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# Preparation of sulfonated porous carbon nanotubes/activated carbon composite beads and their adsorption of low density lipoprotein

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**Abstract** The high level of low density lipoprotein (LDL) in plasma is the main cause of atherosclerosis. Hemoperfusion is an ideal therapy to lower the level of LDL in human blood system while therapeutic effect is determined by the adsorbent. The adsorbent must have suitable pore structure and specific functional groups. Carbon nanotubes (CNTs) could be a new adsorbent material because CNTs have high specific surface area and they can be modified by a variety of functional groups. Porous carbon composite beads with the CNTs and phenolic resin mixture were synthesized by suspension polymerization, following with carbonization and steam-activation. Then the porous composite beads were sulfonated with a sulfanilic acid anhydrous by diazotization and coupling reaction. The potential application of the sulfonated porous composite beads in adsorbing low density lipoprotein (LDL) from human serum was investigated. The results showed that the sulfonic acid groups on the composite beads could lower LDL levels greatly by electrostatic interaction with electropositive LDL. The higher 20–100 nm pore volume the composite beads had, the more LDL they could adsorb. The 20–100 nm pore volume was enhanced by adding more CNTs and improving CNTs dispersion (ultrasonic crushing). The sulfonated composite beads containing 45 wt% CNTs presented the highest adsorption capacity to LDL 10.46 mg/g, showing a good prospect as LDL adsorbent in hemoperfusion.

## 1 Introduction

Researchers always concern about how to reduce low density lipoprotein (LDL) level because of the linear relationship between it and incidence of atherosclerosis [1–3]. Recent studies have shown that blood purification therapy can effectively lower blood LDL levels [4]. While the hemoperfusion is the main stream technology for blood purification therapy in recent years, adsorbent is the key material in hemoperfusion. A few adsorbents for LDL hemoperfusion have already been commercially available in the market and subjected to clinical treatment. For example, two typical negatively charged systems, Japan' Kaneka Corporation Liposorber LA [5–7] and Germany's Fresenius company DALI system [8–11], have been used to reduce LDL level by electrostatic interactions because electropositive Apo-B exists on the surface of LDL molecules [12]. Although these LDL adsorbents have good

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effects [6–11], the systems are expensive and difficult to promote extensive application. It is necessary to find a low cost LDL adsorbent to meet the requirement of hemoperfusion.

A mesoporous activated carbon has been developed by Mikhalovsky et al. with the capacity to remove cytokines TNF, IL-6, IL-8 and IL-1b from human plasma in hemoperfusion [13–17]. Their results showed that the carbon adsorbents had good biocompatibility and the further development for the treatment of sepsis [13]. So the mesoporous carbon materials is a promising new large particle blood perfusion materials. Carbon nanotubes (CNTs), one-dimensional carbon allotropes, not only has the unique hollow structure, but also can form a large number of "aggregated pore" [18], it has good adsorption capacity for middle molecule toxin and high adsorption rate, implied the great potential in the application of CNTs in hemoperfusion [19]. In addition, CNTs possess excellent chemical and thermal stability. Its surface can be modified by a variety of functional groups. There has reported about functionalized CNTs respect for cholesterol biosensor [20–23]. However, to the authors' knowledge, adsorption of LDL in hemoperfusion on CNTs has not yet been reported. At present, CNTs can be grown as a forest using a variety of methods by a low price. So CNTs is considered to be a highly effective new adsorbent material for hemoperfusion.

Powdery CNTs cannot be used in hemoperfusion application, because developed porous structure, high mechanical strength and spherical shape are basic requirements for the adsorbents in hemoperfusion [24, 25]. So in this paper, we prepared spherical porous carbon composite beads with the CNTs and phenolic resin (PF) mixture by suspension polymerization [26], carbonization and steam-activation. The porous composite beads had high specific surface area, well developed porous structure, excellent mechanical properties with the enhancement of CNTs. Then the porous composite beads were functionalized by sulfanilic acid anhydrous with the method of diazotization and coupling reaction [27], and applied to adsorb electropositive LDL.

## 2 Experimental

### 2.1 Materials

The CNTs were first prepared by chemical vapor deposition at 650°C with propylene as carbon source and Ni as catalyst. Then they were purified with nitric acid ($HNO_3$, 65%, v/v, A.R., Beijing Chemical Works) and hydrofluoric acid (HF, A.R., Beijing Chemical Works). After that they were treated with nitric acid (65%, v/v) and sulfuric acid ($H_2SO_4$, 96%, v/v, A.R., Beijing Chemical Works) ($HNO_3$:$H_2SO_4$ = 1:3 v:v) for 30 min at boiling temperature. The average diameter of the CNTs was about 40 nm. The PF was a novolac-type resin with a softening point of 95–105°C (Institute of Chemistry, Chinese Academy of Sciences). Hexamethylenetetramine (HEXA) (A.R., Sinopharm Chemical Reagent Co., Ltd) was used as the crosslinking agent. Sodium dodecyl sulfate (SDS) (C.P., Sinopharm Chemical Reagent Co., Ltd) and polyvinyl alcohol (PVA) (average degree of polymerization 1750, Beijing Yili Fine Chemicals Co., Ltd) were used as dispersants in suspension polymerization. Sulfanilic acid anhydrous ($H_2NC_6H_4SO_3H$, chemical reagent, Tianjin Fu Chen Chemical Reagent Works), sodium nitrite ($NaNO_2$, A.R., Beijing Chemical Works), azobisisobutyronitrile (AIBN) (C.P., Shanghai 4 Hervey Chemical Co., Ltd) and N,N′-dimethylformamide (DMF) (A.R., Beijing Chemical Works) were used to sulfonate composite beads. The sodium chloride injection (saline) (Shangdong Qidu Pharmaceutical Co., Ltd) was used to equilibrate the adsorbents. The human serum with high LDL level was obtained from Tsinghua University Hospital.

### 2.2 Synthesis of porous composite beads

Suspension polymerization was used to produce CNTs/PF composite beads. Firstly, the CNTs was dispersed in ethanol by general sonication (ICAN Ultrasonic Cleaning Machine, 600W, Beijing Aiken Institute of Mechanical and Electronic Equipment, China) or ultrasonic crushing (KS-900F Kesheng Sonics Vibra Cell, 900W, Ningbo Ultrasonic Equipment Co., Ltd, China) for 9 h. Then PF, HEXA were dissolved in CNTs ethanol to form a homogeneous dispersed phase. 1.89 wt% PVA and 0.3 wt% SDS mixed aqueous solution was prepared as continuous phase. Then the dispersed phase was injected into the continuous phase at 70°C with mechanical stirring of 600–650 rpm for 20 min. Secondly, the system was heated to 96°C for 3 h for the crosslinking of PF with the help of HEXA. Then the synthesized CNTs/PF beads were washed by deionized water, ethanol and dried at 100°C. Finally, the porous CNTs/activated carbon composite beads (CNTs/AC beads) were obtained from the CNTs/PF beads by carbonization at 600°C and steam-activation at 850°C for more than 90 min in a tube furnace under an argon flow.

### 2.3 Sulfonation of CNTs/AC beads

General procedure for sulfonating the CNTs/AC beads was as follow. A mixture of sulfuric acid (96%, v/v, 250 ml) with sulfanilic acid anhydrous (21.650 g) was homogenized by magnetic stirring until no large particle was visible. This was followed by addition of sodium nitrite (10.350 g) at 10–15°C and held for 30 min. The oxidized

CNTs/AC beads (in nitric acid (65%, v/v) at 70°C for 2 h) and AIBN were added, and then the reaction was held at 40°C for 6 h. The suspension was poured over ice and the mixture was filtered. The functionalized CNTs/AC beads were washed with DMF and acetone, and dried in vacuum at 80°C to obtain sulfonated CNTs/activated carbon composite beads (S-CNTs/AC beads).

### 2.4 Characterization

The size and size distribution of CNTs/PF beads were counted by a Mastersizer2000 laser particle size analyzer (UK Malvern company). The morphology and microstructure of the beads were analyzed by a LEO-1530 field emission scanning electron microscope (SEM) (Germany LEO company). In addition, nitrogen adsorption–desorption isotherms at 77 K from a Sorpomatic 1990 apparatus (USA Thermo Electron company) were used to calculate the specific surface area and pore size distribution with Brunauer–Emmett–Teller method ($S_{BET}$) and Barrett–Joyner–Halen method, respectively. The compressive strength was used to characterize the strength of the beads. The upper pressure head fixed in the worktable, the under pressure head was a electronic balance. The compressive strength of 30 samples with the diameter of 1 mm in each group were measured, the average value was the strength of the beads. Fourier Transform Infrared (FTIR) spectra were obtained using a PerkinElmer Spectrum Gx (USA Perkin-Elmer company, resolution 4 $cm^{-1}$). Raman spectra were obtained using a RM2000 spectrometer (UK Renishaw company) employing a He–Ne laser of 1mW radiating on the sample operating at 632.8 nm. X-ray photoelectron spectroscopy (XPS) analysis was conducted with a PHI5300 X-ray photoelectron spectroscopy (USA Perkin-Elmer Physics Electronics company). The negative charge of the S-CNTs/AC beads was characterized by zeta potential using Zetasizer 3000HS (UK Malvern company) in pH 7.4 phosphate buffer solution.

### 2.5 Adsorption of LDL

Adsorption of LDL was conducted by static adsorption experiment in vitro. S-CNTs/AC beads (0.0400 g) were equilibrated in saline (2 ml) overnight prior to removal of saline and addition of 1 ml human serum. And the adsorbent was incubated at 37°C for 2 h while shaking (150 rpm). The LDL levels were analyzed before and after adsorption with 7170 automatic biochemical analyzer (Japan Hitachi Instrument Co., Ltd). The adsorption experiment was repeated three times. The LDL adsorption amount ($AQ$) was calculated by

$$\begin{aligned} AQ &= \frac{V(C_0 - C_t)}{W}\left(10^{-3}\,\mathrm{mmol/g}\right) \\ &= \frac{V(C_0 - C_t)/0.0259}{100W}\left(\mathrm{mg/g}\right) \end{aligned} \tag{1}$$

Where $C_0$ and $C_t$ (mmol/l) were the LDL concentrations of the serum before adding adsorbents and after 2 h of adsorption, respectively; $V$ (ml) was the volume of the serum and $W$ (g) represented the weight of the adsorbent.

## 3 Results and discussion

### 3.1 Preparation of CNTs/AC beads

The as-prepared CNTs/PF beads had not only perfect sphericity with smooth surface but also narrow size distribution (between 400 and 1000 μm) (Fig. 1a), which could meet the requirements as adsorbents for hemoperfusion. The highest content of CNTs that could be added into the beads was 45 wt%. More CNTs would lead to formation of irregular particles. After carbonization at 600°C and then steam-activation at 850°C, the developed porous CNTs/AC beads were obtained (Fig. 1b). The pore size distribution of the beads produced with CNTs was in the range of 20–100 nm (Fig. 2). The 20–100 nm pore volume increased when more CNTs were added and ultrasonic crushing method was used to disperse CNTs. At the same time the CNTs/AC beads had good strength. The strength of 30 wt% CNTs beads achieved 9.8 N, and 45 wt% CNTs beads reached 10.5 N, which was approximate 2.3 times and 2.5 times that of beads without CNTs respectively.

### 3.2 Sulfonation of CNTs/AC beads

The CNTs/AC beads were sulfonated by sulfanilic acid anhydrous with the method of diazotization and coupling reaction. The reaction scheme was shown in Fig. 3. At first, the beads were oxidated by nitric acid to obtain groups containing oxygen on the beads in order to promote the follow-up coupled reaction. Secondly, sulfanilic acid anhydrous was diazotized by sodium nitrite in concentrated sulfuric acid at low temperature, and then the diazonium salt was coupled to oxidated CNTs/AC beads with the help of initiator (AIBN), forming the functionalized composite beads.

The FTIR spectrum (Fig. 4a) of CNTs/AC beads shows the 1568 $cm^{-1}$ peak, which was $sp^2$ carbon E1u infrared fundamental frequency mode [28], there had also a weak O–H stretching vibration (3407 $cm^{-1}$), which was mainly water vapor in a weak oxidation effect. After nitric acid oxidation, there were a O–H stretching vibration

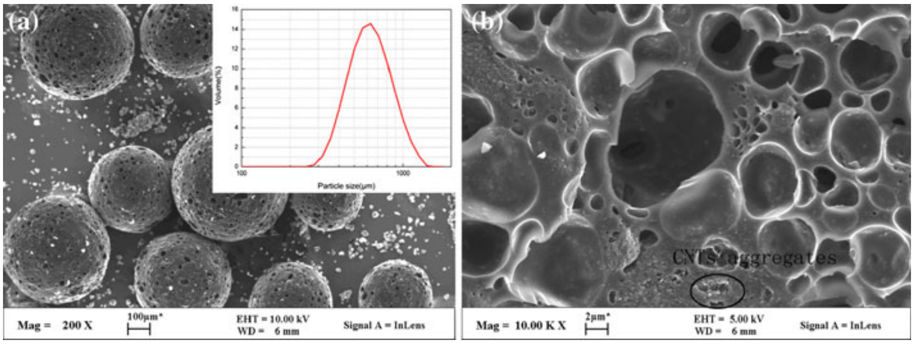

**Fig. 1** Appearance morphology with narrow size distribution (**a**) and the microstructure of CNTs/AC beads (**b**)

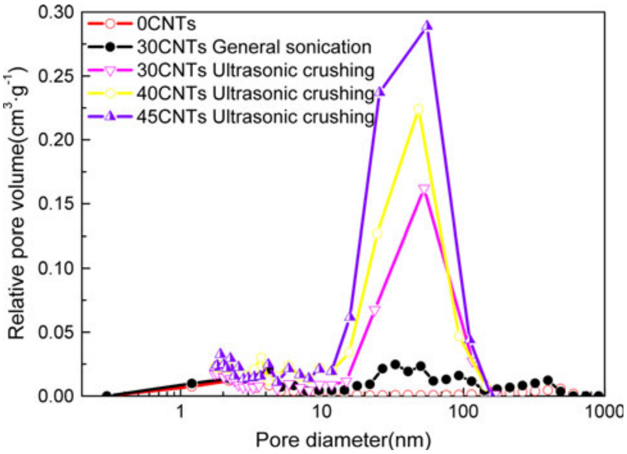

**Fig. 2** Pore size distributions of CNTs/AC beads with different CNT contents and prepared by different CNT dispersion methods

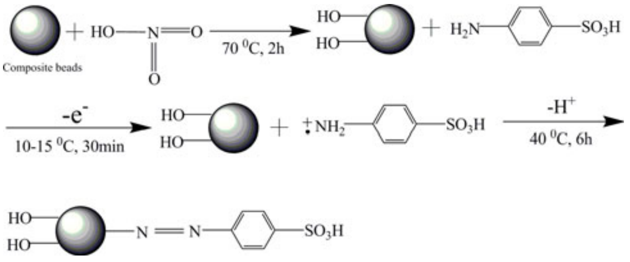

**Fig. 3** Schematic diagram of sulfonation of CNTs/AC beads

(3418 $cm^{-1}$), a C=O stretching vibration (1728 $cm^{-1}$) and a C–O stretching vibration (1195 $cm^{-1}$), suggesting that the nitric acid oxidize the surface of the CNTs/AC beads and form hydroxyl and carboxyl groups. After sulfonation treatment, there was a 1217 $cm^{-1}$ peak in addition to the spectrum of the oxidized CNTs/AC beads, which was the sulfonic acid groups in the S=O asymmetric stretching vibration [29]. These clearly indicated that sulfanilic acid anhydrous had been coupled to the CNTs/AC beads.

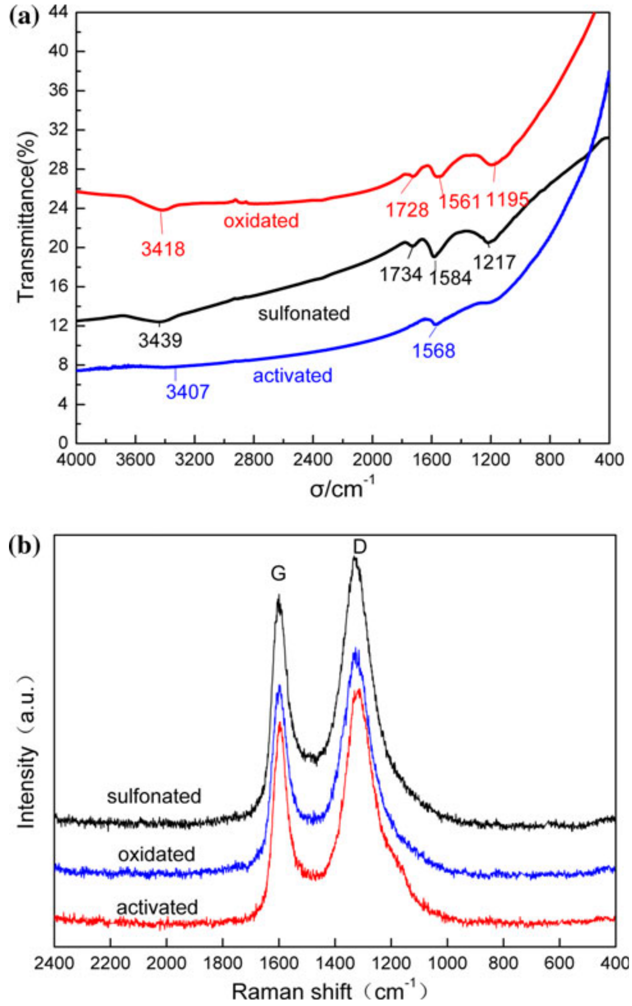

**Fig. 4** FTIR (**a**) and Raman (**b**) spectra of 30 wt% CNTs composite beads

Figure 4b were Raman spectrum of the composite beads with 30 wt% CNTs. The Raman spectrum consisted of two peaks, one at around 1330 $cm^{-1}$ was called D peak (brought about by amorphous carbon), and the other at about 1590 $cm^{-1}$ was called G peak (indication of graphitic laminar structure). So the composite beads consisted of a crystalline structure imbedded in an amorphous carbon matrix. The ratio (R) of D peak to G peak has been used to give a direct measure of crystallization degree in carbonaceous materials. Greater the R value was, more amorphous carbon matrix was [30]. For 30 wt% CNTs

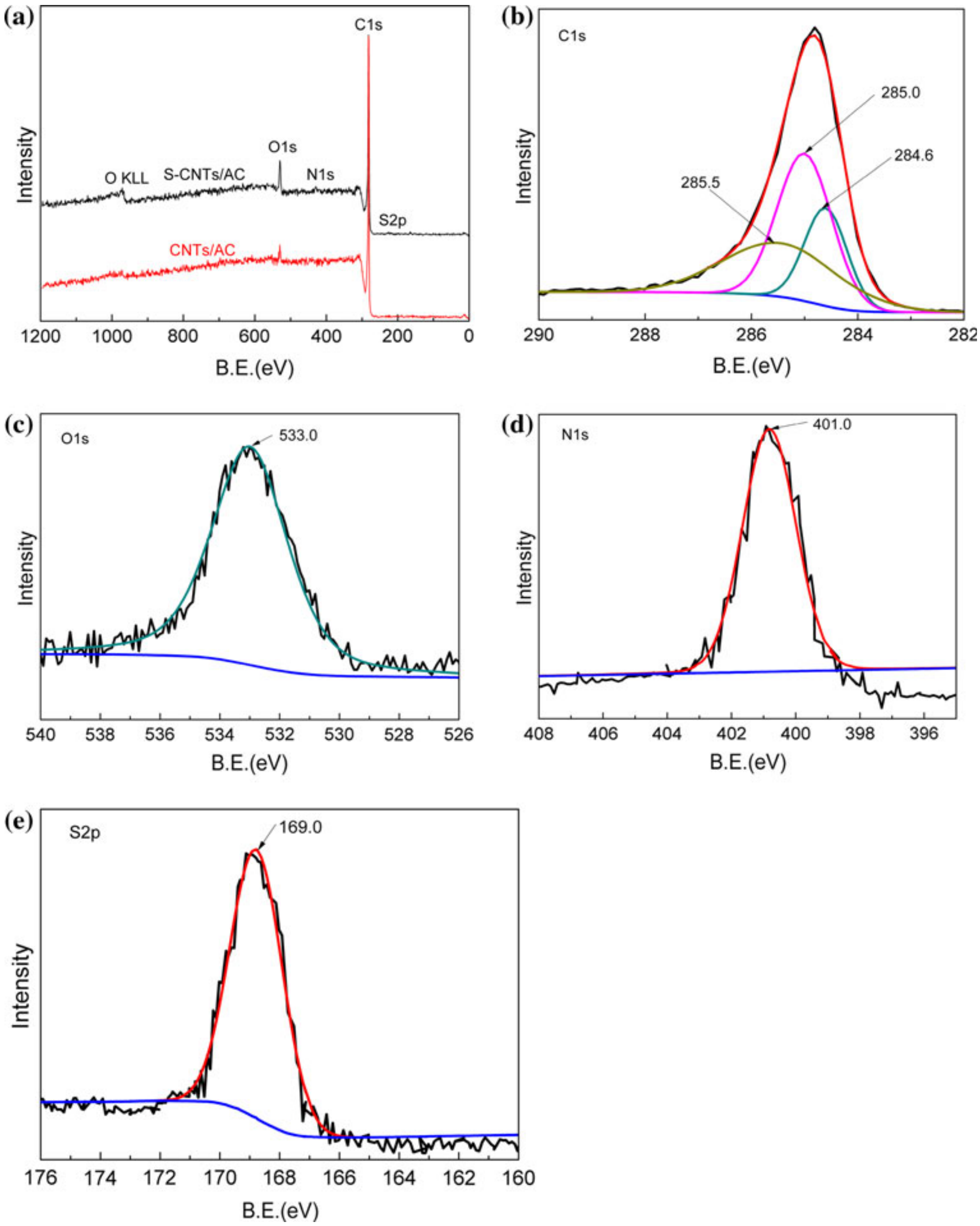

**Fig. 5** The XPS spectra of the S-CNTs/AC beads **a** full spectra, **b** C1s core spectra, **c** O1s core spectra, **d** N1s core spectra and **e** S2p core spectra

composite beads, *R* value increased from 2.206 (activated) to 2.468 (oxidated) and 2.772 (sulfonated), implying that crystallization degree decreased significantly by functionalization. It meant that larger amount of unsaturated carbon atoms and heterogeneous atoms in the composite beads were achieved by functionalization.

The XPS full spectrum of S-CNTs/AC beads (Fig. 5a) confirmed the existence of N and S elements and increase of O element content. XPS (as a semi-quantitative analysis method for surface element) shows that the O/C molar ratio increased from 3.7 to 7.0% after the sulfonation treatment. The C1 s peaks in the XPS narrow spectrum of the S-CNTs/AC beads could be decomposed into 284.6, 285.0, 285.5 eV (Fig. 5b) and are attributed to C–C, C–H, C–N [30] based carbon. O1s binding energy is 533.0 eV (Fig. 5c), indicating the surface of the S-CNTs/AC beads have C–OH based oxygen. N1 s peak at 401 eV (Fig. 5d) is due to $\sigma^*$ (N–H) response [31]. The peak at 169.0 eV shows the presence of S2p which sufficiently characterized the chemical structure with S=O species (Fig. 5e) [32]. These all confirmed that the sulfonic acid had been successfully grafted to the CNTs/AC beads.

## 3.3 Adsorption of LDL

LDL concentrations were analyzed before and after adsorption. Figure 6 shows the adsorption amount of LDL on the S-CNTs/AC beads. The adsorption capacity of the

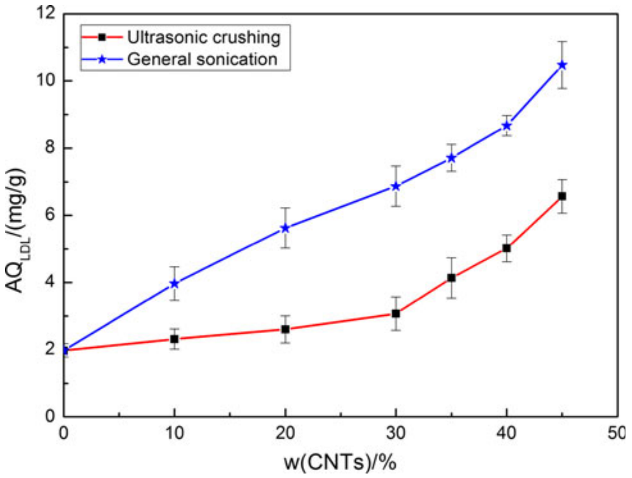

**Fig. 6** Adsorption amount of LDL on the S-CNTs/AC beads with different CNT contents and by different CNT dispersion methods

S-CNTs/AC beads to LDL increased with the increase of CNTs content. The amount of LDL adsorbed on the S-CNTs/AC beads containing 45 wt% CNTs dispersed by general sonication was 6.56 mg/g, which was 3.3 times that of the beads without CNTs. When CNTs was dispersed in ethanol by ultrasonic crushing, it could improve the adsorption capacity of the S-CNTs/AC beads to LDL. The adsorption capacity of the S-CNTs/AC beads containing 45 wt% CNTs dispersed by ultrasonication reached 10.46 mg/g, which was 1.6 times that of the S-CNTs/AC beads containing 45 wt% CNTs dispersed by general sonication. The result was higher than current reports [33–37] and was close to the Germany's Fresenius company DALI system [8–11]. Such as, Li et al. [36] reported that LDL adsorption amount reached 4.69 mg/g on the heparin immobilized PAN-based resin. Wang et al. [37] synthesized different LDL adsorbents containing sulfonic groups, phosphoric groups, L-lysine and carboxyl groups as the ligand on the cellulose beads, the most LDL adsorption amount reached 1.43 mg/ml by the sulfonic groups immobilized. It indicated that the CNTs could be a new LDL adsorbent material to replace the traditional polymer materials.

For LDL adsorbent, the key factors are the surface charged groups and the pore structure [15]. Firstly, the beads with different surface groups had different negative charges, thus different adsorption capacity to LDL. The zeta potential of the S-CNTs/AC beads was −26.3 mV, and their adsorption capacity to LDL was 3.07 mg/g. The zeta potential of the oxidated composite beads was −18.5 mV, and their adsorption capacity to LDL was only 2.24 mg/g. The negative charge of sulfonic acid group was stronger than hydroxyl and carboxyl groups thus enhanced the electrostatic interaction of the beads to the electropositive LDL from the serum. Secondly, the S-CNTs/AC beads (the zeta potential of the S-CNTs/AC beads with different CNTs contents was about −26 mV) had developed porous structure (20–100 nm pore size) which fitted to the LDL (LDL is a particle of about 20 nm). As Table 1 shows, the more CNTs were added, the more the total pore volume and 20–100 nm pore volume were. Especially, the more 20–100 nm pores volume was, the more adsorption amount of LDL was. When the CNTs dispersed by general sonication, the S-CNTs/AC beads containing 30 wt% CNTs had 0.0767 $cm^3$/g 20–100 nm pores, which was 47 times that of beads without CNTs, and the adsorption amount of LDL was 1.5 times. Additionally, when the CNTs dispersion was improved by ultrasonic crushing, the 20–100 nm pore volume was more. For the S-CNTs/AC beads containing 30 wt% CNTs, the 20–100 nm pore volume increased from 0.0767 $cm^3$/g (general sonication) to 0.273 $cm^3$/g (ultrasonic crushing), the adsorption amount of LDL was improved from 3.07 to 6.87 mg/g. The highest adsorption capacity of S-CNTs/AC beads to LDL reached 10.46 mg/g when 45 wt% CNTs were added (CNTs dispersed by ultrasonic crushing) because of their high 20–100 nm pore volume (0.407 $cm^3$/g).

## 4 Conclusions

Porous carbon composite beads with the CNTs and PF mixture were synthesized by suspension polymerization, following with carbonization and steam-activation. The porous composite beads were sulfonated with a sulfanilic acid anhydrous by diazotization and coupling reaction to obtain S-CNTs/AC beads. And they were applied to adsorbing LDL from human serum. The results showed

**Table 1** Pore volume, specific surface area ($S_{BET}$) and $AQ_{LDL}$ of S-CNTs/AC beads by different dispersion methods

| CNTs content (wt.)% | CNTs dispersion method | $V_{tot}$ ($cm^3$/g) | $V_{20\text{–}100\ nm}$ ($cm^3$/g) | $S_{BET}$ ($m^2$/g) | $AQ_{LDL}$ (mg/g) |
|---|---|---|---|---|---|
| 0 | – | 0.0542 | 0.00161 | 426 | 1.98 |
| 30 | General sonication | 0.244 | 0.0767 | 492 | 3.07 |
| 30 | Ultrasonic crushing | 0.600 | 0.273 | 613 | 6.87 |
| 40 | Ultrasonic crushing | 0.719 | 0.323 | 610 | 8.67 |
| 45 | Ultrasonic crushing | 0.811 | 0.407 | 723 | 10.46 |

that the electronegative sulfonic acid groups (–$SO_3H$) on the S-CNTs/AC beads could lower LDL levels greatly by electrostatic interaction between electropositive LDL and the adsorbents. The more 20–100 nm pore volume was, the higher adsorption amount of LDL on the S-CNTs/AC beads was. The 20–100 nm pore volume was increased by adding more CNTs and improving CNTs dispersion (ultrasonic crushing). The highest adsorption capacity of the S-CNTs/AC beads to LDL was 10.46 mg/g while 45 wt% CNTs were mixed (CNTs were dispersed by ultrasonic crushing).

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