Flexible route to fabricate excellent adsorbents for vitamin B$_{12}$ by specially designed oil-drop process

Bingzhi Guo[1,2,3,4], Yilun Huang[1,2,3], Qianming Gong[1,2,3], Junjie Wang[1,2,3], Daming Zhuang[1,2,3], Ji Liang[5]

[1]*School of Materials Science and Engineering, Tsinghua University, Beijing 100084, Peoples Republic of China*
[2]*State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, Peoples Republic of China*
[3]*Key Laboratory for Advanced Materials Processing Technology, Ministry of Education, Beijing 100084, Peoples Republic of China*
[4]*School of Chemical Engineering and Material Science, Beijing Institute of Technology, Zhuhai 519088, Peoples Republic of China*
[5]*Department of Mechanical Engineering, Tsinghua University, Beijing 100084, Peoples Republic of China*
E-mail: gongqianming@mail.tsinghua.edu.cn

This work presented the preparation of an excellent adsorbent composed of carbon nanotubes (CNTs) and activated carbon (AC) with hierarchical porous structure by specially designed oil-drop process. In this process, CNTs were pre-dispersed in the ethanol diluted phenolic formaldehyde resin and subsequently, the uniform suspension was injected dropwise into the stratified liquids. These liquids were composed of paraffin, polydimethyl siloxane and poly(ethylene glycol) (PEG)-6000 aqueous solution with different densities. After being semi-cured in the three-layered liquids at 70°C, the spheres were carbonised at 600°C and further activated at 800°C with steam. Scanning electron microscope observations indicated that compared with those prepared by two-layered oil bath in the authors' previous work, the CNTs/phenolic resin spheres acquired by the modified oil-drop method would absorb PEG-6000 instead of polydimethyl siloxane and hence no residue of silica spheres produced in the final CNTs/AC spheres. Meanwhile, pore structure analyses indicated that the average diameter of the pores in the CNTs/AC spheres increased from 8.1 to 23.3 nm, which could be ascribed to the pore forming effect of PEG-6000. The adsorption capacity for vitamin B$_{12}$ by the porous CNTs/AC spheres reached 52.98 mg/g, which was much higher than commercial AC beads and macroporous resin spheres. This implied that the CNTs/AC spheres could have potential applications in hemoperfusion.

1. Introduction: Haemoperfusion is an indispensable medical treatment for patients with renal failure, acute intoxication, hyperlipidemia and so on, for it can remove middle or big molecular weight toxins which cannot be removed by regular hemodialysis [1–9]. Obviously, the curative effects would be determined by the adsorption capacity of the adsorbents. Currently, activated carbon (AC) and macroporous resin (MR) beads are the dominant adsorbents in hemoperfusion, but the pores in AC beads are mainly micropores of less than 2 nm in diameter, which leads to poor adsorption capacity of middle or big molecular toxins [10, 11]. Differently, most pores in MR beads are tens of nanometres and this limits its adsorption for small molecular toxins. Therefore, developing adsorption materials containing both mesopores and macropores are the key to improve the curative effects of hemoperfusion [12, 13].

It is well known that in recent years, carbon nanotubes (CNTs) have been proved to be a new efficient adsorption material [14–16]. Besides their special hollow structure, they could develop many 'aggregated mesopores' through self-assembly process via Van der Waals' forces and thus brought about rather high adsorption capacity for different substance, especially for middle molecule toxins [17, 18]. Probably it could be developed to be a promising adsorbent for hemoperfusion [13, 19–21].

Nevertheless, the challenge is how to turn the powdery CNTs into tough porous blocks or spheres without lowering their excellent adsorption capacity because powdery CNTs might result in secondary pollution for the difficulty of separation or recycling. Ye *et al.* [13] prepared CNTs/AC composite spheres by adding CNTs into ethanol diluted phenol–formaldehyde (PF) resin solution and then smashing the dried CNTs/PF blocks into small pieces. After being sieved, some particles with desirable sizes were further cured in an autoclave during which the irregular shaped particles would turn into spheres on account of the surface tension of

resin. Followed by carbonisation and activation, the obtained CNTs/AC spheres with 22.5 wt% CNT exhibited an adsorption capacity for vitamin B$_{12}$ (VB$_{12}$) of about 19.92 mg/g. Lu *et al.* [14] synthesised CNTs/AC composite spheres by suspension polymerisation. Since the sizes of the obtained spheres were in normal distribution, desirable spheres had to be selected by sieving process. The VB$_{12}$ adsorbed by the composite spheres with about 45 wt% CNT was 32.38 mg/g. Inevitably, the ratio of CNTs in the spheres could not be increased too much, because the surface tension of resin was limited during the curing process in the two methods aforementioned. Recently, Wang *et al.* [10] reported a new method to fabricate CNTs/carbon spheres by combining freezing casting, chemical vapour infiltration and water vapour activation, the adsorption of VB$_{12}$ could achieve 51.48 mg/g. In contrast to this relatively complex technology, Guo *et al.* [22] proposed an oil-drop strategy to make porous CNTs/AC spheres with two layers of stratified oils. As a whole, the adsorption of VB$_{12}$ was rather high and the process was simplified, while after activation, in the surface layer of the spheres, there produced a lot of SiO$_2$ microbeads derived from the adsorbed polydimethyl siloxane and the spheres had to be cleaned further with diluted alkali solution. In addition, if the average pore size of 8.1 nm for the CNTs/AC spheres could be increased a little, it would be more conducive to the adsorption of larger molecular toxins like low density lipoprotein (18–25 nm).

Besides spheres, CNTs based bulk materials like foams [23] or sponges [24] might also be feasible in future applications, but it will not be discussed in this Letter. Herein, we dispersed CNTs in ethanol diluted PF resin and then injected the suspension dropwise into the three-layered liquids of paraffin liquid (PL)/polydimethyl siloxane fluid (PSF)/PEG aqueous solution based on their different densities. Then the CNTs/phenolic resin (CNTs/PF) composite microspheres were semi-cured in the hot liquid phase. After being

carbonised at 600°C and activated with steam at 800°C, the resultant CNTs/AC composite spheres with hierarchical porous structure were acquired. Compared with our previous work [22], in this modified oil-drop method, we added the third layer of PEG-6000 aqueous solution, so that PEG-6000 replaced the adsorbed PSF in the two-layered PL/PSF system in the CNTs/PF microspheres, thus we could cut out the final alkali washing process. At the same time, PEG-6000 could play the role of pore forming agents and so the porous structure of CNTs/AC could be adjusted further.

2. Experimental: In this work, the CNTs were multi-walled CNTs which had been pre-treated by acid. The diameter of the CNTs was about 8–15 nm and the specific surface area of them was about 150 m^2/g. PF resin, curing agent paratoluensulfonyl chloride, PL, PSF and PEG-6000 were of analytical grade. VB_{12} (biochemical reagent) was provided by Sinopharm Chemical Reagent Co., Ltd.

Fig. 1 shows the schematic diagram of the fabrication process. 1.0 g acid-pre-treated CNTs and 3.0 g PF were mixed in 40 ml ethanol solution (75 wt% ethanol/25 wt% deionised water). The mixture was further ultrasonic treated for 2 h. Then curing agent (0.6 g, 20 wt% of PF resin) and another 15 ml of ethanol were added into the uniform CNTs suspension. Subsequently, a syringe was used to inject the suspension dropwise into the three-layered liquids of PL, PSF and PEG-6000 at 70°C. After 5 h of gradual sinking in the stratified liquids, the spheres got semi-cured and could keep spherical during the next separation process. Then the semi-cured beads were put into an oven for 12 h at 70°C. Subsequently, the intermediate spheres were carbonised at 600°C and activated at 800°C with water vapour for 75 min in Ar atmosphere. Then the final porous CNTs/AC spheres were obtained.

Scanning electron microscope (SEM, Germany Carl Zeiss Company) was used to investigate the morphology and microstructure of the spheres. An image Analyser for 5051, which was designed by Tsinghua University, was used to analyse the degree of sphericity and size distribution of the spheres. The specific surface area and pore size distribution were analysed by nitrogen adsorption/desorption isotherms with the Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halen method, respectively (TriStar II 3020, USA). Thermogravimetric analyses (TGA, Q5000IR, USA) were adopted to analyse the carbonisation process.

The method we used to characterise the adsorption ability of the spheres was referred to the former work of our group [13, 14, 22]. The adsorption amount of VB_{12} could be calculated by the following equation

$$q = \left(\frac{C_0 - C_t}{W}\right)V \qquad (1)$$

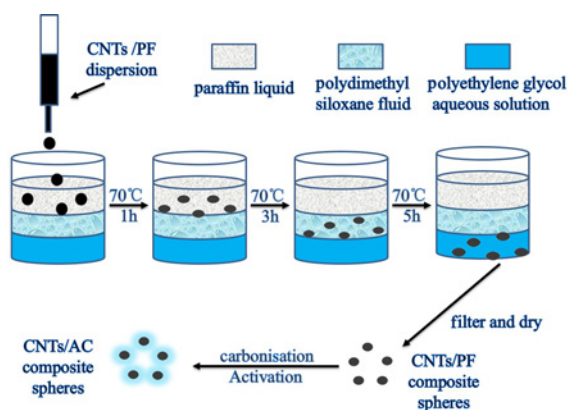where q is the adsorption amount; C_0 and C_t are the concentrations of the VB_{12} solution before and after adding the spheres; V is the volume of the solution (50 ml); and W is the weight of the spheres.

3. Results and discussion: The CNTs/PF suspension droplets dripped from syringe are spherical due to surface tension, but the soft droplets would easily deform before curing if the densities of the droplets and the liquids did not match. In other words, if the density of the droplets is much lower than that of the liquids, they will float and deform to be thick disc-shaped. Alternatively, if the density of the droplets is much higher than that of the liquids, they will plunge and hit the bottom of the vessel directly to be debris or deform. So the three layers of liquids with gradient densities were specially selected in order to keep the droplets suspending instead of floating on the surface or plunging immediately during solidifying process. Only in this case, the droplets could keep spherical shape under the balance among the surface tension, gravity and the buoyancy. Since at 70°C, the density of the droplets would enhance little by little because of the evaporation of ethanol and H_2O in the droplets. Actually, the droplets fell slowly down to the interface of PL and PSF first and then, after 1 h, they sank into PSF under a new balance of the three forces. After another 2 h, the droplets would fall gradually to the PEG-6000 aqueous solution layer. Before they fell on the bottom of the container finally, the droplets were semi-cured and became solidified spheres. After being separated, the CNTs/PF spheres were dried in oven for another 12 h to make them tougher.

Fig. 2 shows the TGA results of PF, CNTs/PF, PL, PSF and PEG-6000 at a heating rate of 10°C/min in nitrogen atmosphere. It can be noted that in the range of 50–350°C, the weight loss of CNTs/PF, PEG-6000 and PL are about 5, 2 and 100 wt%, respectively. In contrast, the weight loss of CNTs/PF obtained by two-layered oil bath is more than 20 wt% [22]. This indicates that certain amount of PEG-6000, instead of PL, is adsorbed by the CNTs/PF spheres got by modified oil-drop method. In the range of 350–400°C, the weight loss of PSF is remarkable, while the weight loss of CNTs/PF spheres is not noticeable. Then in the range of 400–450°C, the weight loss of CNTs/PF is synchronous to that of PEG-6000, so it is reasonable to infer that the adsorbed substance by CNTs/PF spheres is mainly PEG-6000 instead of PL or PSF. Probably, the adsorbed PEG-6000 may also change the carbonisation and the following activation of the resin [11] and correspondingly, alter the pore structure of the resultant spheres. The CNTs in the final spheres is about 50 wt%.

Fig. 3 shows the surface morphology of CNTs/AC microspheres prepared by two-layered oil bath (Figs. 3a and b) and modified oil-drop method (Figs. 3c and d). Statistically, the degree of sphericity for the spheres got by modified process is a little higher than that by previous oil-drop method [22]. More significant is that, the
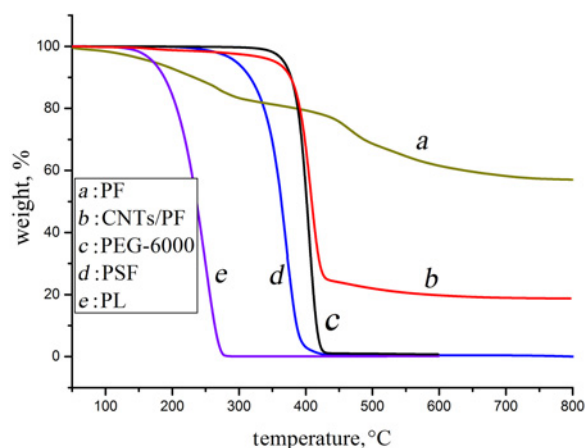

Fig. 1 *Schematic diagram of preparation of the CNTs/AC composite spheres by oil-drop process in three-layered liquids*

Fig. 2 *TGA curves of PF, CNTs/PF, PEG-6000, PSF and PL*
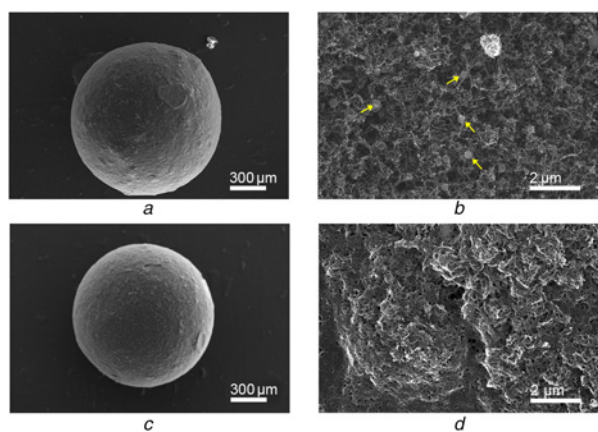
Fig. 3 *SEM images of apparent morphology of CNTs/AC microspheres prepared by oil-drop method (a, b) and modified oil-drop method (c, d). Silica beads are highlighted by yellow arrows*

surface of the CNTs/AC spheres by modified process is uniformly distributed with some macropores (Fig. 3*d*) rather than widely dispersed SiO₂ microspheres (Fig. 3*b*, marked with yellow arrows). In fact, this indicates that adsorbed PEG-6000 from the third layer can not only replace PSF to a great extent, which helps to omit the alkali washing process, but also plays the role of pore forming agent which conduces to acquire a more developed pore structure.

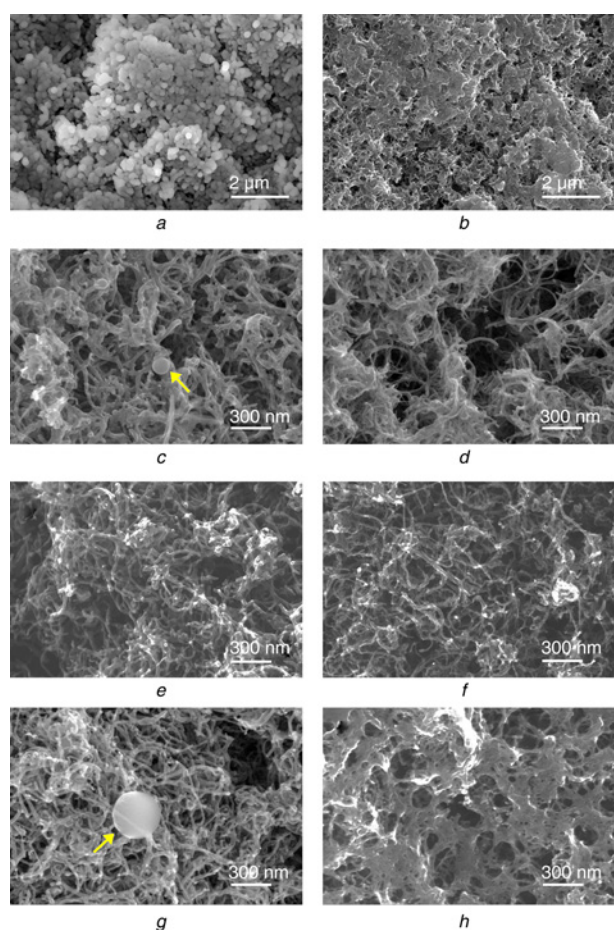Fig. 4 demonstrates the pore structure evolution from CNTs/PF to CNTs/AC spheres. The surface morphology of CNTs/PF is quite different for the samples prepared by two-layered system (Fig. 4*a*) and modified process (Fig. 4*b*). It is probably that the adsorbed PSF was incompatible with PF resin and it acted as the separate of PF resin during curing process, so the surface of the sample prepared by previous oil-drop method looks like aggregated powders. The internal microstructure is similar to that of the surface for both simples. Generally, both the surface and the internal zone are short of pores for CNTs/PF beads. After carbonisation, both the surface and the internal part turned from solid into porous structure (Figs. 4*c*–*f*). Nevertheless, it should be noted that there produced some silica beads in the surface of the samples got by two-layered oil bath (Fig. 4*c*) [22]. Even after being activated, the silica beads were still inlaid in the surface (Fig. 4*e*). In contrast, PEG-6000 is a thermally unstable polymer, although the adsorbed PEG-6000 might be integrated with PF resin during curing process, it would crack to be gaseous substances according to TGA (Fig. 2) and lead to a higher porosity during carbonisation. This may be attributed to the more active residual carbon derived from adsorbed PEG-6000 after carbonisation [11]. Although qualitatively, the pore structure looks like each other by SEM observation, it should be different based on quantitative BET analyses.

Fig. 5*a* shows the N₂ adsorption–desorption isotherms of the porous composite spheres. It is obviously that the isotherm is type IV curve which contains a multi-stage adsorption process in the samples. A hysteresis loop might be related to capillary condensation in mesopores [17]. The facts that the hystersis loop is shown in the pressure range of $p/p_0 = 0.85$–0.99 and the adsorption amount of N₂ rose abruptly suggests that, drastic capillarity appears in the bigger mesopores (>20 nm) and macropores [17]. Fig. 5*b* shows
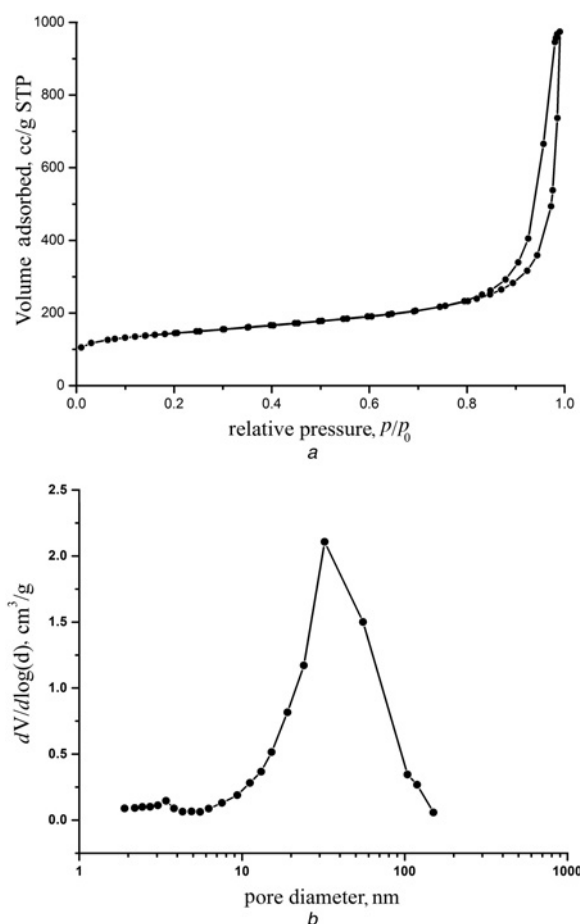

Fig. 4 *SEM images about the pore structure evolution for the spheres prepared by two-layered oil system (a, c, e, g) and modified process (b, d, f, h), surface morphology of CNTs/PF beads (a, b), carbonised CNTs/PF spheres (c, d), activated CNTs/PF spheres (g, h) and internal microstructure of carbonised CNTs/PF spheres (e, f). Silica beads are highlighted by yellow arrows*

Fig. 5 *N₂ adsorption–desorption isotherms and pore size distribution plots of CNTs/ AC spheres*
a N₂ adsorption–desorption isotherms
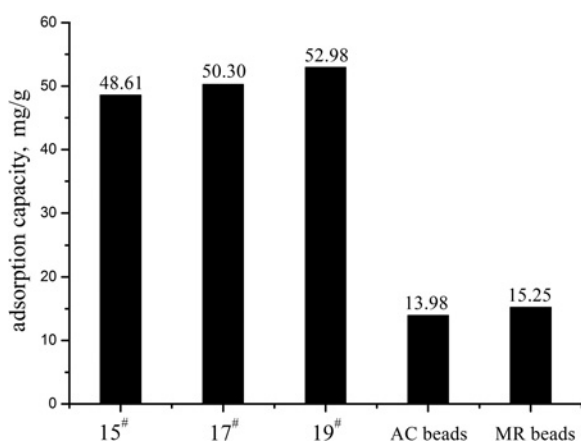*b Pore size distribution of CNTs/AC spheres*

Fig. 6 *Adsorption of VB12 by CNTs/AC spheres, AC and MR beads*

the pore size distribution and the average diameter of the composite spheres is about 23.3 nm, which is about two times larger than 8.1 nm for the spheres prepared by previous oil-drop method [22]. Obviously, larger pores are beneficial for the adsorption of bigger molecular toxins. Meanwhile, the total pore volume of resultant CNTs/AC spheres is 1.38 cm^3/g, which is about four times that of the spheres prepared in two-layered oil bath [22]. Hereto the pore forming effects of PEG-6000 are proved quantitatively besides SEM observations. In addition, the diameters of the composite spheres could be controlled by the needles. For example, the equivalent diameter of the spheres got by No.15 needle (with the internal diameter of 1.45 mm) is 1.56 mm and that by No.19 needle (with the internal diameter of 0.7 mm) is 1.18 mm. The degree of sphericity denoted by dimension ratio is 0.93–0.94.

In the application of hemoperfusion, presently, AC and MR beads are the primary adsorbents. As the control, the adsorption capacities of VB$_{12}$ were 13.98 and 15.25 mg/g for AC and MR beads, respectively. In this Letter, the corresponding adsorption capacity for VB$_{12}$ could reach 52.98 mg/g, which is more than three times of AC and MR beads (Fig. 6). Although the specific areas of AC beads (810 cm^2/g) and MR beads (960 cm^2/g) are much higher than that of CNTs/AC spheres (498 cm^2/g), the average diameter of the pores in the first two beads are about 1.4–1.5 nm [10], which is a little smaller than the size of VB$_{12}$ (2.09 nm). For AC beads, the pores are mainly micropores and for MR beads, the pore distribution is too single that they lack mesopores with larger size or macropores which could act as diffusing channels during adsorption process. Then accordingly, the larger average pore size (23.3 nm) own to the pore forming effects of PEG-6000 should be the key factor that is favourable for the distinguished adsorption capacity for the CNTs/AC spheres.

4. Conclusion: CNTs/PF microspheres were prepared by special designed oil-drop method in three-layered liquids and the porous CNTs/AC composite spheres were obtained by carbonising and activating the CNTs/PF composite spheres. The added third layer of PEG-6000 aqueous solution could replace the adsorption of PSF during curing process in the oil bath and thus the post-treatment of alkali washing for residual SiO$_2$ microbeads could be cut out. Moreover, the adsorbed PEG-6000 could act as pore forming agent during carbonisation and activation process, in this way the average pore diameter of the resultant spheres was as high as 23.3 nm. Besides, the diameter and the sphericity of the spheres were also controllable. The adsorption of VB$_{12}$ was up to 52.98 mg/g for the resultant porous CNTs/AC spheres, which was 3.79 and 3.47 times of AC and MR beads, respectively. Probably, they are expected to have potential applications in hemoperfusion.

5 References

[1] Babb A.L., Farrell P.C., Uvelli D.A., ET AL.: 'Haemodialyzer evaluation by examination of solute molecular spectra', *ASAIO Trans.*, 1972, **18**, pp. 98–105

[2] Liu X., Zhang D.L., Liu W.H.: 'Progress of middle molecular weight uremic toxins and removal', *Progr. Mod. Biomed.*, 2012, **12**, (18), pp. 3581–3583

[3] Wang H., Yuan Z., Teng X.L., ET AL.: 'Investigations on the adsorbents for uremic middle molecular toxins (I) glutaraldehyde-cross inked chitosan adsorbent', *Chem. J. Chin. Univ.*, 2002, **23**, (1), pp. 75–77

[4] Zhang J.D., Yuan Z.: 'Progress in hemoperfusion material', *Chin. J. Polym. Bull.*, 2006, **4**, pp. 23–28

[5] Sandeman S.R., Howell C.A., Mikhalovsky S.V., ET AL.: 'Inflammatory cytokine removal by an activated carbon device in a flowing system', *Biomaterials*, 2008, **29**, pp. 1638–1644

[6] Li G.F., Wan J.X., Huang X.Q., ET AL.: 'Comparison study on adsorption of middle molecular substances with multiwalled carbon nanotubes and activated carbon', *J. Biomed. Eng.*, 2011, **28**, (4), pp. 758–762

[7] Chu J.G., Yuan Z., He B.L.: 'Separation and analysis of uremic middle molecules', *Ion Exch. Adsorpt.*, 2001, **17**, (6), pp. 553–560

[8] Malik D.J., Warwick G.L., Mathieson I., ET AL.: 'Structured carbon haemoadsorbents for the removal of middle molecular weight toxins', *Carbon*, 2005, **43**, pp. 2317–2329

[9] Malik D.J., Warwick G.L., Venturi M., ET AL.: 'Preparation of novel mesoporous carbons for the adsorption of an inflammatory cytokine (IL-1β)', *Biomaterials*, 2004, **25**, pp. 2933–2940

[10] Wang J.J., Gong Q.M., Zhuang D.M., ET AL.: 'Chemical vapor infiltration tailored hierarchical porous CNTs/C composite spheres fabricated by freeze casting and their adsorption properties', *RSC Adv.*, 2015, **5**, (22), pp. 16870–16877

[11] Yang J.B., Ling L.C., Liu L., ET AL.: 'Preparation and properties of phenolic resin-based activated carbon spheres with controlled pore size distribution', *Carbon*, 2002, **40**, pp. 911–916

[12] Ye C., Gong Q.M., Lu F.P., ET AL.: 'Adsorption of middle molecular weight toxins on carbon nanotubes', *Acta Phys. Chim. Sin.*, 2007, **23**, (9), pp. 1321–1324

[13] Ye C., Gong Q.M., Lu F.P., ET AL.: 'Preparation of carbon nanotubes/phenolic-resin-derived activated carbon spheres for the removal of middle molecular weight toxins', *Sep. Purif. Technol.*, 2008, **61**, pp. 9–14

[14] Lu Y.M., Gong Q.M., Liang J.: 'Preparation of carbon nanotubes/activated carbon composite microspheres and their application to adsorption of VB12', *Acta Phys. Chim. Sin.*, 2009, **25**, (8), pp. 1697–1702

[15] Lu C.Y., Guan W.S., Zhang G.H., ET AL.: 'TiO2/Fe2O3/CNTs magnetic photocatalyst: a fast and convenient synthesis and visible-light-driven photocatalytic degradation of tetracycline', *Micro. Nano Lett.*, 2013, **8**, (10), pp. 749–752

[16] Xia P.X., Zhang M., Zheng J., ET AL.: 'Facile route to synthesise larger mesoporous nickel silicate coated on carbon nanotubes and application for dye removal', *Micro. Nano Lett.*, 2014, **9**, (3), pp. 184–188

[17] Yang Q.H., Hou P.X., Bai X., ET AL.: 'Adsorption and capillarity of nitrogen in aggregated multi-walled carbon nanotubes', *Chem. Phys. Lett.*, 2001, **345**, pp. 18–24

[18] Lu Y.M., Gong Q.M., Lu F.P., ET AL.: 'Preparation of sulfonated porous carbon nanotubes/activated carbon composite beads and their adsorption of low density lipoprotein', *J. Mater. Sci., Mater. Med.*, 2011, **22**, pp. 1855–1862

[19] Lu Y.M., Gong Q.M., Lu F.P., ET AL.: 'Synthesis of porous carbon nanotubes/activated carbon composite spheres and their application for vitamin B12 adsorption', *Sci. Eng. Compos. Mater.*, 2014, **21**, (2), pp. 165–171

[20] Stefan R., Dorota L., Wojciech P.: 'Application of mass transfer coefficient approach for ranking of active carbons designed for hemoperfusion', *Carbon*, 2004, **42**, pp. 2139–2146

[21] Ye C., Gong Q.M., Lu F.P., ET AL.: 'Adsorption of uraemic toxins on carbon nanotubes', *Sep. Purif. Technol.*, 2007, **58**, pp. 2–6

[22] Guo B.Z., Gong Q.M., Wang J.J., ET AL.: 'Fabrication of uniform porous CNTs/activated carbon composite spheres by oil-drop method in stratified oils and their adsorption of VB12', *RSC Adv.*, 2015, **5**, (58), pp. 46997–47003

[23] Ji L.J., Stevens M.M., Zhu Y.F., ET AL.: 'Preparation and properties of multi-walled carbon nanotube/carbon/polystyrene composites', *Carbon*, 2009, **47**, (11), pp. 2733–2741

[24] Asima S., Abeerah S., Rohama G.: 'Silica decorated CNTs sponge for selective removal of toxic contaminants and oil spills from water', *J. Environ. Chem. Eng.*, 2015, **3**, (2), pp. 892–897