

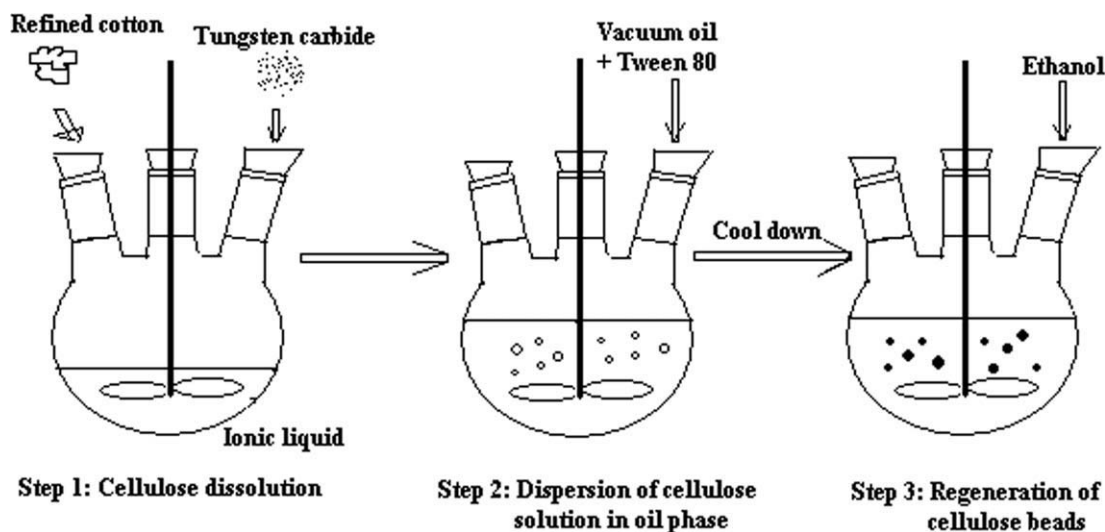


Figure 1 Scheme of the main procedures for the preparation of the cellulose composite beads.

rpm, and the appropriate ratio of the oil phase to the cellulose solution was in the range 3–6.

For the regeneration of cellulose beads from IL, a combination of cooling and solvent addition was used in this study. The cooling procedure was optimized by a decrease of 5°C/15 min from 90 to 40°C. However, after cooling, the beads formed were loose and easy to break. The reason might have been the slowness of cellulose regeneration from BmimCl. To accelerate the regeneration procedure, some solvents for BmimCl were added, including water, ethanol, and acetone. After comparison, the spherical shape of the composite beads was improved significantly when some of ethanol was added as a regeneration solvent. Typically, the addition of 100 mL of ethanol for 200 mL of the oil phase was suitable. Compared to the traditional method of cellulose xanthate vis-

cose, which exhausts some toxic gases (e.g., hydrogen sulfide) during the regeneration procedure, the new technology with IL dissolution in this study is more environmentally friendly, especially for a large-scale process.

Figure 2 shows the prepared cellulose composite beads. The prepared composite beads had a spherical appearance and a certain particle size distribution, which are essential for EBA application. It was hard to find crack and adhesion of particles during the preparation. Figure 3 shows the morphology of the composite beads as determined by scanning electron microscopy. The results demonstrate the new method with IL (BmimCl), as the direct-dissolution solvent was technically feasible and the spherical cellulose composite beads could be prepared in a relative easy, time-saving, and environmentally

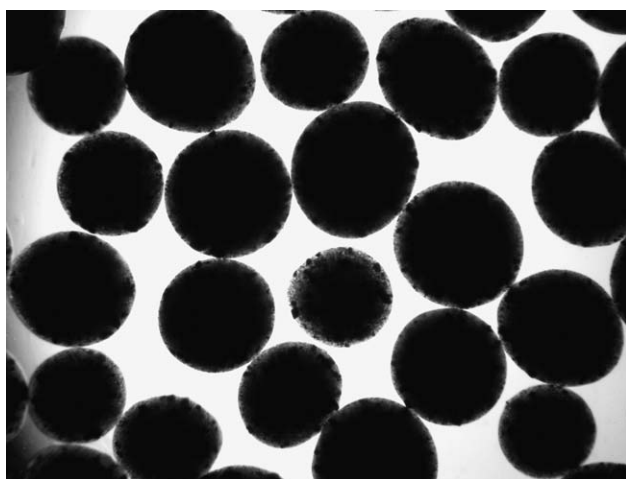


Figure 2 Photographs of the composite bead appearance.

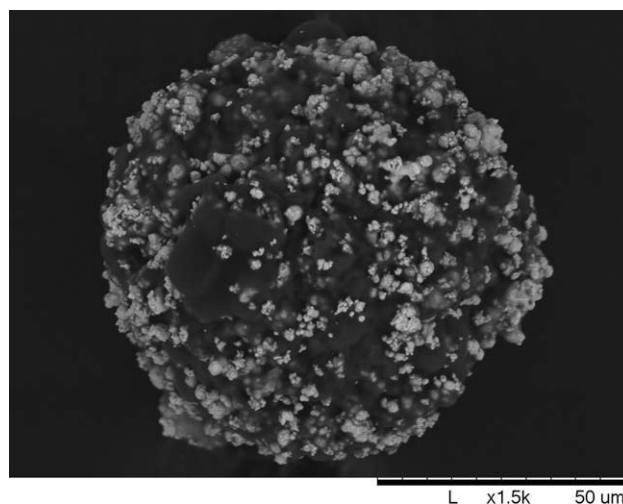
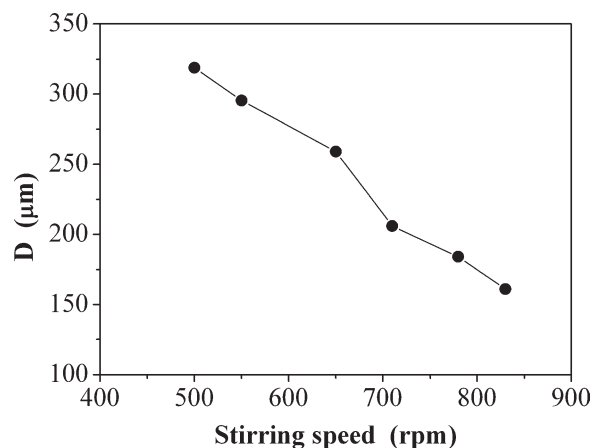


Figure 3 Morphology of the composite beads as determined by scanning electron microscopy.



**Figure 4** Effect of the stirring speed on the mean particle diameter ( $D$ ) of the cellulose beads. The cellulose concentration was 3%, the ratio of the oil phase to the cellulose solution was 5, and the addition of tungsten carbide was 0.3 g/g of cellulose solution.

friendly way. In the following study, some important preparation factors, such as the cellulose concentration, densifier addition, stirring speed, and ratio of the oil to the cellulose solution, were studied further to meet the requirements of applications as EBA matrices. Three aspects of the bead properties, including the bead size and size distribution, wet density, and porous structure, were explored.

#### Bead size and size distribution

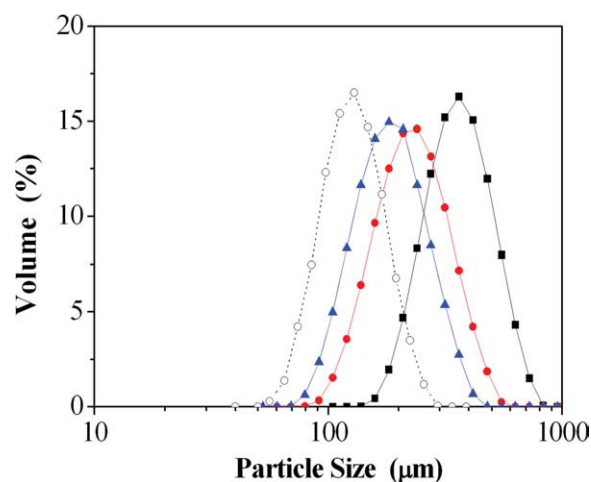
The bead size is one of most essential properties for the chromatographic matrix and determines the separation efficiency. Several factors that affected the bead size during preparation were studied; these included the cellulose concentration, ratio of the oil to the cellulose solution, stirring speed, and addition of tungsten carbide powder. The stirring speed was found to be the key factor in controlling the bead size. As shown in Figure 4, the mean size of the composite beads decreased significantly as the stirring speed increased. With a low stirring speed of 500 rpm, the dispersion of the cellulose solution in the oil phase was inadequate, and the resulting beads were a little large, with a mean diameter of 320  $\mu\text{m}$ . As we know, large beads have strong limitations on the mass transport for adsorption processes. When the stirring speed was higher than 700 rpm, the mean particle size was lower than 200  $\mu\text{m}$ , which would be suitable for EBA application. Therefore, the optimum stirring speed was chosen as 780 rpm in this study to control the mean bead size at about 200  $\mu\text{m}$ ; this is a normal bead size for EBA application, as in previous studies.<sup>12–15</sup> In addition, the ratio of the oil/water phase also influenced the dispersion of the cellulose solution in the oil phase and played an important role in the beads size. The results indicate that the mean beads

size increased from 150 to 260  $\mu\text{m}$  when the oil/water ratio increased from 3 : 1 to 6 : 1. The suitable oil/water ratio was chosen as 5 : 1. Furthermore, the cellulose concentration and tungsten carbide addition in the ranges tested in this study had little impact on the bead size.

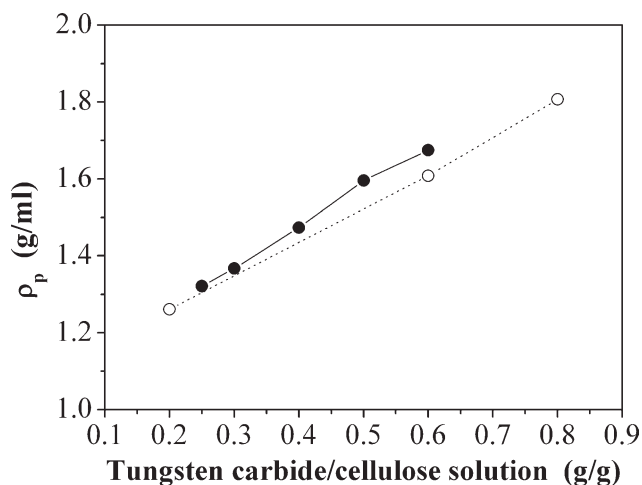
The size distribution of the composite beads is another important characteristic for EBA to form perfectly classified fluidization in the column. Generally, the beads should have a symmetrical size distribution, and the ratio of the largest particle diameter to the smallest one should be higher than 2.2.<sup>2</sup> The size distributions of prepared composite beads are shown in Figure 5. The composite beads showed a good logarithmic, symmetrical, and relatively wide distribution of particle size. For example, with a cellulose concentration of 4%, a ratio of the oil to the cellulose solution of 5 : 1, a stirring speed of 780 rpm, and the addition of tungsten carbide powder of 30%, the prepared beads had a size distribution of 80–300  $\mu\text{m}$  with a mean size of 180  $\mu\text{m}$ ; this should be suitable for EBA application. As shown in Figure 5, compared to the cellulose–tungsten carbide composite beads prepared with cellulose xanthate viscose, the composite beads prepared in this study had a little larger size and wider size distribution.

#### Wet density

The wet density of composite beads determines the operational velocity of the fluid phase in expanded



**Figure 5** Size distribution of the composite beads prepared with different stirring speeds: (▲) 780, (●) 710, and (■) 500 rpm. The cellulose concentration was 3%, the ratio of the oil phase to the cellulose solution was 5, and the addition of tungsten carbide was 0.3 g/g of cellulose solution. For comparison, (○) the size distribution of the composite beads prepared with cellulose xanthate viscose is also shown. The data are from the literature.<sup>15</sup> [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6** Wet density ( $\rho_p$ ) values of the composite beads as the function of tungsten carbide addition. The cellulose concentration was 4%, the ratio of the oil phase to the cellulose solution was 5, and the stirring speed was 780 rpm. For comparison, (○) the wet density values of the composite beads prepared with cellulose xanthate viscose are also shown. The data are from the literature.<sup>29</sup>

beds. To increase the productivity of the EBA process, adsorbents with high densities have recently been in demand. In this study, tungsten carbide powder with a density of 15.0 g/mL was used as the densifier, so the adjustment of tungsten carbide addition during the preparation might have been the main factor in controlling the wet density of the prepared composite beads. The wet density values of the composite beads prepared as a function of tungsten carbide addition are shown in Figure 6. The wet density increased linearly with increasing tungsten carbide addition. The results indicate that the tungsten carbide as the densifier was successfully entrapped within the cellulose skeleton to gradually increase the wet density of the composite beads. For comparison, the wet density values of cellulose–tungsten carbide composite beads prepared with cellulose xanthate viscose in the previous study<sup>29</sup> are also shown in Figure 6. The two different methods had the same trends and similar values of wet density with the addition of tungsten carbide powder.

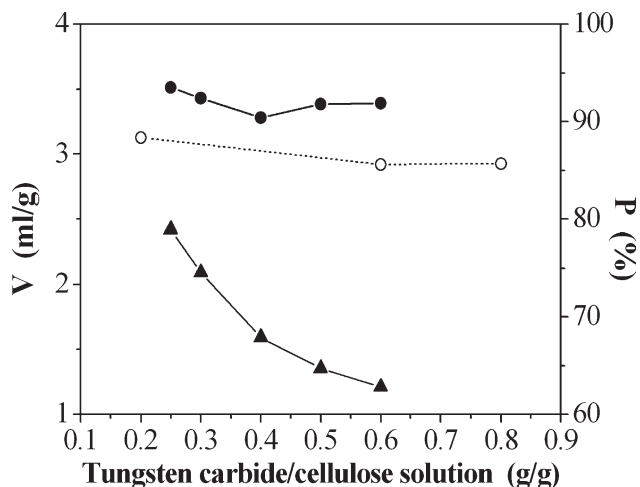
Other factors, such as the cellulose concentration, ratio of the oil phase to the cellulose solution, and stirring speed, had little impact on the wet density of the composite beads. When the ratio of tungsten carbide to the cellulose solution was fixed at 0.3 and the ratio of the oil phase to the cellulose solution was adjusted from 3 to 6, the wet density of the composite beads changed in the range 1.36–1.39 g/mL. As the cellulose concentration was changed from 2.5 to 4.5%, the wet density was between 1.37 and 1.40 g/mL. When the stirring speed was increased from 500 to 850 rpm, the wet density decreased slightly from 1.46 to 1.35 g/mL. Therefore,

it was possible to design and control the wet density of the composite beads directly with the adjustment of the ratio of tungsten carbide to the cellulose solution.

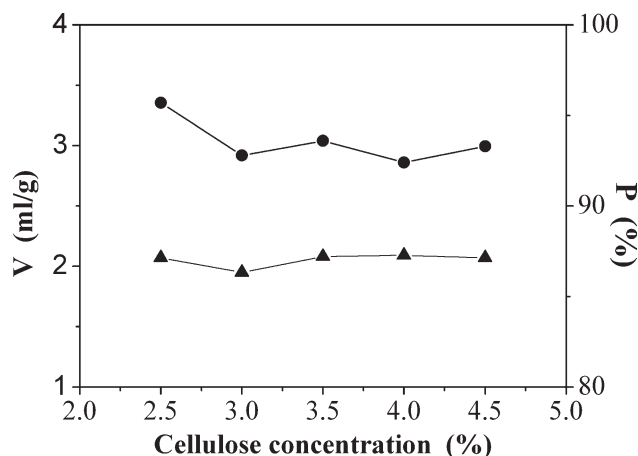
### Pore properties and specific surface area

The pore properties are quite essential for a porous matrix used for chromatographic separation and determine the effective passage and the binding space for target adsorbates. The porosity, pore volume, specific surface area, and mean pore size were examined in this study. For EBA application, the matrices should have a high porosity and pore volume and appropriate specific surface areas and mean pore sizes to match the demand of increasing productivity.

The effects of tungsten carbide addition, cellulose concentration, ratio of the oil phase to the cellulose solution, and stirring speed on the porosity and pore volume of the composite beads are shown in Figures 7–10. As shown in Figure 7, the porosity changed in the range 90–95% with all preparation conditions tested; this was slightly larger than those of the composite beads prepared with the cellulose xanthate viscose.<sup>29</sup> The results indicate that the cellulose regenerated from IL had a good porous structure and could be used as a chromatographic matrix. The pore volume was about 2 mL/g of dry beads; this was similar to that of the cellulose beads based on xanthate viscose.<sup>10</sup> As shown in Figure 7, the pore volume decreased with increasing tungsten carbide addition; this might have been caused by the



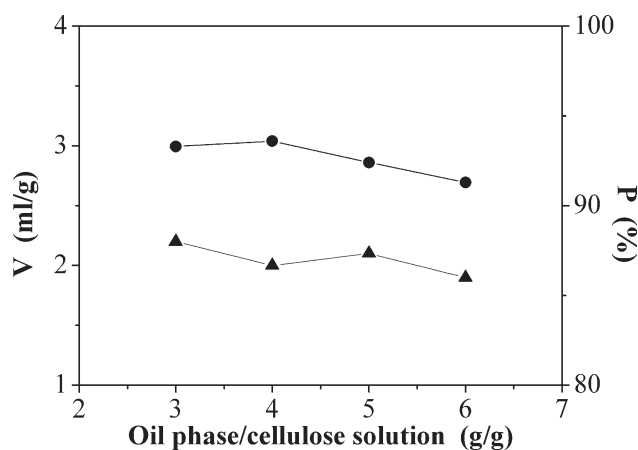
**Figure 7** (●) Porosity and (▲) pore volume of the composite beads as the function of tungsten carbide addition. The cellulose concentration was 4%, the ratio of the oil phase to the cellulose solution was 5, and the stirring speed was 780 rpm. For comparison, (○) the porosity of the composite beads prepared with cellulose xanthate viscose are also shown. The data are from the literature.<sup>29</sup>



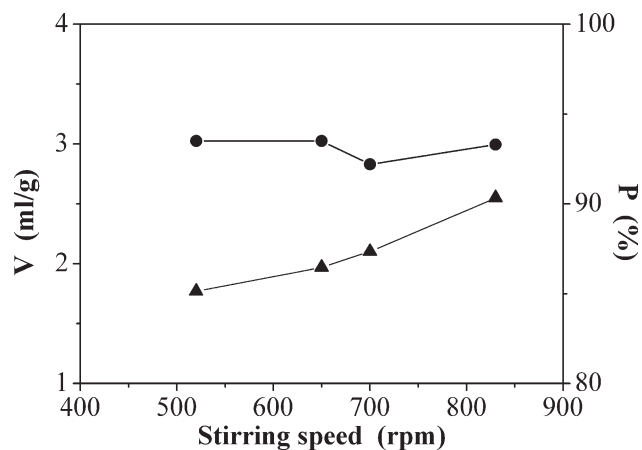
**Figure 8** (●) Porosity and (▲) pore volume of the composite beads as a function of cellulose content. The addition of tungsten carbide was 0.3 g/g of cellulose solution, the ratio of the oil phase to the cellulose solution was 5, and the stirring speed was 780 rpm.

increase in the wet density of the composite beads. As shown in Figures 8 and 9, when the cellulose concentration and the ratio of the oil phase to the cellulose solution increased, the pore volume changed slightly between 1.9 and 2.2 mL/g with an average of about 2.0 mL/g of dry beads. The pore volume increased from 1.8 to 2.5 mL/g with increasing stirring speed from 520 to 830 rpm.

Figures 11–14 show the effects of tungsten carbide addition, the cellulose concentration, the ratio of the oil phase to the cellulose solution, and the stirring speed on the specific surface area and mean pore radius. The addition of tungsten carbide had less of an effect on the pore structure, and the specific surface area and the mean pore radius were about 33 m<sup>2</sup>/mL and 55 nm, respectively. The mean pore radius

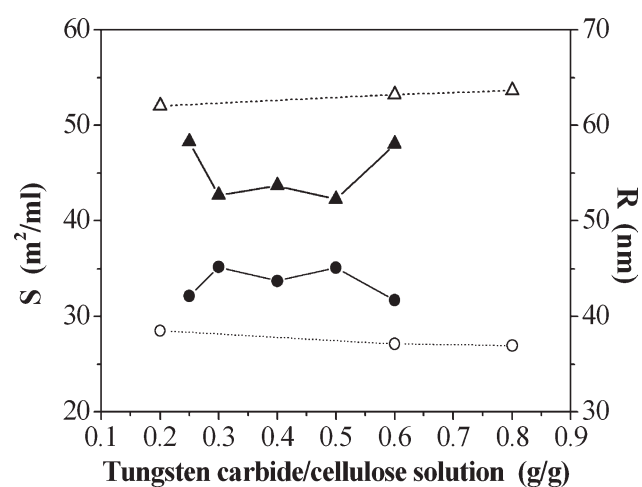


**Figure 9** (●) Porosity and (▲) pore volume of the composite beads as a function of the ratio of the oil phase to the cellulose solution. The cellulose concentration was 4%, the addition of tungsten carbide was 0.3 g/g of cellulose solution, and the stirring speed was 780 rpm.

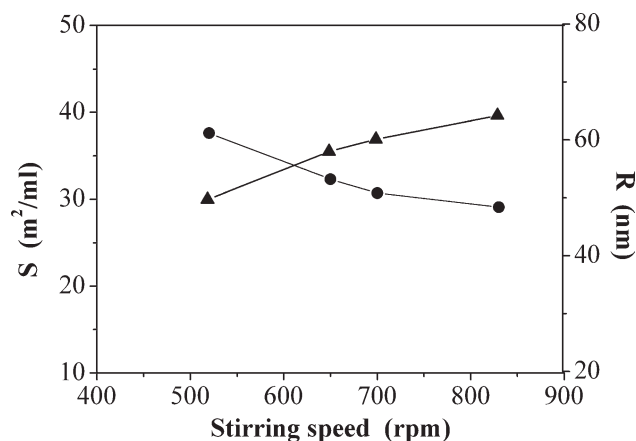


**Figure 10** (●) Porosity and (▲) pore volume of the composite beads as a function of the stirring speed. The cellulose concentration was 4%, the addition of tungsten carbide was 0.3 g/g of cellulose solution, and the ratio of the oil phase to the cellulose solution was 5.

increased significantly from 49.5 to 64.2 nm when the stirring speed increased from 520 to 830 rpm. The increase of the stirring speed enhanced the contact surface of the oil and cellulose solution, decreased the bead size, and enlarged the pore diameter; this caused the decrease in the specific surface area. On the contrary, the high viscosity caused by the high cellulose concentration or greater addition of the oil phase might have increased the stirring resistance. As shown in Figure 13, the specific surface area increased from 34.0 to 41.4 m<sup>2</sup>/mL and the mean pore radius decreased from 56.3 to 45.0 nm when the cellulose concentration increased



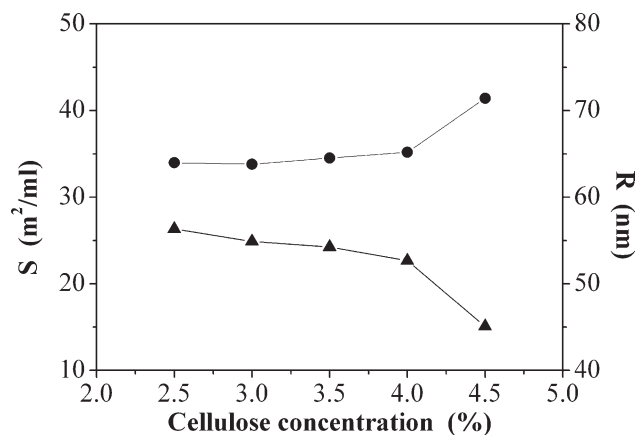
**Figure 11** (●) Specific surface area and (▲) mean pore radius of the composite beads as a function of the tungsten carbide addition. The cellulose concentration was 4%, the ratio of the oil phase to the cellulose solution was 5, and the stirring speed was 780 rpm. For comparison, (○) the specific surface area and (△) mean pore radius of the composite beads prepared with cellulose xanthate viscose are also shown. The data are from the literature.<sup>29</sup>



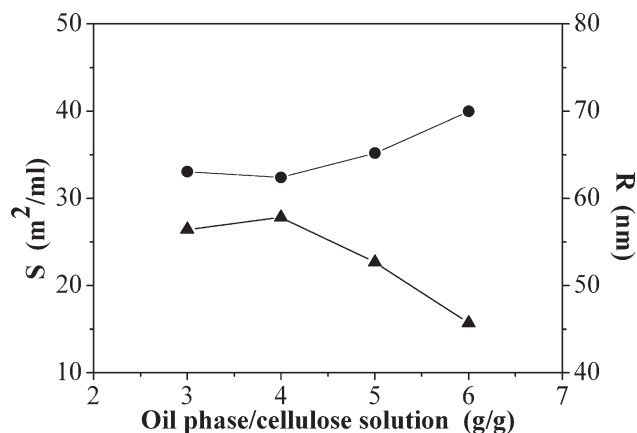
**Figure 12** (●) Specific surface area and (▲) mean pore radius of the composite beads as a function of the stirring speed. The cellulose concentration was 4%, the addition of tungsten carbide was 0.3 g/g of cellulose solution, and the ratio of the oil phase to the cellulose solution was 5.

from 2.5 to 4.5%. When the ratio of the oil phase to the cellulose solution increased from 3 to 6, the specific surface area increased from 33.1 to 40.0 m<sup>2</sup>/mL, and the mean pore radius decreased from 56.5 to 45.7 nm.

In general, the prepared cellulose–tungsten carbide composite beads showed a high specific surface area of 35 m<sup>2</sup>/mL with a relatively large pore radius of about 50 nm; this should be suitable for adsorptive chromatography. As shown in Figure 11, the mean pore radius of the carbide composite beads in this study was a little smaller than that of cellulose–tungsten carbide composite beads prepared with cellulose xanthate viscose, whereas the specific surface area was slightly higher. This may have been due to pore enlargement with cassava starch as the porogenic agent in the previous study.<sup>29</sup>



**Figure 13** (●) Specific surface area and (▲) mean pore radius of the composite beads as a function of the cellulose concentration. The addition of tungsten carbide was 0.3 g/g of cellulose solution, the ratio of the oil phase to the cellulose solution was 5, and the stirring speed was 780 rpm.



**Figure 14** (●) Specific surface area and (▲) mean pore radius of the composite beads as a function of the oil–viscose ratio. The cellulose concentration was 4%, the addition of tungsten carbide was 0.3 g/g of cellulose solution, and the stirring speed was 780 rpm.

The main preparation conditions and properties of the prepared composite beads are summarized in Tables I and II. In general, the composite particles had a spherical appearance, suitable size distribution, and appropriate wet density, porosity, pore radius, and specific surface area. Most of the properties were comparable to those of cellulose–tungsten carbide composite beads prepared with cellulose xanthate viscose. The results show that the composite particles prepared in this study had potential application as matrices for chromatographic separation.

## CONCLUSIONS

In this study, cellulose–tungsten carbide composite beads were prepared by a new method. With IL (BmimCl) as a nonderivatizing dissolution solvent for cellulose and with tungsten carbide powder as the densifier, composite particles were formed through the method of water-in-oil suspension and cooling/ethanol regeneration. The bead size could

**TABLE I**  
Summary of the Main Conditions Optimized for the Preparation of the Cellulose–Tungsten Carbide Composite Beads

Preparation condition	Controlled value
Dissolution temperature (°C)	95
Dissolution time (min)	40
Regeneration reagent added	Ethanol
Cellulose content (%)	4
Tungsten carbide/cellulose solution ratio (g/g)	0.25–0.6
Oil phase/cellulose solution ratio (g/g)	5
Stirring speed (rpm)	780



**TABLE II**  
**Summary of the Main Properties of the Prepared Cellulose–Tungsten Carbide Composite Beads**

Property	Value
Mean bead size ( $\mu\text{m}$ )	$\sim 200$
Wet density (g/mL)	1.32–1.68
Porosity (%)	90–96
Specific surface area ( $\text{m}^2/\text{mL}$ )	30–42
Mean pore radius (nm)	45–65

be controlled by the stirring speed and the ratio of the oil phase to the cellulose solution. The wet density of the beads was influenced mostly by the addition of tungsten carbide powder, and there was a linear relationship between them. The pore properties were affected little by the cellulose content and the addition of tungsten carbide powder, but increasing the stirring speed or decreasing the oil/water ratio caused a larger pore radius and reduced the specific surface area. In general, the composite particles had a spherical appearance, suitable size distribution, and appropriate wet density, porosity, pore radius, and specific surface area. Compared to the traditional technology with cellulose xanthate viscose, the new method with IL as the nonderivatizing dissolution solvent was technically easier and more environmentally friendly. The results show that the composite particles prepared in this study have potential application as matrices of EBA adsorbents. More information on the properties of bed expansion, fluid mixing, and hydrodynamics in the column will be studied in a coming work.

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