Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 19(2007) 451–457
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Comparison of four supports for adsorption of reactive dyes by immobilized *Aspergillus fumigatus* beads

WANG Bao-e, HU Yong-you*

School of Environmental Science and Engineering, South China University of Technology, Guangzhou 510640, China.
E-mail: baoewang@163.com

Received 10 May 2006; revised 5 July 2006; accepted 24 July 2006

Abstract

Four materials, sodium carboxymethylcellulose (Na-CMC), sodium alginate (SA), polyvinyl alcohol (PVA), and chitosan (CTS), were prepared as supports for entrapping fungus *Aspergillus fumigatus*. The adsorption of synthetic dyes, Reactive Brilliant Blue KN-R, and Reactive Brilliant Red K-2BP, by these immobilized gel beads and plain gel beads was evaluated. The adsorption efficiencies of Reactive Brilliant Red K-2BP and Reactive Brilliant Blue KN-R by CTS immobilized beads were 89.1% and 93.5% in 12 h, respectively. The adsorption efficiency by Na-CMC immobilized beads was slightly lower than that of mycelial pellets. But the dye culture mediums were almost completely decolorized in 48 h using the above-mentioned two immobilized beads (exceeding 95%). The adsorption efficiency by SA immobilized beads exceeded 92% in 48 h. PVA-SA immobilized beads showed the lowest adsorption efficiency, which was 79.8% for Reactive Brilliant Red K-2BP and 92.5% for Reactive Brilliant Blue KN-R in 48 h. Comparing the adsorption efficiency by plain gel beads, Na-CMC plain gel beads ranked next to CTS ones. SA and PVA-SA plain gel beads hardly had the ability of adsorbing dyes. Subsequently, the growth of mycelia in Na-CMC and SA immobilized beads were evaluated. The biomass increased continuously in 72 h. The adsorption capacity of Reactive Brilliant Red K-2BP and Reactive Brilliant Blue KN-R by Na-CMC immobilized beads was 78.0 and 86.7 mg/g, respectively. The SEM micrographs show that the surface structure of Na-CMC immobilized bead is loose and finely porous, which facilitates diffusion of the dyes.

Key words: adsorption; *Aspergillus fumigatus*; immobilization; reactive dyes

Introduction

It is estimated that there are over 7×10^5 t of dyestuffs produced annually worldwide (Young and Yu, 1997). Colored industrial effluents not only produce visual pollution but also risk ecological and public health. Recently, the use of biomass for removal of dyes has been extensively studied (Walker and Weatherley, 2000; Ozfer *et al*., 2003; Harazono and Nakamura, 2005). Unfortunately, the use of freely suspended biomass is plagued with problems, including the need for separation of the suspended biomass from the aqueous medium, and the possible clogging of pipelines and filters (Khoo and Ting, 2001). In general, the natural mycelial pellets are not mechanically strong and varied in size, which can lead to problems, such as channelling in column operation. Immobilization of microorganism overcomes many of these problems. It also provides other advantages, such as high cell density, strong endurance of toxicity, easy separation of produce, low operating expenses, simple maintenance management, lower residual sludges. Applications of immobilization of microorganism have been shifted to wastewater treatment (Nina *et al*., 1995; Chen *et al*., 2002; Suhail *et al*., 2005).

The research on decolorization of dye effluents using immobilized microorganism centralizes in biodegradation (Chen *et al*., 2003; He *et al*., 2004; Nurdan *et al*., 2005) due to the particular mechanism of biodegradation decolorization by certain discovered microorganisms, such as white rot fungus. The immobilized microorganisms are able to degrade dyes efficiently and can be recycled. Recently, biodegradation was difficult by immobilized microorganism owing to the use of resisting light degradation and bio-oxidation dyes. The difficulty brought about promising alternatives for adsorption by immobilized microorganism because fungus is efficient in adsorption of diverse dyes (O'Mahony *et al*., 2002). Moreover, adsorption offers many other advantages: reusability of valuable materials, no or little secondary pollution (Zümriye and Secilay, 2005).

Relatively few studies have been done on adsorption of dyes using immobilized microorganisms. The plant supports like corn core (Dong and Zhou, 2005) and synthetic polymers like polysulphone (Fu and Viraraghavan, 2003) are described to immobilize fungus for adsorption dyes efficiently. However, the use of these supports needs further practical confirmation.

The adsorption of dyes using immobilized microorgan-

Project supported by the Science and Technology Foundation of Guangzhou Municipal Environment Protection Bureau (No. 006). *Corresponding author. E-mail: ppyyhu@scut.edu.cn.

ism is not widely applied because, for one thing, there is unsuitable immobilization support. Seeking supports fitting adsorption of dye is a matter of great concern. Many natural polymers like carboxymethylcellulose (Glay *et al*., 2003), sodium alginate (Yalup *et al*., 2003), and agar (Liu *et al*., 2003) as immobilization supports are used for adsorption of heavy metals. These polymers are known for low prices, rich source, nontoxicity, being biodegradable in environment and simple immobilization operation. But are these natural polymers suitable for as supports immobilizing fungi for adsorption of dye? It is the key problem to solve in this study.

Aspergillus fumigatus was previously isolated. It has shown high adsorptive capacity of five kinds of dyes, including reactive dyes, acid dyes, alkaline dyes, direct dyes, and disperse dyes. Reactive Brilliant Blue KN-R was decolorized by more than 95.6% using *A. fumigatus* pellets at an initial dye concentration of 200 mg/L within 96 h (Xiao *et al*., 2004; Xiao and Hu, 2005). On the basis of the previous study, the aim was the adsorption of reactive dyes by *A. fumigatus* immobilized in Na-CMC, SA, PVA-SA, and CTS gel beads in this study. Na-CMC, SA and CTS are natural polymers. The synthetic polymer PVA added into SA was to enhance the strength of the beads. The two selected dyes, Reactive Brilliant Blue KN-R, and Reactive Brilliant Red K-2BP were typical and in common use in textile, dyeing, and printing industries in China. The best entrapped support was obtained by comparing the physical characters, immobilization operation, adsorption efficiency, and so on.

1 Materials and methods

1.1 Materials

The dyes, Reactive Brilliant Blue KN-R (C.I. Reactive Blue 19) and Reactive Brilliant Red K-2BP (C.I. Reactive Red 24), in commercial purity, was obtained from Guangzhou Yongzhi Dyeing Chemical Industry Co., Ltd (Guangzhou, China). They were used without further purification. Their chemical structures are shown in Fig.1.

The immobilization supports: sodium carboxymethylcellulose (Na-CMC; high viscosity; 2.0% in H_2O at 25°C: 300–600 mPa·s; content of sodium: 6.5%–6.8%) was supplied from Fuchen Chemical Enterprise Co. in Tianjin, China. Sodium alginate (SA; viscosity: 150 mPa·s) was chemically pure grade, and polyvinyl alcohol (PVA) was analytically pure grade. Chitosan (CTS) (degree of deacetylation: 75%) was prepared with chitin.

Enriched culture medium of following composition was used in this study: glucose 15 g/L, KH_2PO_4 1 g/L, $(NH_4)_2SO_4$ 1 g/L, $MgSO_4{\cdot}7H_2O$ 0.5 g/L, NaCl 0.5 g/L and yeast extract 1 g/L. Dye culture medium comprises of 10 g/L of glucose, 1 g/L of KH_2PO_4, 1 g/L of $(NH_4)_2SO_4$, 0.5 g/L of $MgSO_4{\cdot}7H_2O$, 0.5 g/L of NaCl and 0.2 g/L of Reactive Brilliant Blue KN-R or Reactive Brilliant Red K-2BP. The pH of the enriched culture medium was 5.18, which was in the range of suitable pH for the growth of fungus. So the pH value of the medium was not adjusted.

The fungus, *A. fumigatus*, was isolated from an activated-sludge system to treat wastewater from a dyeing factory located in Guangzhou, China.

1.2 Spore suspension preparation

The five days slants were transferred into conical flasks containing culture and beadings and surged on a rotary shaker at 30°C and 150 r/min for 5 h. The concentration of spore suspension was adjusted to 10^7/ml using a haemacytometer.

1.3 Immobilization methods

Aseptic technique was demanded in the process of entrapped immobilizations at room temperature. All the solutions except iron chlorides solution (filtration sterilization) were autoclaved at 121°C for 20 min.

Entrapped in Na-CMC gel: 100 ml of Na-CMC solution (2%, w/v) and 1 ml of spore suspension was mixed until homogeneous. The mixture was dropped into iron chlorides solution (0.1 mol/L) using an injector (10 ml) with 9-sized pinhead, forming beads. The spore-immobilized beads were cured for 30 min to enhance their mechanical stabilities.

Entrapped in SA gel: 100 ml of SA solution (2%, w/v) and 1 ml of spore suspension was mixed until homogeneous. The mixture was dropped into a solution of calcium chloride (4%, w/v) using the same-sized injector, forming beads. The spore-immobilized beads were cured for 4 h to enhance their mechanical stabilities.

Entrapped in PVA-SA gel: 100 ml of PVA (6%, w/v) and SA (2%, w/v) solution and 1 ml of spore suspension was mixed until homogeneous. The mixture was dropped into a solution of calcium chlorides (4%, w/v) using the same-sized injector, forming beads. The spore-immobilized beads were also cured for 4 h to enhance their mechanical stabilities. Thereafter, the beads were collected and rinsed with phosphate buffer (pH 7.0, the concentration 0.05 mol/L) until the effluent liquid was clarified.

Entrapped in CTS gel: 5 g of CTS were dissolved in 50 ml acetum (5%). The mixture was diluted in 100 ml of distilled water, stirred severely and placed statically for 6

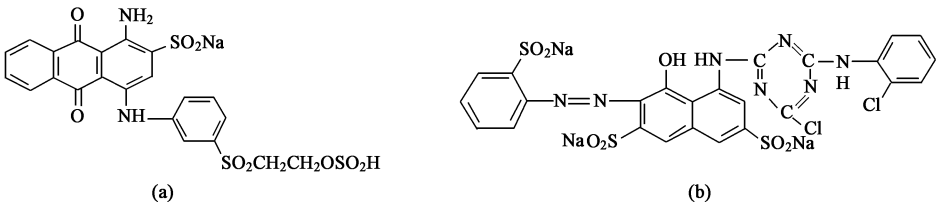

Fig. 1 Chemical structures of dyes (a) Reactive Brilliant Blue KN-R (λ_{max}=591 nm); (b) Reactive Brilliant Red K-2BP (λ_{max}=534 nm).

h. Then it was mixed with 1 ml of spore suspension until homogeneous, and dropped into sodium polyphosphate solution (1%, w/v) using the same-sized injector, forming beads. The spore-immobilized beads were cured for 3 h to enhance their mechanical stabilities.

The above-prepared spore-immobilized beads were collected, rinsed with sterilized water thrice and transferred into enriched culture medium. The inocula were placed on a rotary shaker at 30°C and 150 r/min for 3 d. Thereafter, the freshly beads were harvested and rinsed in the same way, and stored in physiological saline at 4°C.

The four plain immobilization methods were the same as that recounted above, respectively except that the support solutions were not mixed with spore suspension.

1.4 Adsorption experiment

Water on the surface of stored immobilized beads was blotted using filter paper. One gram of beads were transferred to 50 ml of dye culture medium and incubated on a rotary shaker at 30°C and 150 r/min. The dye concentration of culture medium was analyzed spectrophotometerically at several time intervals.

Control tests using plain gel beads without fungus were carried out similarly as mentioned above. The only different factor from adsorption by immobilized beads was that the beads were transferred into 50 ml of dye solutions and the whole process did not require aseptic operation.

All the experiments were carried out at least for two replicates.

1.5 Mass concentration of immobilized beads measurement

The samples were taken out at several time intervals of adsorption. The beads were collected by centrifugation at 5000 r/min for 15 min and washed thrice with distilled water. Thereafter, the beads were dried in an oven at 80°C for 12 h until constant weight, which was the overall mass. The dry mass was the overall mass subtracted adsorbed dye mass. Hereby, the mass concentration of immobilized beads in each sample was measured.

1.6 Comparison of physical characters of immobilized beads

Strength of immobilized beads: two methods were used to compare the strength of immobilized beads in this study. One was that a compressive stress was placed on the immobilized beads placed in an injection. The other was that the immobilized beads were transferred into distilled water and surged at a high rotary rate. The damages of immobilized beads were observed.

Stability of immobilized beads: the immobilized beads were placed in batch solutions including 0.01, 0.1, 1 mol/L hydrochloric acid and sodium hydroxide, 1 mol/L sodium chloride, sodium sulfate, potassium dihydrogenphosphate and calcium chlorides for 24 h. The changes in strength and apparent surface were observed.

Saturated wet density of immobilized beads: the saturated wet density of immobilized beads was calculated by the volume of beads saturated water in solution and the wet weight of beads.

1.7 Adsorption capability

Adsorption efficiency (P) expresses the adsorption ability of immobilized beads. It was calculated utilizing the following equation:

$$P = \frac{A_0 - A_1}{A_0} \times 100\% \tag{1}$$

Where, A_1 is the absorbance of residual dye in culture media; A_0 is the absorbance of initial dye in culture media. The absorbance was measured at maximum absorbing wavelength of dyes (λ_{max}=534 nm) (Fig.1) by an ultraviolet visible spectrometer (TU-1800SPC). If the absorbance was beyond the demanded range (0–1), the sample was diluted with distilled water.

Adsorption capacity q (mg/g) was expressed approximately as:

$$q = \frac{C_0 V_0 P}{m} \tag{2}$$

Where, m is the dry mass of beads after adsorption; C_0 is the initial concentration of dyes; V_0 is the initial volume of dye culture medium.

2 Results and discussion

2.1 Adsorption of dyes by different immobilized beads and mycelial pellets

As shown in Figs.2a and 2b, the adsorption efficiency of Reactive Brilliant Red K-2BP and Reactive Brilliant Blue KN-R by CTS immobilized beads was the highest. It was 89.1% and 93.5% in 12 h, respectively. The adsorption efficiency by Na-CMC immobilized beads was lower slightly than that of mycelial pellets. But the dye culture mediums were almost completely decolorized in 48 h using the above-mentioned two immobilized beads (exceeding 95%). The adsorption efficiency by SA immobilized beads exceeded 92% in 48 h. PVA-SA immobilized beads showed the lowest adsorption efficiency. It was 79.8% for Reactive Brilliant Red K-2BP and 92.5% for Reactive Brilliant Blue KN-R in 48 h.

There is the same phenomenon observed in adsorption systems by the four immobilized beads that the adsorption efficiencies of Reactive Brilliant Red K-2BP were lower than that of Reactive Brilliant Blue KN-R. It owes to the different chemical structure of the two dyes (Fig.1). The larger space resistance exists in adsorption reaction between immobilized beads and Reactive Brilliant Red K-2BP due to the more complicated structure. Moreover, there are more sulfonic groups in Reactive Brilliant Red K-2BP. Sulfonic groups can produce negative charge by ionization. Generally, mycelia surface present negative charge, which make the immobilized bead surface electronegative. Mutual repulsion forces between dyes and immobilized beads hinder the process of adsorption.

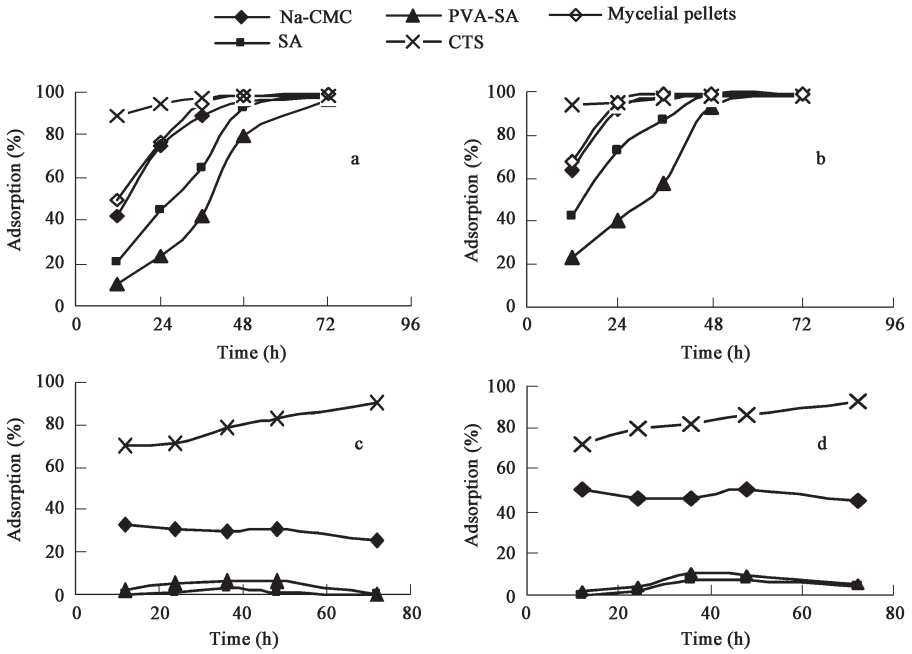

Fig. 2 Adsorption efficiency by immobilized beads and mycelial pellets (a and b) and plain gel beads (c and d). (a) and (c) are adsorption of Reactive Brilliant Red K-2BP; (b) and (d) are adsorption of Reactive Brilliant Blue KN-R.

2.2 Adsorption of dyes by plain gel beads

Figs.2c and 2d show that CTS plain gel beads had significant 71.9% Reactive Brilliant Blue KN-R removal and 70.2% Reactive Brilliant Red K-2BP removal in 12 h and both exceeding 90% in 72 h. Adsorption efficiency by Na-CMC plain gel beads was also relatively high (50.4% Reactive Brilliant Blue KN-R; 33.1% Reactive Brilliant Red K-2BP in 12 h). It fluctuated slightly at a later stage. SA and PVA-SA plain gel beads both had low dye removal (less than 10%).

That the supports participate with the adsorption of dyes would lead to increase in the adsorption of immobilized beads. It can be supported from the comparison of adsorption efficiency of gel beads in Fig.2. CTS immobilized beads had the highest adsorption efficiency due to high adsorption efficiency by CTS plain gel beads, which accorded with the result of high adsorption of indigo blue by chitin and CTS (Alexandre *et al*., 2004). CTS obtained from chitin have high contents of amine and hydroxyl functional groups, resulting in Coulomb force between these functional groups and sulfonic groups on dyes. Similarly, there is Coulomb force between functional groups like carboxyl of Na-CMC plain gel beads and the dyes.

The adsorption efficiencies of dyes by Na-CMC, PVA-SA, and SA plain gel beads fluctuated slightly with time due to the rapid metabolism-independent adsorption between plain gel beads and dyes. The adsorption saturation state was homeostasis with adsorption and desorption, so the adsorption efficiency decreased when the desorption rate exceeded the adsorption rate. The adsorption efficiency by CTS plain gel beads increased all through because of constant inner diffusion of dye and higher adsorption rate than desorption rate.

2.3 Growth of immobilized mycelia

Although the culture components in dye-containing culture media may be adsorbed by immobilized beads, they mostly were utilized for the metabolism of growing entrapped mycelia. Thus, the mass concentration of immobilized beads at time intervals in the process of adsorption could be characterized by the growth of immobilized mycelia. The growth curves of mycelia in the adsorption system of Na-CMC and SA and dyes are shown

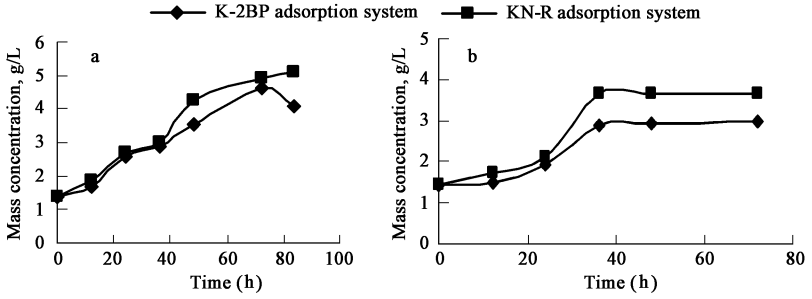

Fig. 3 Growth curves of immobilized beads. (a) SA immobilized beads; (b) Na-CMC immobilized beads.

in Fig.3. The mycelia entrapped in the two immobilized beads in Reactive Brilliant Blue KN-R system grew faster than in Reactive Brilliant Red K-2BP system, due to the greater toxic restrains of Reactive Brilliant Red K-2BP than that of Reactive Brilliant Blue KN-R. It also explains the adsorption efficiency of Reactive Brilliant Blue KN-R by two immobilized beads being higher than that of Reactive Brilliant Red K-2BP in the same environment. In addition, Fig.3 also shows that the growth mass of mycelia entrapped in SA immobilized beads in two kinds of dyes adsorption system is greater than that of mycelia entrapped in Na-CMC immobilized beads, respectively.

The relationships between adsorption efficiency and growth mass are shown in Fig.4. The growth curve of SA immobilized beads adsorption system kept ascending in 72 h. The growth of mycelia entrapped in Na-CMC immobilized beads increased slightly after 36 h. Moreover, the slope of adsorption efficiency curve disaccorded with that of growth curve. It means that the increase of adsorption efficiency owes to other unknown factors besides the growth of mycelia.

2.4 Adsorption capacity of Na-CMC and SA immobilized beads

Fig.5 shows the adsorption capacity of dyes by Na-CMC and SA immobilized beads. The maximum adsorption capacity of Reactive Brilliant Red K-2BP and Reactive Brilliant Blue KN-R by Na-CMC immobilized beads was 78.0 mg/g and 86.7 mg/g, respectively. The values were larger than that reported in the published reports (Fu and Viraraghavan, 2003). Fu and Viraraghavan (2003) reported that the immobilized *Aspergillus niger* beads had adsorption capacities of 64.7 mg/g for Acid Blue 29, 8.3 mg/g for Basic Blue 9. Fig.5 also indicates that the SA immobilized beads had maximum adsorption capacity of 52.2 mg/g for Reactive Brilliant Red K-2BP and 58.5 mg/g for Reactive Brilliant Blue KN-R.

2.5 Comparison of physical characters of immobilized beads

As shown in Table 1, all the immobilized beads remained integral in acid, alkali, and salt solutions. However, certain beads became soft, sparkling, and fragile. It shows that Na-CMC and SA immobilized beads can adapt to the

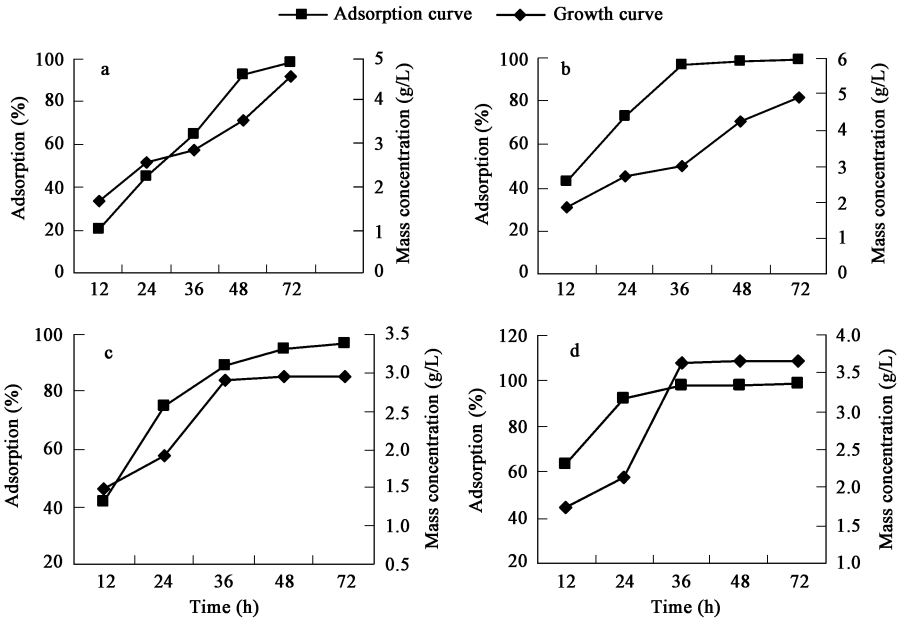

Fig. 4 Adsorption and growth curves of SA immobilized beads (a and b) and Na-CMC immobilized beads (c and d). (a) and (c) in Reactive Brilliant Red K-2BP adsorption system; (b) and (d) in Reactive Brilliant Blue KN-R adsorption system.

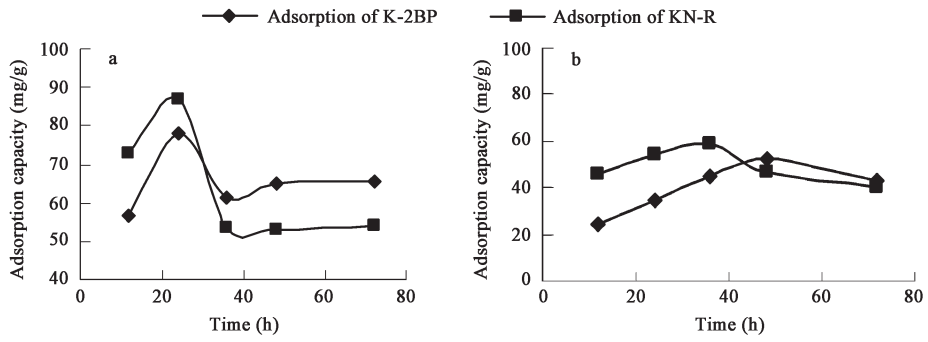

Fig. 5 Adsorption capacity of immobilized beads. (a) Na-CMC immobilized beads; (b) SA immobilized beads.

Table 1 Change in the physical characters of immobilized beads in acid, alkali, and salt solutions

	HCl (mol/L)			NaOH (mol/L)			NaCl (mol/L)	$CaCl_2$ (mol/L)	KH_2PO_4 (mol/L)	Na_2CO_3 (mol/L)
	0.01	0.1	1	0.01	0.1	1	1	1	1	1
Na-CMC	+	+	+	+	++	+++	0	0	++	+++
SA	0	0	0	+	++	+++	+	0	+++	+++
PVA-SA	++	++	++	++	++	+++	+++	+	+++	++
CTS	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++

(0) No change; (+) softer, sparkler, and lower flexibility slightly; (++) softer, sparkler, and lower flexibility; (+++) sparkle, loose, and fragile.

change in the environment.

The results indicate that it inhibits the practical use of CTS immobilized beads due to low strength and instability in acid, alkali, and salt solutions though the adsorption efficiencies of them are the highest. PVA-SA immobilized beads have advantages of easy operation of immobilization and high strength. But they are instable in acid, alkali, and salt solutions and adsorption efficiencies by them are the lowest. SA and Na-CMC are alternative to be supports according to better physical characters of their immobilized beads.

The order of strength of immobilized beads was: PVA-SA>SA>Na-CMC >CTS (Table 2). The order of saturated wet density was: SA>PVA-SA>Na-CMC>CTS>mycelial pellets.

Table 2 Comparison of strength and saturated wet density of immobilized beads and mycelial pellets

Beads	Integrality	Relative strength	Saturated wet density (g/ml)
Na-CMC	0	++	0.287
SA	0	+++	0.541
PVA-SA	0	++++	0.362
CTS	–	+	0.2
Mycelial pellets	0	+	0.1

Strength comparison: Integrality after surged at 300 r/min, damaged degree after pressed; (0)integrity; (–) damaged slightly; (+) low strength, soft; (++)good strength; (+++)better strength; (++++) hard.

2.6 Apparent change of immobilized beads before and after adsorption

The solution became colorless after adsorption. The immobilized beads appeared in the color of the dyes after adsorption demonstrates that the main reaction is adsorption by supports and mycelia and not biodegradation by mycelia.

Mycelial disassembly phenomenon existed in the adsorption system using SA immobilized beads, and not distinct in adsorption system using Na-CMC immobilized beads. The reason is that the growth mass of mycelia of the former are greater than that of the latter. The excess growth results in mycelia escaping from immobilized beads. In addition, the mycelial pellets varied in size and were agglomerated easily unlike Na-CMC immobilized beads.

2.7 Microstructure of Na-CMC plain gel beads and Na-CMC immobilized beads

As shown in Fig.6, the SEM micrographs of Na-CMC plain gel bead and Na-CMC immobilized bead indicate the different surface structures of them. Na-CMC plain gel bead surface was rough and showed no obvious pore. The surface structure of Na-CMC immobilized bead was loose and finely porous, which facilitated the diffusion of dyes. Moreover, there was a uniform rich fungal growth on the surface of the beads, which indicated that the immobilization of spores was not localized. This uniform distribution of fungus means the proper biosorption of dyes on the whole surface area of the Na-CMC immobilized beads.

3 Conclusions

Four entrapped supports were chosen to immobilize *A. fumigatus*. The adsorption efficiency of Reactive Brilliant Red K-2BP and Reactive Brilliant Blue KN-R using CTS immobilized beads was the highest. It was 89.1% and 93.5% in 12 h, respectively. The adsorption efficiency by Na-CMC immobilized beads was lower slightly than that of mycelial pellets. But the dye culture mediums were almost completely decolorized in 48 h using the above-mentioned two immobilized beads. The adsorption efficiency by SA immobilized beads exceeded 92% in 48 h. PVA-SA immobilized beads showed the lowest adsorption efficiency.

CTS plain gel beads had significant removal efficiency of 71.9% Reactive Brilliant Blue KN-R and 70.2% Reactive Brilliant Red K-2BP in 12 h and both exceeded 90% in 72 h. Adsorption efficiency of Reactive Brilliant Blue KN-R and Reactive Brilliant Red K-2BP by Na-CMC plain gel beads was 50.4% and 33.1% in 12 h, respectively. SA

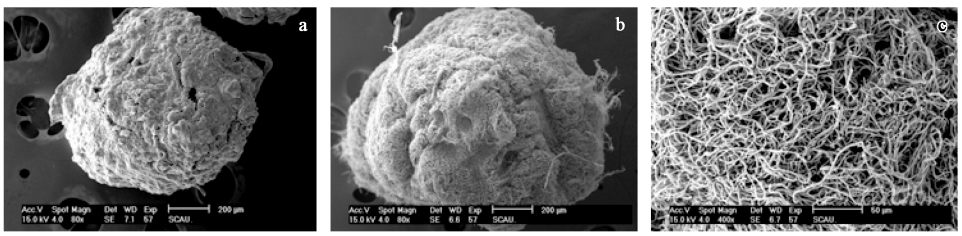

Fig. 6 SEM micrographs of Na-CMC gel beads. (a) Na-CMC plain gel bead (× 80); (b), (c) Na-CMC immobilized bead (× 80, × 400).

and PVA-SA plain gel beads indicated low dye removals, which were less than 10% in 72 h.

The biomass in Na-CMC and SA immobilized beads kept increasing in 72 h. The slope of adsorption efficiency curve disaccorded with that of growth curve.

The maximum adsorption capacity of Reactive Brilliant Red K-2BP and Reactive Brilliant Blue KN-R using Na-CMC immobilized beads was 78.0 mg/g and 86.7 mg/g, respectively. The values were larger than that reported in the published reports.

CTS and PVA-SA unfit as immobilization supports compared with Na-CMC and SA. Na-CMC immobilized beads offer more advantages compared with SA: higher adsorption efficiency, no distinct mycelial disassembly phenomenon, lower material cost. Moreover, the surface structure of Na-CMC immobilized bead is loose and finely porous. These results show that Na-CMC is an excellent support.

Acknowledgements: Financial support for this research was provided by Environmental Protection Bureau of Guangzhou, Guangdong, China in the form of project entitled "Screening microbe for biosorption and establishing strain library". The authors are also thankful to School of Life Science, South China Agricultural University, China for providing the SEM technology aids.

References

Chen K C, Wu J Y, Yang W B *et al*., 2002. Evaluation of effective diffusion coefficient and intrinsic kinetic parameters on azo dye biodegradation using PVA-immobilized cell beads[J]. Biotech Bioeng, 83: 821–832.

Chen K C, Wu J Y, Huang C C *et al*., 2003. Decolorization of azo dye using PVA-immobilized microorganisms[J]. J Biotechnol, 101: 241–252.

Dong X J, Zhou G L, 2005. Study on decolorization of Reactive Brilliant Blue KN-R by the adsorption of immobilized *Penicillinm jensenii*[J]. China Environmental Science, 25: 494–498.

Fu Y Z, Viraraghavan T, 2003. Column studies for adsorption of dyes from aqueous solutions on immobilised *Aspergillus niger* fungal biomass[J]. Water SA, 29: 465–472.

Gülay B, Sema B, Yakup A M, 2003. Biosorption of heavy metal ions on immobilized white-rot fungus *Trametes versicolor*[J]. J Hazard Mater, 101: 285–300.

Harazono K, Nakamura K, 2005. Decolorization of mixtures of different reactive textile dyes by the white-rot basidiomycete *Phanerochaete sordida* and inhibitory effect of polyvinyl alcohol[J]. Chemosphere, 59: 63–68.

He F, Hu W R, Li Y Z, 2004. Investigation of isolation and immobilization of a microbial consortium for decoloring of azo dye 4BS[J]. Wat Res, 38: 3596–3604.

Khoo K M, Ting Y P, 2001. Biosorption of gold by immobilized fungal biomass[J]. Biochem Eng J, 8: 51–59.

Liu N, Liao J L, Luo S Z *et al*., 2003. Biosorption of ^{241}Am by immobilized *Saccharomyces cerevisiae*[J]. J Radioanal Nucl Chem, 258: 59–63.

Nina C, Hanne V H, Kimmo T J *et al*., 1995. Degradation of chlorinated aromatic compounds in UASB reactors[J]. Water Sci Technol, 31: 249–259.

Nurdan K P, Raziye O U, Fulya E, 2005. Biodecolourization of Direct Blue 15 by immobilized *Phanerochaete chrysosporium*[J]. Process Biochem, 40: 1923–1929.

O'Mahony T, Guibal E, Tobin J M, 2002. Reactive dye biosorption by *Rhizopus arrhizus* biomass[J]. Enzyme Microb Tech, 31: 456–463.

Ozfer Y, Dilek A, Seval C, 2003. Decolorization of textile dyes by fungal pellets[J]. Process Biochem, 38: 933–938.

Prado A G S, Torres J D, Faria E A, 2004. Comparative adsorption studies of indigo carmine dye on chitin and chitosan[J]. J Colloid Interf Sci, 277: 43–47.

Suhail A, Amjad A K, Qayyum H, 2005. Potential of immobilized bitter gourd (*Momordica charantia*) peroxidases in the decolorization and removal of texitile dyes from polluted wastewater and dyeing effluent[J]. Chemosphere, 60: 291–301.

Vaidya A A, Datye K V, 1982. Environmental pollution during chemical processing of synthetic fibers[J]. Colourage, 14: 3–10.

Walker G M, Weatherley L R, 2000. Biodegradation and biosorption of acid anthraquinone dye[J]. Environnental Pollution, 108: 219–223.

Xiao J B, Hu Y Y, Tian J, 2004. Studies on decolorization by adsorption of Reactive Brilliant Blue KN-R[J]. China Environmental Science, 24: 63–67.

Xiao J B, Hu Y Y, 2005. Adsorption of various dyes by mycelial pellets[J]. Acta Scientiae Circumstantiae, 25: 525–529.

Yalup A M, Çigdem A, Aysun E *et al*., 2003. Ca-alginate as a support for Pb(II) and Zn(II) biosorption with immobilized *Phanerochaete chrysosporium*[J]. Carbohyd Polym, 52: 167–174.

Young L, Yu J, 1997. Ligninase-catalyzed decolorization of synthetic dyes[J]. Wat Res, 31: 1187–1193.

Zümriye A, Secilay T, 2005. Biosorption of reactive dyes on the green alga *Chlorella vulgaris*[J]. Process Biochem, 40: 1347–1361.