Novel carbonaceous nanocomposite pellicle based on bacterial cellulose

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A novel carbonaceous nanocomposite pellicle was prepared by one-step mild hydrothermal carbonization of bacterial cellulose pellicle soaked in glucose solution. The nano-fibrous structure of bacterial cellulose remains intact while carbonaceous spheres with nanometre sizes were generated from glucose during hydrothermal carbonization at 180 °C for 3 h. The carbonaceous spheres formed *in situ* and anchored on the nanofibers' surface expanded the nanostructure of bacterial cellulose and the water-holding capacity decreased slightly from 98% to 93%. Approximately 80% w/w of the dried carbonaceous pellicle was found to be nanometre sized carbonaceous spheres. The size of carbonaceous spheres decreased significantly but had a 60% increase of surface carboxyl groups when the carbonaceous pellicle was prepared in the presence of acrylic acid. The carbonaceous spheres in the never-dried pellicle demonstrate a high adsorption capacity towards heavy metal ions. Approximately, 200 mg of Pb(II) and 1134 mg of Fe(III) can be adsorbed per gram of carbonaceous pellicle, respectively.

Introduction

It is known that cellulose can be produced by many bacteria as a three-dimensional network of nano-fibrils with very high water content (98–99%).[1] When cultured statically, a bacterial cellulose (BC) pellicle is formed at the air-liquid interface by cellulose-producing bacteria such as *Acetobacter xylinus*. Many biomedical applications of this BC pellicle have been explored because of its good physical properties, biocompatibility and strong water-holding capacity.[2] BC pellicle mainly consists of randomly webbed cellulose nanofibers of 20–30 nm in diameter. Like plant cellulose, the BC nanofiber possesses a highly crystalline structure. The high crystallinity provides BC with very good physical and chemical stability. Furthermore, the nano-structured pellicle also provides a very high specific surface area. Probably due to these merits, recently BC has become a very popular matrix for the production of functional composites. These functional composites find their applications mostly in the area of biomedical or tissue engineering.[3–8] Specifically, composites made of BC and hydroxyethylcellulose,[4] polylactide,[5] and hydroxyapatite[6,8] have been developed for orthopedic applications. Hydroxyapatite-BC nanocomposites with a 3-dimensional network was used as a scaffold for cartilage regeneration.[9] BC nanocomposites impregnated with silver nanoparticles have also been used for antimicrobial wound dressing.[10] In addition to biomedical applications, BC pellicles impregnated with noble metal nanoparticles such as Ag, Pt, Pd have been used as catalytic membranes in fuel-cells.[11] Iron oxide nanoparticles have also been incorporated into BC pellicles to prepare magnetic membranes.[12]

Carbonaceous particles prepared by hydrothermal processes have been an appealing topic in recent years, because of their wide variety of applications as adsorbents, catalysts, electrode materials, and stationary phase in liquid chromatography.[13,14] The hydrothermal carbonization of glucose and other carbohydrates is becoming a well-known process to produce monodispersed carbonaceous spheres featuring a hydrophilic surface with mostly carboxyl and carbonyl functionalities.[15,16] The mechanism of carbonaceous sphere formation involves the dehydration of the carbohydrate into furan-like molecules (furfural aldehyde and/or 5-(hydroxymethyl)-2-furaldehyde) as the first step and subsequent polymerization and carbonization as a second step. It has been demonstrated that this carbonaceous nanosphere has a high adsorption capacity toward heavy metal ions.[17,18] Porous active carbon has been used as a carrier for carbonaceous nanospheres as it easily handles the nanospheres during the adsorption operation.[17] In order to improve the surface functionality of the carbonaceous nanospheres, acrylic acid has also been employed during hydrothermal carbonization of glucose to increase the surface carboxyl content and enhance its metal ion adsorption capacity.[17]

Since the direct application of carbonaceous nanoparticles for heavy metal ion adsorption usually encounters some difficulty in recovery, in this work an easily retrievable carbonaceous pellicle (BC@C) was prepared by mild hydrothermal carbonization of BC pellicle soaked in glucose solution. In addition to the carbonaceous spheres formed in the bulk glucose solution, the formation of carbonaceous nanospheres along the nanofibers of BC is expected since the high specific surface area of BC pellicle will provide additional nucleation sites for the decomposed glucose to polymerize into carbonaceous nanospheres during hydrothermal carbonization of glucose in the presence of BC. In this work, the effect of the nanofibrous structure of BC on the size of carbonaceous spheres formed inside the pellicle was studied. In addition, the effects of employing acrylic acid in the hydrothermal carbonization on the morphology

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Table 1 Composition and yield of carbonaceous particles in BC pellicles prepared by hydrothermal carbonization at 180 °C for 3 h

Sample[a]	C produced in absence of BC/g	C yield based on glucose (%)	BC@C composite/g	C in BC@C/g	C fraction of composite (%)
BC@C, 3 h	0.0510	3.800	0.1110	0.090	81.44
BC@C, 6 h	0.5400	40.00	0.1220	0.101	83.11
BC@C–Ac, 3 h	0.1350	10.00	0.1015	0.081	79.70
BC@C–Ac, 6 h	0.7480	55.40	0.1161	0.096	82.26

[a] BC 1.8 g, glucose 1.35 g, acrylic acid 1.5 mL in 15 mL solution.

of carbonaceous pellicle as well as on the heavy metal ion adsorption capacity were also investigated.

Results and discussion

Carbonaceous microspheres

Glucose solution of 0.5 M autoclaved at 180 °C for 3 h generated a black fine particulate suspension. The particulate was observed by FESEM (Fig. 1a) to be spherical with a very smooth surface. The smooth surfaced spherical particles have a high degree of uniformity with micrometre diameter size (5–8 µm) which agrees well with that observed by previous investigators.[17,18] Extending the hydrothermal time to 6 h did not increase the size of the microspheres. However, production yield significantly increased from 3.8% w/w to 40.0% w/w, which means about 0.4 g of carbonaceous microspheres can be obtained from 1 g of glucose employed. As can be seen in Fig. 1b, many smaller spheres with diameter size around 1–2 µm appeared along with the dominant spheres (5–8 µm) after 6 h carbonization. Evidently, the size uniformity obtained at 6 h is quite inferior to that at 3 h. It is believed that the well-known decomposed product of glucose, 5-(hydroxymethyl)-2-furaldehyde (HMF), probably reacts *via* a polymerization-condensation-dehydration cascade to form the final carbonaceous spheres.[15] With the depletion of HMF during extended hydrothermal carbonization, the spheres could not grow to their ultimate diameter size (5–8 µm) leading to the non-uniformity of microspheres obtained at 6 h.

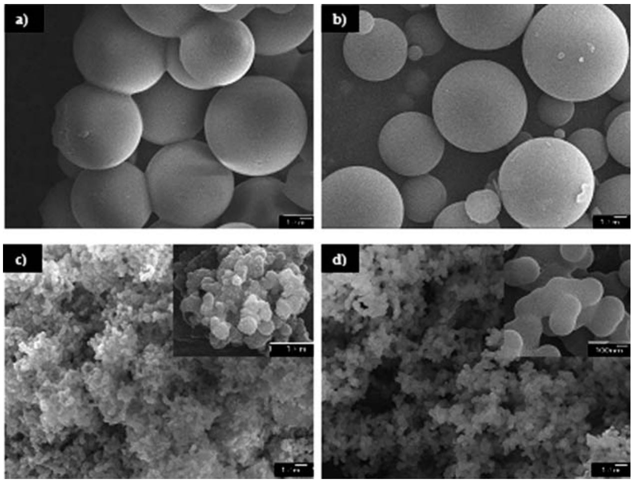

Fig. 1 FESEM micrograph of 0.5 M glucose hydrothermal carbonization (a) 3 h, (b) 6 h, (c) with acrylic acid 3 h, (d) with acrylic acid 6 h.

Addition of co-monomer to the reaction mixture of the hydrothermal carbonization process can obtain carbonaceous materials with a specific surface functional group.[18] Carbonaceous particles with surface functionalized with carboxylic groups (C–Ac) were synthesized by hydrothermal carbonization of 0.5 M glucose in the presence of 10% w/v acrylic acid. As shown in Fig. 1c, addition of acrylic acid induces a significant change in particle morphology. The smooth particles surface can no longer be observed, instead submicron particles aggregated into a raspberry-like micrometre sized particles. This phenomenon has been explained by Demir-Cakan *et al.*[18] that acrylic acid tends to stabilize the newly formed particles and prevent them from further growth as in the pure glucose case. Later on in the process, the submicron particles aggregate into micron-sized particles. However, the high acrylic acid loading (10% w/v) in this case demonstrates that the stabilized submicron particles will not aggregate into the spherical micrometer sized species due to steric effects.[18] As expected in the pure glucose case, prolonging the hydrothermal time to 6 h increased the carbonaceous particle yield from 10% to 55.4% (Table 1). The prolonged reaction time also promotes the fusion of the submicron particles into a peanut-like structure as observed in Fig. 1d.

The hydrothermal carbonization of glucose has already been demonstrated as an effective process to produce micrometre sized spheres with core-shell structures consisting of a hydrophobic aromatic nucleus and a hydrophilic shell, which contains a high density of oxygen functional groups (hydroxyl, phenol, carbonyl, carboxylic, *etc.*).[15] It is interesting to obtain the information about the surface charge of the carbonaceous particles, so zeta potential was measured at different pH values. As shown in Fig. 2, the point of zero charge (PZC) of all the prepared particles is around pH 2. The zeta potential decreases with pH and levels-off at neutral pH to a value about −35 to

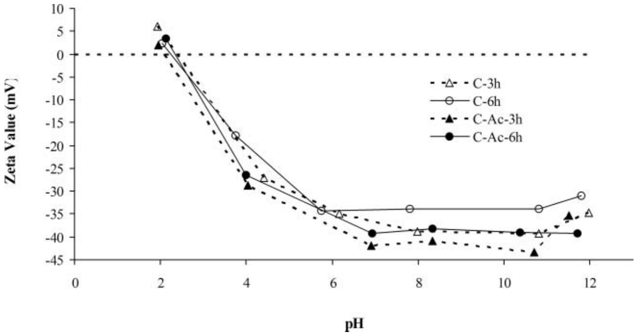

Fig. 2 Surface charge of plain and carboxylic acid functionalized carbonaceous particles.

−42 mV. Extending the hydrothermal time from 3 h to 6 h seems to slightly decrease the zeta potential from −40 mV to −35 mV for the plain carbonaceous C-particles and −42 mV to −40 mV for acrylic acid modified C–Ac particles at neutral pH. It is out of our expectation that the acrylic acid addition did not contribute a significant decrease of zeta potential, since carbonization of glucose in the presence of acrylic acid has been demonstrated to be able to enrich the carboxylic acid content on the surface of carbonaceous particles.[18] Therefore, the acid content on the particle surface was determined by titration.[19] For particles obtained after 3 h of hydrothermal carbonization, the acid equivalent increased 60% from 1.22 to 1.96 mmol g^{-1} when acrylic acid was added. This significant increase of acidic groups can not be truly reflected by the measured zeta potential value because the zeta potential is a surface technique and can not measure the carboxylic groups located within the pores of the C–Ac particles obtained in the presence of acrylic acid (Fig. 1c).

Carbonaceous pellicles (BC@C)

The highly crystalline structure of cellulose ensures bacterial cellulose can withstand the mild hydrothermal carbonization conditions for glucose (180 °C, 3 h) so the BC nanostructure is well preserved. The nanostructure of BC can be observed by FESEM (Fig. 3a) and consists of nanofibers with diameter much less than 100 nm randomly but tightly intertwined and forming a three-dimensional network, as observed in the cross-section micrograph (Fig. 3b). BC pellicle was immersed in 0.5 M glucose solution overnight to ensure glucose concentration was uniformly distributed inside of pellicle. After 3 h hydrothermal carbonization in the glucose solution, the white BC pellicle turned brownish and the integrity of the pellicle was still well-maintained. As observed by FESEM (Fig. 3c and d), most of the carbonaceous spheres in the pellicle (BC@C) are coupled to the nanofibers but with diameter sizes in the submicron range, which is much smaller than that obtained in the absence of BC pellicle (Fig. 1a and b). The size of the spheres formed *in situ* were also affected by their location in BC pellicle. The size of the spheres in the surface layer is around 0.1–1 μm (Fig. 3c), which is much larger than that formed in the interior of BC pellicle (Fig. 3d). The effect of location on the size of the spheres can be attributed to the mass transfer resistance inside BC pellicle. In the surface layer, decomposed glucose product HMF attaches to nucleation sites provided by nanofibers and polymerizes into a carbon sphere. The depleted HMF can be readily supplied by transferring from bulk solution so that the carbonaceous sphere can keep growing to its ultimate size. On the other hand, the carbonaceous sphere initially formed in the interior of BC pellicle stops growing once HMF is depleted and without ready supply from bulk solution because of the high mass transfer resistance. As shown in Table 1, without considering the amount produced in the bulk solution, the amount of carbonaceous spheres formed in the pellicle BC@C (90 mg) already exceeds that produced in the absence of BC (51 mg). Evidently, the very high surface area of BC will provide a large amount of nucleation sites to facilitate the carbonaceous spheres formation. As mentioned in the previous section, prolonging the hydrothermal time to 6 h can have a 10-fold increase of the amount of carbonaceous spheres produced. However, the amount carbonaceous spheres formed in the carbonaceous pellicle BC@C did not have a significant increase (as shown in Table 1) because the BC pellicle only has limited space and surface to accommodate the carbonaceous spheres formed *in situ*. BC@C pellicle still possesses a high water-holding capacity as indicated by its water content only slightly reduced from 98.8% w/w of original BC pellicle to 97.0% and 93.1% of carbonaceous pellicles prepared after 3 h and 6 h carbonization, respectively.

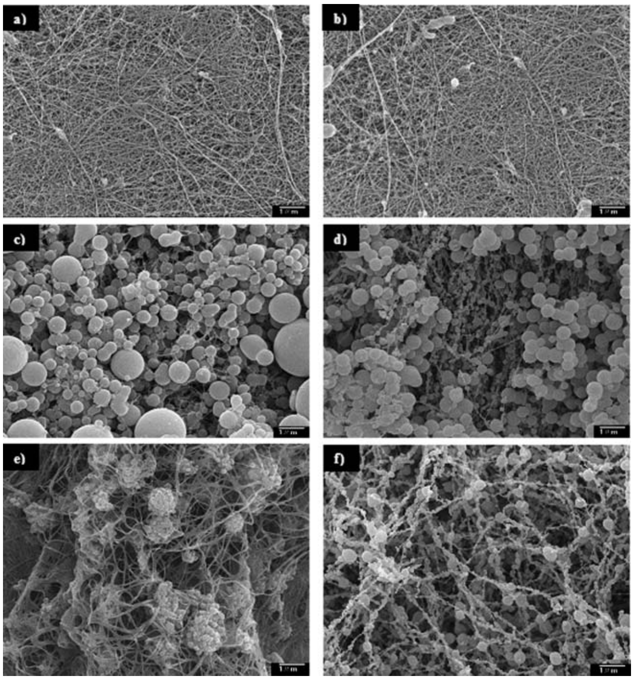

Fig. 3 FESEM micrograph of hydrothermal carbonization bacterial cellulose for (a) original BC top view, (b) BC cross-sectional views, (c) BC@C top view, (d) BC@C cross-sectional views, (e) carboxylic acid fuctionalized BC@C–Ac top view, (f) BC@C–Ac cross-sectional views.

The carbonaceous pellicle was also prepared in the presence of 10% w/v acrylic acid. As shown in Fig. 3e, an appreciable amount of micrometre sized aggregates of nano-spheres are formed with cellulose nanofibers in the surface layer of BC pellicle. Most of the nanofibers' surface is free of carbonaceous particles. However, as observed in the cross-sectional area of the acrylic acid modified BC@C (Fig. 3f), most of the nanofibers are coated with nanometre sized spheres. The size of these nanospheres is much smaller than that of their counterparts prepared in the absence of acrylic acid (Fig. 3d). This is in good agreement with what was observed when the carbonaceous spheres were prepared by adding acrylic acid as co-monomer, the acrylic acid tends to stabilize the newly formed carbonaceous particles and prevents them from further growth. The steric effect of the nanofibers in the interior of BC pellicle also prevents the nanospheres from assembling into micrometre sized aggregates as present on the surface layer. Similar to BC@C, the carbonaceous particle content in BC@C–Ac did not increase much as carbonization time was extended from 3 h to 6 h. Despite acrylic acid addition and extending carbonization to 6 h, the carbonaceous particle content remains at a constant level approximately 80% w/w in the dried carbonaceous pellicle. It is very clear that the nanofibers of BC can provide a very high surface area for carbonaceous spheres to grow with resulting size significantly smaller than their counterparts in the bulk solution. In comparison with the original BC pellicle, the BC@C and BC@C–Ac pellicles have a more porous and expanded nanostructure. Evidently, the original tightly packed nanofibers are expanded by the formation of nano or submicron sized carbonaceous spheres in between. The porous structure of the carbonaceous pellicle should facilitate the carbonaceous nanospheres as an easily retrievable adsorbent.

Adsorption of heavy metal ions (Fe^{3+}, Pb^{2+})

The carbonaceous particles prepared from hydrothermal carbonization of glucose with[18] and without[17] acrylic acid have been demonstrated to have good adsorption capacity towards heavy metal ions. Fe(III) and Pb(II) were used as model heavy metal ions for equilibrium adsorption by carbonaceous spheres and BC@C pellicle. The adsorption for Fe(III) was carried out at pH 1.8 for 5 days to ensure the adsorption equilibrium. Since BC pellicle itself did not show any adsorption capability towards those metal ions, the amount of metal ion removed from the supernatant was considered to be adsorbed by the carbonaceous nanospheres incorporated in BC@C. As shown in Fig. 4, the adsorption performance of plain C is much better than that of acrylic acid modified C–Ac even after they are incorporated into the BC pellicle as BC@C and BC@C–Ac nanocomposites. The acrylic acid modified C–Ac is known to have an outer surface enriched with carboxylic acid groups[18] The carboxylic acid will be completely protonated at pH 1.8 employed for Fe(III) adsorption. Probably, the protonated carboxylic acid at the outer surface of C–Ac particles is not favorable for forming a complex with Fe(III).

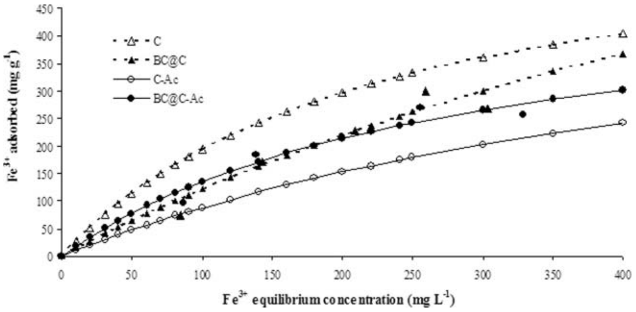

Fig. 4 Adsorption isotherm of Fe(III) solution at pH 1.8.

The adsorption isotherms were fitted with the Langmuir adsorption model as shown in eqn (1).

$$q_e = \frac{Q^\circ b C_e}{1 + bC_e} \quad (1)$$

where q_e, Q^o, C_e and b are the amount of metal ion adsorbed by carbonaceous particles, maximal adsorption capacity, equilibrium concentration and adsorption constant, respectively. As shown in Table 2, the isotherms are well-fitted with the Langmuir model as demonstrated by the square of correlation coefficients being close to unity ($r^2 > 0.95$). Despite of its 80% carbonaceous particle content, the BC@C pellicle shows the maximum adsorption capacity (1134.5 mg g^{-1}) approximately 1.8 fold higher than that of its counterpart, plain C microspheres (634 mg g^{-1}) and 2.2 fold higher than that of BC@C–Ac (511.8 mg g^{-1}). Presumably, the carbonaceous nanospheres formed inside BC@C pellicle rather than microspheres provide a higher carbonaceous surface area that leads to a significantly enhanced Fe(III) adsorption capacity.

Table 2 Langmuir isotherm parameters of adsorption for Fe(III) and Pb(II) on carbonaceous materials

	Fe(III)			Pb(II)		
Sample	Q^o/mg g^{-1}	b/L mg^{-1}	r^2	Q^o/mg g^{-1}	b/L mg^{-1}	r^2
C	634.411	0.0044	0.9898	224.776	0.3450	0.9497
C–Ac	577.148	0.0018	0.9839	687.208	0.0075	0.9601
BC@C	1134.49	0.0012	0.9557	108.606	0.1226	0.9987
BC@C–Ac	511.799	0.0036	0.9658	213.707	0.0937	0.9399

Fig. 5 shows the adsorption isotherms of Pb(II) after 72 h incubation at pH 6.0 and room temperature. Except acrylic acid modified C–Ac particles, plain C microspheres and carbonaceous pellicles (BC@C and BC@C–Ac) achieve adsorption saturation at quite low equilibrium concentration (<100 mg L^{-1}). The isotherms were also well-fitted with the Langmuir adsorption model as shown in Table 2. The C–Ac particles show Q^o of 680 mg g^{-1}, approximately 3-fold higher than their counterparts plain C microspheres. This is contradictory to what was observed for Fe(III) adsorption. The very different adsorption capacity probably arises from pH 6 rather pH 1.8 employed for Pb(II) adsorption. At pH 6, the carboxylic acid on C–Ac surface is fully dissociated which may favor forming a complex with Pb(III). In contrast to Fe(III) adsorption, neither plain C nor acrylic acid modified C–Ac has a better adsorption performance once incorporated into BC as a carbonaceous pellicle. BC@C–Ac has a Q^o close to that of plain C microspheres at about 220 mg g^{-1}. BC@C however shows the poorest adsorption performance with Q^o about 110 mg g^{-1}. Evidently, BC as a matrix deteriorates the adsorption performance of carbonaceous pellicle toward Pb(II). The very different effect of BC matrix on adsorption performance of carbonaceous particles formed in the nanocomposites towards Fe(III) and Pb(II) is probably due to the very different metal ion properties such as ionic radius, electro-negativity, and ionization potential.[20] The larger radius size, higher ionic potential and electro-negativity may limit the accessibility of Pb(II) to the carbonaceous nanoparticles embedded inside of the BC pellicle. The adsorption capacities of the as-prepared carbonaceous particles and pellicles towards Fe(III) and Pb(II)

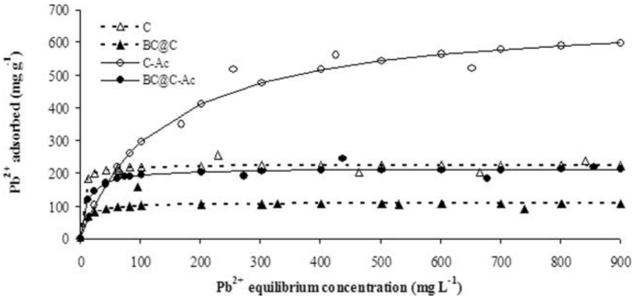

Fig. 5 Adsorption isotherm of Pb(II) at pH 6.0.

Table 3 Comparison of Fe(III) and Pb(II) adsorption capacities in different adsorbents

Adsorbent	Fe(III)/mg g^{-1} [a]	Pb(II)/mg g^{-1} [b]	Reference
C (180 °C, 3 h)	349.784	223.65	this study
C–Ac (180 °C, 3 h)	193.084	562.26	this study
BC@C (180 °C, 3 h)	284.787	107.15	this study
BC@C–Ac (180 °C, 3 h)	256.599	209.97	this study
C–Ac (190 °C, 16 h)	—	351.4	18
Calcination Carbon (400 °C)	34.63	—	17
Active Carbon @C (180 °C, 6 h)	39.10	—	17
Low-rank coal	—	250.7	20
Lignite	—	8.49	20
Leonardite	—	250.7	20
Active Carbon	27.93	—	21
Clinoptilolite (Treated with HNO_3 at 20 °C)	64.5	—	22
Blast furnace sludge	—	64.17	23

[a] Equilibrium concentration of Fe(III) at 280 mg L^{-1}. [b] Equilibrium concentration of Pb(II) at 600 mg L^{-1}.

were compared with those reported by other investigators using different adsorbents. As shown in Table 3, when compared at the same equilibrium metal ions concentration, the adsorption capacities of carbonaceous pellicle are approximately 7-fold higher for Fe(III) but about 70% lower for Pb(II).

Experimental

Materials

Bacterial cellulose pellicle was obtained by statically culturing *Acetobacter xylinum* (BCRC12334) in Hestrin–Schramm medium at 27 °C for 7 days. The harvested BC pellicle was soaked in 1 N NaOH and heated to 95 °C for 30 min followed by washing thoroughly with deionized water to neutral pH. The rest of chemicals are analytical grade and used without any further treatment.

Synthesis of carbonaceous spheres and nanocomposites

Plain carbonaceous particles (C) was produced by heating 15 mL of 0.5 M glucose solution in a 40 mL Teflon container sealed by a stainless steel autoclave at 180 °C for 3 h. After cooling to room temperature, the precipitate was thoroughly washed with alcohol followed by deionized water. For the preparation of carboxylic acid functionalized carbonaceous particle (C–AC), 10% w/v acrylic acid was employed in the 0.5 M glucose solution for hydrothermal carbonization. Carbonaceous pellicles BC@C and BC@C–Ac were synthesized by soaking 1.8 g never-dried BC pellicle in 15 ml 0.5 M glucose solution and with 10 w/v% acrylic acid addition, respectively, for 24 h under stirring before hydrothermal carbonization was carried out at 180 °C for 3 h. After cooling to room temperature, the BC composites were separated from the fine precipitate by a mesh screen and washed thoroughly with deionized water. The carbonaceous particles and pellicles were stored in deioninzed water for further characterization and application.

Adsorption of Fe(III) and Pb(II)

The plain and carboxylic acid functionalized carbonaceous particles along with carbonaceous BC pellicle counterparts were tested for the adsorption of Fe(III) and Pb(II). Typically, 10 mg of samples were added to 1.5 ml of metal ion solution of different concentrations with pH adjusted to 1.8 for Fe(III) and 6.0 for Pb(II) by 0.1 N HCl or NaOH solution. The adsorption was carried out under shaking for 6 days for Fe(III) and 3 days for Pb(II) with pH adjusted every 24 h to 6.0 ± 0.1 at room temperature. The supernatant of the suspension obtained by filtering through a 0.45 μm membrane filter was immediately analyzed by inductively coupled plasma spectrophotometer for metal ion concentration determination.

Characterization methods

Surface charges of carbonaceous particles in solution were determined by zeta potential analyzer (Malvern, Zetasizer 2000). A suspension of 50 mg of particles dispersed in 15 ml deionized water with pH adjusted 2 to 12 by 0.1 N HCl or NaOH solution were used for zeta potential measurement. The acidic groups content of plain and carboxylic acid functionalized particles were determined using titration method. Carbonaceous particles (10 mg) were dispersed in 20 ml NaCl solution for 24 h before titration with 0.5 N NaOH solution previously standardized with 0.05 N $H_2C_2O_4$ solution. Field emission scanning electron microscopy (FESEM) images of the samples were obtained by scanning electron microscope (JEOL, JSM-6390 LV). Critical point drying (Samdri PVT-3D) was employed to prepare the BC and its nanocomposites (BC@C and BC@C–Ac) sample for FESEM observation. Inductively coupled plasma spectrophotometer (Horiba Jobin Yvon, ICP-AES JY2000) was used for metal ion concentration determination.

Conclusions

In summary, novel carbonaceous pellicles have been synthesized by anchoring carbonaceous nanospheres onto nanofibers of BC pellicle in a one-pot hydrothermal carbonization reaction. The presence of cellulose nanofibers facilitates carbonaceous nanosphere formation during hydrothermal carbonization of glucose and also enhances the adsorption capacity of the incorporated carbonaceous nanospheres towards Fe(III) and Pb(II). In comparison with the fine and dispersed carbonaceous particles, the BC pellicle-based carbonaceous nanocomposites provide an efficient and convenient recyclable tool for heavy metal ion removal. In addition, the high surface area, good chemical stability and carboxylic acid functionalized surface of the as-prepared nanocomposite of carbonaceous pellicle will enable them to be used for other potential applications such as in the fields of catalysis, drug delivery, and enzyme immobilization.

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