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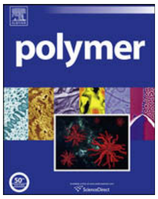

Assembled alginate/chitosan micro-shells for removal of organic pollutants

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ABSTRACT

Natural polyelectrolyte micro-shells were constructed through layer-by-layer (LbL) assembling of alginate sodium (ALG) and chitosan (CHI) onto weakly cross-linked melamine formaldehyde (MF) colloidal particles and subsequent removal of core. The assembled materials presented good film formation ability. It was found that under moderate conditions (room temperature, pure water solution) the ALG/CHI micro-shells can effectively load organic pollutants such as 2,4-dichlorophenol (DCP) and salicylic acid (SA). SEM and AFM images confirmed that the loading behavior of pollutants in the shells occurred and displayed that the feature of shell architecture changes before and after loading. The loading amount of pollutants into shell system was calculated and characterized through HPLC. The loading kinetics analysis showed that the loading process can reach an equilibrium state after approximately 4 h. Compared to the conventional polyelectrolyte $(PSS/PAH)_5$ shells, the $(ALG/CHI)_5$ shells had stronger adsorption capacity and faster adsorption rate for pollutant loading. The adsorption isotherm result of organics in the ALG/CHI micro-shells can be well described by Langmuir equation. Advantages of the assembled natural micro-shells composed of ALG/CHI i.e. efficient loading ability to pollutants in aqueous ecosystem, good stability responded to external stimuli as well as fast loading process render them potentially applicable as environmental-friendly micro-container for the treatment of organic pollutants from aqueous solution.

1. Introduction

With the development of chemical and pharmaceutical industries, many recalcitrant and non-biodegradable organics, like chlorophenol, salicylic acid and certain dye, accumulate in water and suffer the risk of contamination of the underground sources in an irreversible way [1–3]. The existence of these pollutants in excess of a few parts per billion (ppb) in water could lead to serious health problem [4]. Conventional biological and chemical processes are insufficient in removing these contaminants [5], and various adsorption technologies are being widely developed and used for wastewater remediation due to their versatile and efficient capability to separate a wide range of chemical compounds and easily operational procedure [6]. Adsorption on granulated activated carbon is one of the most commonly used methods to concentrate organic pollutant and lower their concentration from effluents. Notwithstanding, relatively high cost, considerable loss of the substrate and premature expenditure of activated carbon upon dissolved compounds or ions competing for sorption sites on the carbon promote one to search for more efficient and economic purification system for removal of persistent pollutants [7–9].

LbL assembled hydrogel films or films containing micro-gel components have received particular attention because of their high loading capability of guest materials in films, good biocompatibility and stimulus-responsive behavior of the films [10–17]. This LbL technology has been extensively utilized in three-dimensional geometry to produced hollow polymeric microcapsules/micro-shells with various hydrogel components [18–20]. Previous studies on these hydrogel micro-shells mainly focus on gene or drug delivery. In fact, applications of the hydrogel micro-shells can be extended to other domains, especially in wastewater treatment based on the following reasons: 1) the guest materials with/without having charge groups are facile to enter into shell interior by a post-diffusion step; 2) the assembled micro-shells can be easily separated by simple filtration; 3) high expanded shell nature in the media will facilitate to high loading of substrates in LbL assembled shell interior and walls; 4) the micro-shells have been shown to function as micro-reactors that might be favorable for the post-treatment of pollutants upon being loaded in the shells owing to controllable permeability of shell walls and stability of the shells themselves.

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Chitosan (CHI), a natural bio-polymeric cation, is generally obtained by deacetylation of chitin. CHI-based complexes often exhibit good adsorption capability of heavy metal ions and organic species [3,4,21,22]. Therefore, synthesis and assembly of CHI together with alginate sodium (ALG) as hollow micro-shells are of particular importance in developing novel biomaterial toward removal of contaminants. Recently we have constructed hydrogen-bonded cross-linked two component ALG/CHI micro-shells, and found that the as-prepared ALG/CHI shells possessed unexpected high stability and permeability [23]. Further experimental results revealed that the shells might be potentially applicable as micro-reactor for the accumulation and subsequent photodegradation of dye molecules [24]. Here, we chose 2,4-dichlorophenol (DCP, a pervasive environmental pollutant extensively used for the production of herbicides, pesticides and plant growth regulators) and salicylic acid (SA, a pollutant comprehensively present in wastewater from paper milling, cosmetic industry and pharmaceutical field) as pollutant models [25,26]. The loading process of pollutants in the preformed ALG/CHI shells was carried out under moderate conditions in the aqueous solution. Detailed loading behaviors of organics in the ALG/CHI shells were investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM), and high-performance liquid chromatography (HPLC). Effects of pH and initial concentration of organics on loading amount of shell system were explored in detail. Compared with conventional PSS/PAH shells, the natural ALG/CHI shells exhibited higher loading capability and shorter loading process. Adsorption isotherm data indicated that the loading process is fitted to Langmuir model. As far as we know, this is the first report on the use of biodegradable ALG/CHI shell as micro-containers for the removal of phenolic- and salicylic-compounds from aqueous environment.

2. Experimental section

2.1. Materials

Melamine formaldehyde (MF) particles with diameters of about 3 μm were prepared according to the method previously reported in the literature [27]. ALG ($M_w = 12{,}000$–$80{,}000$) was obtained from Sigma, Canada. CHI ($M_w = 30{,}000$) was obtained from Primex Biochemicals, Norway. PSS ($M_w = 70{,}000$) and PAH ($M_w = 70{,}000$) were obtained from Aldrich. The desired pH of the solutions was adjusted by diluted aqueous solution of NaOH or HCl. Millipore water with a resistivity higher than 18.2 MΩ/cm was used throughout the study. DCP, SA and all other reagents were of analytical reagent grade and were used without further purification.

2.2. Shell fabrication

3 mL of alginate solution (1 mg/mL in 0.5 M NaCl) or chitosan solution (1 mg/mL in 0.2 M NaCl at pH 3.8) with an opposite charge to that of either MF templates (3 μm) or the last layer deposited, was added to1 mL of template suspension solution (30 mg/mL) and left to absorb for 1 h. The excess species added was removed after each layer was deposited by performing three centrifugation (2000 *g*)/washing/redispersion cycles. Typically, five (ALG/CHI) bilayers were deposited. Hollow shells were obtained by dissolving the MF cores with HCl (0.16 M, 30 min), centrifuged and washed three times with millipore water.

2.3. Organics loading experiments

The as-prepared micro-shell solutions (aged for approximately 2 days) were centrifuged to remove supernatant liquid. Afterwards, DCP or SA solution was added to the above-mentioned shells, adsorbed for 16 h. By centrifugation, the supernatant fluid and the pollutant-loaded shells were respectively obtained for further characterization.

2.4. Measurements of the loading amount

According to the initial concentration of pollutants added and the amount of non-accumulated pollutants remaining in the supernatant liquid obtained from HPLC, we can calculate the loading ratio, loading amount of organics in single shell and shells constructed from per unit mass of template by quantitative analysis, combined with respective standard curve of different organic contaminates, as well as the known physical parameters of MF particles. The calculation equations are shown as follows:

$$\text{ratio} = \frac{c_0 - c_s}{c_0} \tag{1}$$

$$q = \frac{\text{ratio} \times c_0 \times v_0}{k} \times M \tag{2}$$

$$q' = \frac{\text{ratio} \times c_0 \times v_0}{m} \times M \tag{3}$$

where ratio (%), q (g/shell) and q' (mg/g) represent the adsorption capacity of shell system, c_0 and c_s denote the initial and supernatant liquid concentrations of organic solution, v_0 is the volume of organic solution added, k is the number of the constructed shells evaluated by the known parameters of MF particles; m is the mass of MF particles used for fabricating shells; M is molecular weight of target pollutant.

2.5. Characterization

SEM (Hitachi S-4700, Japan) was utilized to observe the morphology of hollow shells and pollutant-filled shells. For SEM analysis, a drop of each sample solution was applied to a sample holder with sequential drying at room temperature overnight. Then the samples were sputtered by coating a thin gold layer on the as-prepared specimens.

AFM images were recorded at ambient temperature by using a Digital Instrument Nanoscopy IIIa in the tapping mode. Samples were prepared by applying a drop of the shell solution onto a freshly cleaned silicon substrate. After the shells were allowed to settle, the substrate was extensively rinsed with millipore water and then dried under a gentle stream of nitrogen.

The amount of unencapsulated organics remaining in the supernatant was estimated by HPLC on an Inersil Waters SunFire-TM C-18 5 μm column (4.6 × 150 mm) at room temperature for small molecule organic compounds without absorption in visible spectra region such as DCP and SA. The HPLC system consisted of a Waters separation module and a Waters 2996 photodiode array detector detects the signals at the 286.8 nm and 296 nm for DCP and SA respectively by using an effluent composed of methanol/water (7:3 v/v) for DCP and acetonitrile/water (2:8 v/v) for SA at a flow rate of 1.0 mL/min.

3. Results and discussion

3.1. Fabrication and characterization of pollutant-loaded shells

Hollow shells were constructed under mild conditions (pure water media, room temperature) by alternate adsorption of five bilayers of ALG and CHI onto about 3 μm diameter MF particles,

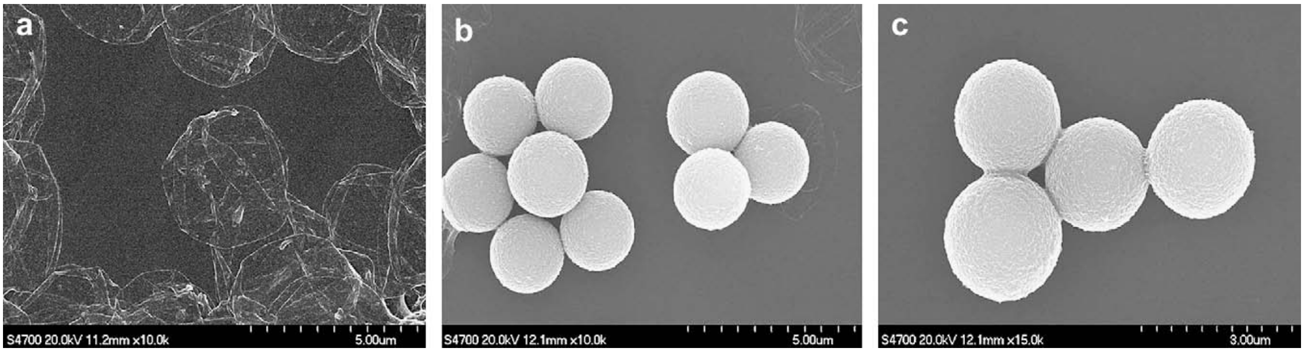

Fig. 1. SEM images of the $(ALG/CHI)_5$ hollow shells (a) and shells upon incubating the preformed shells in various organic solutions in pure water medium: (b) DCP; (c) SA. Scale bars are 5 μm for a, 5 μm for b and 3 μm for c.

followed by removal of template in HCl. As shown in Fig. 1(a), the assembled hollow ALG/CHI shells with a size of ca. 4 μm at the dry state exhibited many folds and creases owing to air-drying. When the obtained shells were loaded with organic compounds i.e. DCP, SA, apparent changes in the morphology of the filled shells appeared (see Fig. 1(b) and (c)). The empty shells look like folded thin shells, but the loaded shells look like filled balloons. All above images provided strong evidence that organic molecules including DCP and SA can migrate across the shell walls and then stay in the interior of the shells. Besides, the profile of each loaded shell is discerned as a spherical shape and this means that the ALG/CHI shells in external environments possess good stability. It is worth mentioning that the diameter of organics-loaded shells at the dry state is approximately 2.3 μm for DCP and 2.0 μm for SA, which is significantly smaller than the original template size of 3 μm. Furthermore, the surface of the DCP- or SA-loaded shells looks like smooth and rigid. This difference in the size and morphology of the shells loaded with organics could be explained by considering the shell wall components and molecular architecture of organic pollutants chosen. In the ALG/CHI shell walls, there should exist some residual charges originated from the carboxylic groups of ALG chains and amino groups of CHI that allow producing hydrogen bonds with organic substrates having suitable functional radicals such as hydroxyl groups and carboxylic groups. In addition, DCP and SA also facilitate forming hydrogen bonds in shell walls in view of their chemical structure. As a result, the interaction of the network structure composed of ALG/CHI and DCP or SA might cause the contraction of shell wall architecture and thus eventually make the framework of shell walls look like rigid and smooth. The changes of morphology and texture of the ALG/CHI films or ALG/CHI beads have been observed by addition of ionic, rigid particles or phenolic derivatives [23,28,29]. All these observations suggest that the ALG/CHI shells just like an elastomer possess loading capacity and strong mechanical property.

In order to gain further insight into the shell texture changes before and after incubation in pollutant-contained solutions, the AFM technique was employed [30]. Fig. 2(a) and (b) displays AFM images (top view) of the ALG/CHI shells before and after incubation in DCP for 16 h. Apparently, the interior of the filled shell is rather bright, indicating that DCP can cross the layer barrier of the shell walls, and accumulate inside the shells. Direct visualization in the above two cases was also provided by AFM measurements on surface plot of the shells. An empty shell looks like a compressed plate (Fig. 2(c)), but a filled shell looks like a small hill (Fig. 2(d)),

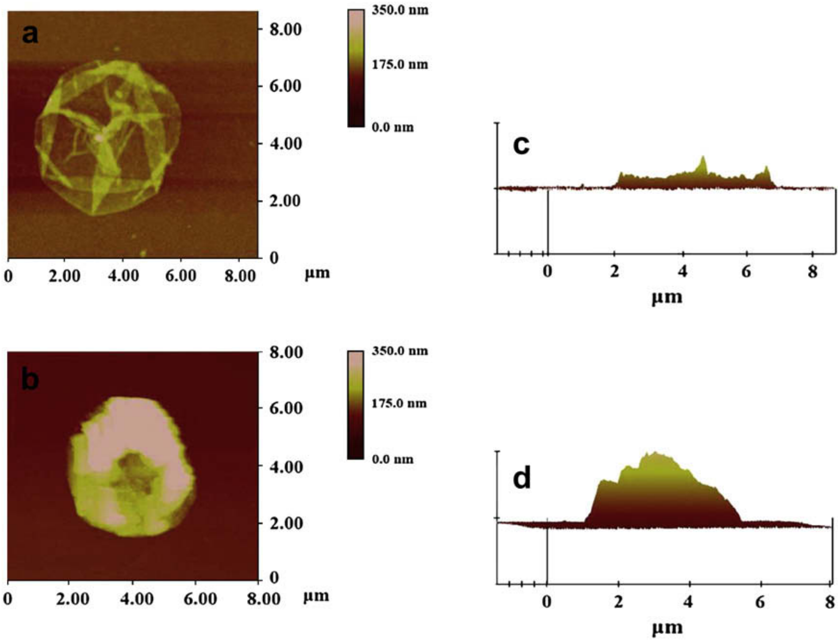

Fig. 2. AFM images of the single multilayer micro-shell of $(ALG/CHI)_5$ (a) before and (b) after incubation in DCP solution. Typical three-dimensional views corresponding to (a) and (b) are shown in (c) and (d), respectively.

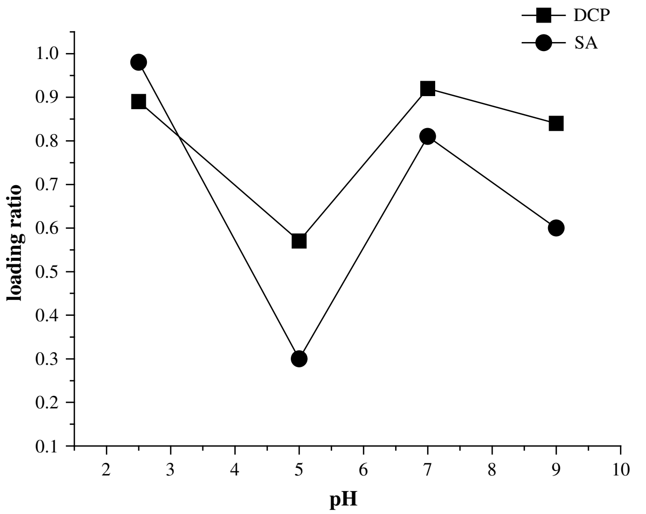

Fig. 3. Effect of pH on loading behavior of organics into the ALG/CHI shells. Note: The loading amount of organics into the shells was obtained by the difference between the initial amount of organic solution added with a known initial concentration of 1.5×10^{-4} M and the amount of unloaded organics from supernatant liquid, in which the amount of unencapsulated organics remaining in the supernatant liquid was examined through HPLC.

Table 1
Loading behavior of DCP with different initial concentrations in the hollow $(ALG/CHI)_5$ shells templated on MF with a diameter of 3 μm, pH 7.

c_0 [$\times 10^{-4}$ M]	0.5	1.5	4.5
q [$\times 10^{-11}$ g/shell]	4.7	11.9	29.1

also suggesting that a great deal of accumulation of DCP had occurred.

3.2. Effects of pH and initial concentration of organic solution on the loading amount

ALG and CHI are two oppositely charged hydrophilic natural polyelectrolyte materials and very sensitive toward changes in external factor such as pH. The effect of pH on the loading amount of DCP and SA in the shells is shown in Fig. 3. One can see that the loading amount of species at pH 5 is relatively low, while the loading amount at acidic media (pH 2.5 shown here) and neutral media (pH 7 shown here) is relatively high. Two aspects of factors i.e. the effect of pH on micro-shell wall components and electrostatic interaction between shell wall and organic species for different loading capacity might be considered here. As we know, the pK_a of ALG is 4.0 and the pK_a of CHI is 7.0 [31,32]. At pH 5 the carboxylate group of ALG mainly exists in the form of COO^- and the amino group of CHI mainly exists in the form of NH_3^+. In this case, the presence of both COO^- and NH_3^+ along polymer backbone could enhance the electrostatic interaction of the network structure of shell wall components, which arose the decrease of the permeability of the shell walls and hence at last led to the reduction of the loading amount [33]. Whereas, at pH 2.5, the carboxylate group of ALG does not carry an electric charge resulting in weakened electrostatic attraction between ALG and CHI and the swelling of shells due to hydration of uncharged ALG segment, which probably causes the formation of a more porous with porosity on the wall architecture that facilitates permeation of species. At pH 7.0, the amino groups of CHI become ionized and in the shell wall there should exist a small quantity of NH_3^+ and excess COO^-. This asymmetric charge density in the wall could also weaken

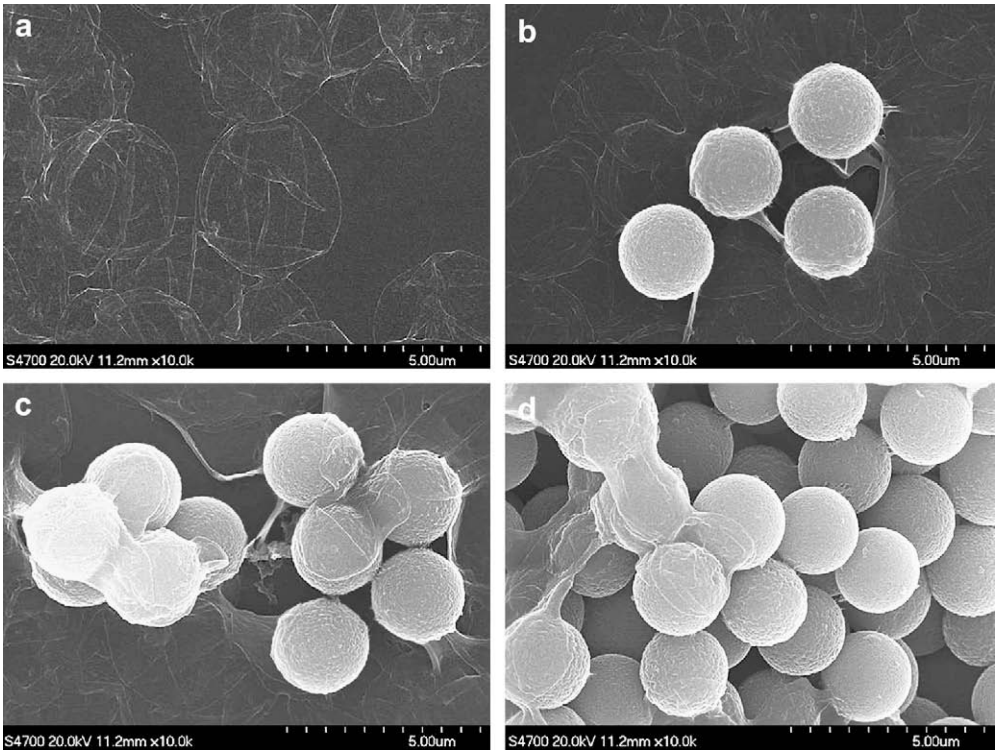

Fig. 4. SEM images of the $(ALG/CHI)_5$ shells upon incubating the preformed shells in DCP solutions with different concentrations of (a) 0, (b) 0.5×10^{-4}, (c) 1.5×10^{-4}, and (d) 4.5×10^{-4} mol/L, respectively.

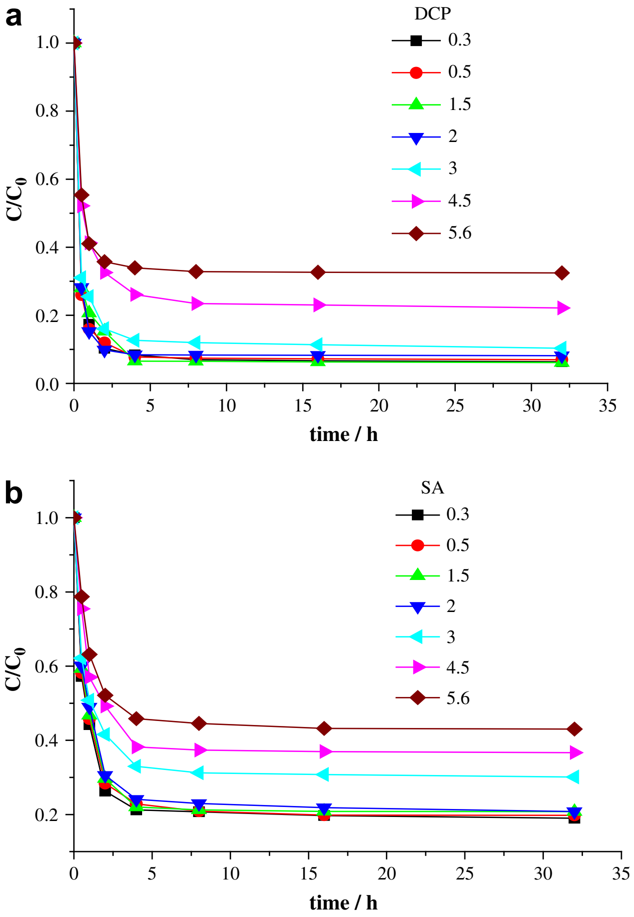

Fig. 5. Loading kinetics of DCP (a) and SA (b) into ALG/CHI micro-shells under different initial concentrations (DCP = 0.3–5.6 × 10^{-4} M and SA = 0.3–5.6 × 10^{-4} M).

electrostatic attraction between two shell components and enhance the penetrating movement of organic through the multilayer wall [19a]. At pH higher than 7, the loading amount of two organic substrates in the shells exhibited a slightly declined trend. Possible reasons are that in this case there are excess negatively charged groups (COO^-) in shell walls as mentioned above; meanwhile two organic pollutants could present in the form of anion species (DCP^-, COO^- of SA) [34]. This thus leads to a strong electrostatic repulsion between wall components and organics. Also, it should be pointed out that in subsequent experiments the optimum pH value of the loading was chosen as 7 on account of high loading capacity of the shells as well as low cost of wastewater treatment process. By quantitative calculation, the loading amount of DCP and SA at neutral medium is 11.9 × 10^{-11} g/shell, and 9.8 × 10^{-11} g/shell, corresponding to 92% of DCP removal and 89% of SA removal.

The effect of the initial concentration of organics on the loading behavior was also explored and the results obtained by quantitative calculation are shown in Table 1. With the increase of the initial concentrations of DCP, the loading amount of organics in the shells gradually increased. This is because the increase of the initial concentrations can enhance the concentration gradient between the bulk and shell interior, hence finally enhancing the loading amount.

Clear observation of the effect of initial concentrations of pollutants on the shell morphology was further obtained by SEM images (Fig. 4). Fig. 4(a) gives a typical SEM image of empty shells. The size of the crumpled shells at the dry state is slightly larger than the original MF template size of 3 μm because of collapse of the shells, which has also been observed in the polyelectrolyte micro-shells of PSS/PAH or PSS/PDDA [35]. With the enhancement of the initial concentrations of DCP, one can see that the hollow folded shells were gradually reduced and the filled shells with spherical structure increased accordingly, which is consistent with the results shown in Table 1.

3.3. Loading kinetics study

To better understand the absorption process, the loading kinetics of pollutants in the ALG/CHI shell system were investigated and are shown in Fig. 5. From these figures, it can be observed that the loading of DCP and SA with different initial concentrations ranging from 0.3 × 10^{-4} M to 5.6 × 10^{-4} M into ALG/CHI shells was a very fast process. In the initial period of about 3 h, the loading amount increased rapidly, reaching up to about 90% of the total loading amount. After that, the enhanced trend of the loading amount becomes slow. After approximately 4 h, an equilibrium loading amount was achieved. In addition, we carried out comparative experiments on the loading kinetics of DCP in the ALG/CHI shells and the PSS/PAH shells (Fig. 6). One can see that the loading of DCP into PSS/PAH was a relatively slow process, and required at least 15 h to reach the loading equilibrium. The equilibrium loading amount (q') of DCP in the PSS/PAH shells is calculated as ~1.09 mg/g, which is apparently smaller than that of the ALG/CHI shells (~1.99 mg/g). This difference can be rationalized by considering the intrinsically high flexibility of ALG/CHI chains compared to that of PSS/PAH. This also suggests that the ALG/CHI system is favour for the treatment of organic pollutants.

3.4. Loading isothermal model

The loading capacity of organics in shell can be evaluated via the loading isothermal experiment. As we know, a loading isotherm describes the relationships between the loading amount of organics with different initial concentrations into the shells and the concentration of unloaded organics in the supernatant liquid at the equilibrium state. The experimental data of loading isotherms from Fig. 5 can be modeled by Langmuir isotherm equation as:

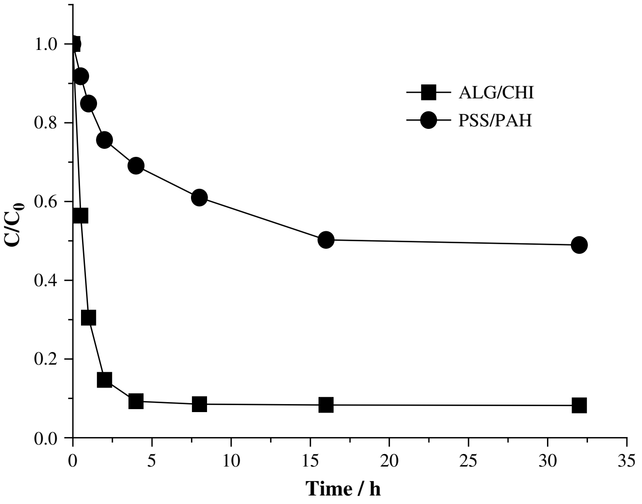

Fig. 6. Comparative study on loading kinetics of DCP into ALG/CHI and PSS/PAH micro-shells (initial organics concentration: 2 × 10^{-4} M, pH 7).

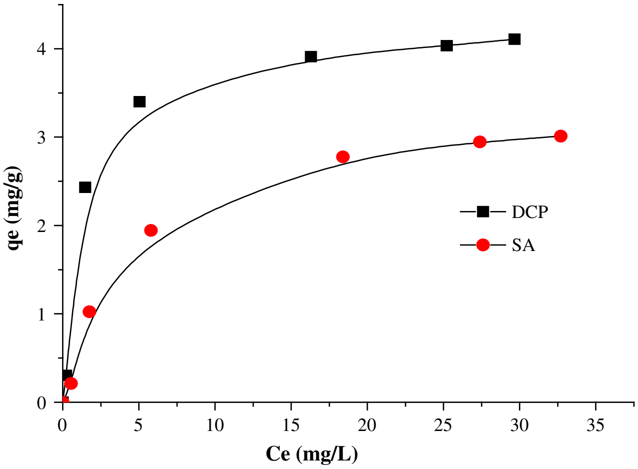

Fig. 7. Loading isotherms of DCP and SA into ALG/CHI shells: experimental equilibrium uptakes and the Langmuir model fitting (pH 7; 25 °C).

$$q_e = \frac{q'_m C_e}{1/b + C_e} \tag{4}$$

in which q'_m is the maximum amount of loading (mg/g); b is the loading equilibrium constant (L/mg); C_e is the equilibrium concentration of organics in the supernatant fluid (mg/L).

The fitted result from the Langmuir equation is displayed in Fig. 7. It was observed that the adsorption isotherm results for the ALG/CHI micro-shell system can be well described by Langmuir equation. From the model fitting, the maximum adsorption capacity, q'_m, of organics into ALG/CHI shells is found to be 4.292 ($R^2 = 0.995$) mg/g for DCP and 3.014 ($R^2 = 0.992$) mg/g for SA. The difference between the maximum adsorption capacities of two organic species into the shells might be originated from their different molecular weights and loading ratios in the shells.

4. Conclusion

We presented an economical and nontoxic system, based on assembled biodegradable micro-shells consisting of ALG and CHI, for removal of organic pollutants from aqueous environment. SEM, AFM and HPLC were employed to verify the successful and efficient loading of organics in confined shells. The loading amount is related to pH and initial concentration of organic solution. The relatively optimum loading can be proceeded under neutral medium, which qualifies the ALG/CHI for potential practical application for treatment of wastewater. Compared with conventional micro-shells, ALG/CHI shells have advantageous ability to load more organics in a faster time. The adsorption isotherm can be well described by Langmuir equation. This study might provide a more efficient and economic purification system for removal of persistent pollutants from wastewater.

Acknowledgements

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