Column studies for biosorption of dyes from aqueous solutions on immobilised *Aspergillus niger* fungal biomass

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Abstract

Biosorption is becoming a promising alternative to replace or supplement the present dye removal processes from dye wastewaters. Based on the results of batch studies on biosorption of the dyes on powdered fungal biomass, *Aspergillus niger*, an immobilised fungal biomass was used in column studies for removal of four dyes, Acid Blue 29, Basic Blue 9, Congo Red and Disperse Red 1 from aqueous solutions. For each dye, the effectively pretreated powdered fungal biomass was immobilised in a polysulphone matrix in the form of spherical beads. In column studies, adsorption and elution tests were conducted for each dye and the regeneration and reuse for Acid Blue 29 were carried out. The breakthrough data from column studies could be described by the Thomas model. Results of t-tests indicated that the Thomas model constants were statistically significant at 95% confidence level for Acid Blue 29 and Basic Blue 9, but not for Congo Red and Disperse Red 1. The beads had adsorption capacities of 64.7 mg/g for Acid Blue 29, 8.3 mg/g for Basic Blue 9, 1.1 mg/g for Congo Red, and 0.1 mg/g for Disperse Red 1, respectively. In the elution tests, Acid Blue 29 and Basic Blue 9 were easily desorbed from the beads, but Congo Red and Disperse Red 1 were minimally desorbed. The beads in the column retained a high adsorption capacity (91%) for Acid Blue 29 in the second cycle, which suggested that the system using *A. niger* biomass can be developed for the removal of certain dyes.

Key words: *Aspergillus niger*, immobilisation, Acid Blue 29, Basic Blue 9, Congo Red, Disperse Red 1.

Introduction

Dye wastewaters discharged from textile and dyestuff industries have to be treated due to their impact on water bodies, and growing public concern over their toxicity and carcinogenicity in particular. Dyes usually have synthetic origins and complex aromatic molecular structures (Banat et al., 1996). According to their dissociation in an aqueous solution, dyes can be classified as follows (Mishra and Tripathy, 1993):

- Anionic: acid, direct and reactive dyes
- Cationic: basic dyes
- Nonionic: disperse dyes.

Dyes such as acid, basic and direct are all water-soluble (Reife, 1990) but disperse dyes have low solubilities and colloidal dispersion properties; thus they are agglomerations (Reife and Freeman, 1996). Many different and complicated molecular structures of dyes make dye wastewaters difficult to be treated by conventional biological and physico-chemical processes. Therefore, innovative treatment technologies need to be investigated.

Biosorption has been studied since 1980s for removing heavy metals, dyes and other organic pollutants by various microorganisms from wastewater. Among these microorganisms, fungal biomass can be produced cheaply and obtained as a waste from various industrial fermentation processes (Kapoor and Viraraghavan, 1995). Decolorisation of dye wastewater by fungal metabolic activities is the subject of many studies (Benito et al., 1997; Knapp et al., 1995; Miranda et al., 1996; Polman and Breckenridge, 1996; Vasdev et al., 1995). Compared with live fungal cells, dead fungal biomass possesses various advantages such as absence of nutrient needs and ease of regeneration (Gadd, 1990). Dried, non-living and physically or chemically pretreated fungal biomass would be an attractive biosorbent for removing dyes from dye wastewaters. However, there are only limited studies on dye removal by dead fungal biomass (Fu and Viraraghavan, 1999; 2000; Gallagher et al., 1997; Polman and Breckenridge, 1996; Zhou and Banks, 1993; Mou et al., 1991). These fungi, which can biosorb diverse dyes, include *Aspergillus niger*, *Rhizopus arrhizus* and *Rhizopus oryzae*.

In batch studies, the dead fungal biomass is normally used in the powdered form, which is convenient and can be separated from a mixture of dye solution and fungal biomass by filters with a fine pore size without difficulty. However, the fungal biomass powder is composed of small particles with low density, low mechanical strength and low rigidity. These properties will cause difficulties in separation of the biomass in practice (Tsezos, 1990). Alternatively, immobilisation of the powdered dead fungal biomass into a solid matrix can overcome this difficulty. It can maintain the native properties of the biomass and has the advantages of improved strength and handling capacity, reduced blockage and head-loss in a column operation and better regeneration characteristics (Tobin et al., 1993; Brierley, 1990; Tsezos, 1990).

Two kinds of fungal biomass, live and dead, are used in immobilisation. Banks and Parkinson (1992) immobilised living fungal cells, *Rhizopus arrhizus* within the reticulated foam biomass support particles and used these immobilsed cells in columns to remove humic acid from the raw water. In the immobilisation of dead fungal biomass for heavy metals removal, various materials can be used as the solid matrix. These are polysulphone, alginate, polyacrylamide, epoxy resin and polyvinyl formal (Kapoor and Viraraghavan, 1998; Spinti et al., 1995; Ferguson et al., 1989; Tobin et al., 1993; Tsezos and Deutschmann, 1990). Polysulphone is an amorphous, rigid, heat-resistant and chemically stable thermoplastic material which is a good immobilising agent (Kapoor and Viraraghavan, 1998). So far no study of dead fungal biomass

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immobilised onto polysulphone solid matrix has been conducted on dye removal from aqueous solutions.

In this study, immobilised dead fungal biomass, *Aspergillus niger*, in polysulphone in the form of spherical beads was used in column studies for removing each of the four dyes, Acid Blue 29, Basic Blue 9, Congo Red and Disperse Red 1 from aqueous solutions, respectively, based on the results of batch studies. A procedure for the immobilisation of dead powdered fungal biomass in polysulphone to form spherical beads was developed. The characteristics of beads such as size distribution and specific surface area were studied. Column studies were conducted to evaluate the adsorption capacity of beads for dye removal. Finally, the dye elution, regeneration and reuse of such beads in columns were examined.

TABLE 1
Summary data on dyes studied

Name	Classification	C.I.	FW	λ_{max} (nm)
Acid Blue 29	Anionic disazo	20460	616.5	600
Basic Blue 9	Cationic thiazine	52015	373.9	660
Congo Red	Anionic direct disazo	22120	696.7	500
Disperse Red 1	Nonionic monoazo	11110	314.3	450

Note: C.I. = color index; FW = formula weight;
λ_{max} = maximum absorbance wavelength.

Materials and methods

Dye solution preparation

The dyes used in this study are presented in Table 1. They were supplied by Sigma Chemical Company, St Louis, MO, USA.

Dye solutions were prepared by dissolving accurately weighed dyes in distilled water at a concentration of 50 mg/ℓ. The pH of each dye solution was adjusted to its effective pH obtained from the results of the batch studies (Table 2). To compare dye removal on the same basis, the pH of all the samples was adjusted to 7.6 before measurement. Dilute HCl or NaOH was used for pH adjustment. The concentration of dye solution was determined using a spectrophotometer (Baush & Lomb-Spectromic 21) operating in the visible range on absorbance mode. Absorbance values were recorded at the corresponding maximum absorbance wavelength (λ_{max}) (given in Table 1) and dye solution was initially calibrated for concentration in terms of absorbance units. The concentration of the dye solution was obtained from its calibration plot.

TABLE 2
Summary of data from batch studies

Name	Effective biomass pretreatment	Effective initial pH	Equilibrium time (h)	Effective elutant
Acid Blue 29	H_2SO_4+Autoclaved	4.0	24	0.1M NaOH
Basic Blue 9	Autoclaved	6.0	30	0.01M HCl
Congo Red	$NaHCO_3$ + Autoclaved	6.0	42	0.01MNaOH
Disperse Red 1	NaOH + Autoclaved	4.0	48	0.05M NaOH

Fungal biomass preparation

The *A. niger* strain used in this study was obtained from the American Type Culture Collection, Rockville, Maryland, USA (ATCC#11414). The culturing procedure, growth media and different pretreatments have been described previously (Fu and Viraraghavan, 1999; 2000). The fungal pellicles were separated by filtering the growth media through a 150 µm sieve and washed with generous amounts of deionised water. They were pretreated by the methods found most effective for enhancement of biosorption of each dye (Table 2) based on batch studies (Fu and Viraraghavan, 1999; 2000). The effectively pretreated biomasses were washed with generous amounts of deionised water until the pH of the wash solution was close to that of deionised water (pH = 6.0), autoclaved for 30 min at 121°C and 124 kPa and then dried in an oven at 60 to 70°C for 36 h. The dry biomass was ground to powder using a mortar and a pestle. The powdered biomass was sieved through a sieve with openings of 150 µm and powder with particles less than or equal to 150 µm was used in immobilisation.

Fungal biomass immobilisation

Fourteen gram of powdered biomass was blended into a solution containing 7 g of polysulphone (obtained from Aldrich Chem., Cat No. 18244-3, avg. mol. wt. 44 000 to 53 000) per 100 mℓ of n, n-dimethyl-formamide (DMF, obtained from Aldrich Chemicals) The mixture was shaken for 24 h on a rotary shaker at 125 r·min^{-1} to dissolve polysulphone completely in DMF and form a uniform and consistent slurry. The slurry was fed through an atomising unit into a deionised water bath. The atomising unit consisted of a stainless steel tube surrounding another stainless center tube of 4 mm diameter. The DMF-polysulphone-biomass slurry was fed into the holding cylinder and then allowed to flow into the centre tube. A needle valve controlled the flow rate of the slurry. Pressurised air was pumped in the annular space between the surrounding and centre tube at a rate of approximately 22.65 ℓ/min. The slurry was atomised at the tip by flowing air. Spherical beads were formed when the atomised slurry contacted with water because of the phase inversion of polysulphone. The biomass was immobilised within the solidified polysulphone matrix. The DMF completely dissolved in water and gradually diffused out which led to the formation of a favourable pore structure for the spherical beads. Beads were cured in a moderately agitated deionised water bath in a rotary shaker at 100 r·min^{-1} for 24 h to diffuse out the DMF. After curing, beads were air-dried for 3 d at room temperature (22 ± 1°C) and irregularly shaped beads were discarded.

Removal by polysulphone beads

To determine the removal effect by polysulphone itself, polysulphone beads were also produced in this study, 14 g of powdered biomass was replaced by 7 g of polysulphone. Other processes were the same as fungal biomass immobilisation. Polysulphone beads were passed through a sieve with 0.6 mm openings. The beads with a diameter smaller than 0.6 mm were used in batch studies for dye removal. Two-tenths of a gram polysulphone beads were added in 75 mℓ of dye solution at its effective initial pH and the mixture was shaken for a period equal to the equilibrium time corresponding to the dye at 125 r·min^{-1}. Meanwhile, as a blank, 75 mℓ of dye solution without the polysulphone beads was also shaken under the same

conditions. The mixture and blank were vacuum filtered through a 0.45 mm filter. The filtrate was analysed for the dye concentration and the dye adsorbed by the polysulphone beads was calculated.

Sieve analysis

Sieve analysis was used to determine the size distribution of the beads. The sieves' openings (mm) were 4.75, 3.35, 2.36, 1.18, 0.85 and 0.6. Beads greater than 4.75 mm and smaller than 0.6 mm were discarded. The uniform coefficient (C_u) was calculated using the following equation (Das, 1997):

$$C_u = \frac{D_{60}}{D_{10}} \quad (1)$$

where:

D refers to the diameter of the beads and the subscripts 10, 60 are the percent finer

D_{10} is referred to as the effective size of the beads.

Measurement of surface area

The surface area of the beads (1.18 to 2.36 mm) was determined by Flowsorb 2300 manufactured by Micromeritics, Georgia, U.S.A. Single point surface area was chosen to measure the surface area of the beads. The gas mixture was composed of 29% mole nitrogen and 71% mole helium. It is a favourable condition for the formation of a monolayer molecules of adsorbed nitrogen on the surface area of porous biomass - polysulphone beads at atmospheric pressure and the temperature of liquid nitrogen. The area covered by each nitrogen gas molecule is known within relatively narrow limits. Therefore, the area of the sample can be directly calculated from the number of adsorbed nitrogen molecules derived from the gas quantity at the prescribed conditions, and the area occupied by each molecule.

Column studies

Four and half gram of the immobilised biomass beads was packed into a glass column which had an inside diameter of 1.27 cm and a height of 40 cm. At the top and bottom of the beads in the column, one layer of gravel with a height of 3 cm was used to distribute influent dye solution and support beads, respectively. To maintain a water head (about 5 cm) above the top of the beads in the column, the outlet was set at a certain level, almost the same as the designed water level in the column. The parameters related to column studies are given in Table 3.

Before the dye solution was passed through the column, deionised water was pumped through the column in a downflow direction to wet the beads completely. Each dye solution was then pumped into the column in a downflow direction by a peristaltic pump at a specified rate (Table 3). Two flow rates for each of the dyes, Congo Red and Disperse Red 1, were used because the higher one caused a rapid breakthrough. Effluent samples were collected at regular intervals (15 min for the first hour, every 30 min from the first hour to the fourth hour, and then at longer intervals) and analysed for pH and dye concentrations. When the concentration ratio of effluent to influent reached a value over 0.8, the column was considered to be exhausted and the pump was stopped.

Dyes adsorbed on the beads in the column were eluted by the elutants found effective (Table 2). The elutant was pumped into the column in the downflow direction with the same flow rate as in the adsorption column test. The eluted samples were collected at intervals varying from 1 min to 30 min (1 min for the first 2 min, every 2 min from 2 min to 6 min, every 4 min from 6 min to 10 min, every 5 min from 10 min to 20 min, every 10 min from 20 min to 30 min, every 15 min from 30 min to 1 h, and every 30 min after 1 h) and analysed for dye concentrations. When the dye concentration of the elutant reached about 1.5 mg/ℓ, the elution test was stopped.

TABLE 3
The parameters of the column studied

Dye	H (cm)	V (mℓ)	Q (mℓ/min)	T (min)
Acid Blue 29	23.5	29.8	6	5.0
Basic Blue 9	24.5	31.0	6	5.2
Congo Red	24.5	31.0	6 (3)	5.2 (10.4)
Disperse Red 1	22.5	28.5	6 (3)	5.2 (10.4)

Note: H = height; V = volume; Q = flow rate;
T = retention time.
The numbers in brackets relate to the second fow rate used.

In the studies on regeneration and reuse, only the beads in the column for removal of Acid Blue 29 were chosen because this dye showed the best results in the batch studies on elution, regeneration and reuse of the biomass among the four dyes. After elution, the biomass beads were regenerated by deionised water based on the results of the batch study. Deionised water was pumped into the column in the downflow direction at the same flow rate as in the adsorption test. When the pH of the regeneration effluent was close to the pH of deionised water, the regeneration process was stopped. The second cycle of the adsorption column test for removal of Acid Blue 29 was conducted as described for the first cycle.

Various mathematical models can be used to describe fixed-bed adsorption. Among these the Thomas (1948) model is simple to use in the design of a fixed-bed adsorption column. Therefore the breakthrough data obtained from the column studies was examined using the kinetic model developed by Thomas (1948). The expression of the Thomas model for an adsorption column is as follows (Reynolds and Richards, 1996):

$$\frac{C}{C_0} \approx \frac{1}{1+\exp\left[\frac{k}{Q}(q_0 M - C_0 V)\right]} \quad (2)$$

where:

C = effluent dye concentration, mg/ℓ
C_0 = initial dye concentration, mg/ℓ
k = Thomas rate constant, ℓ/min.mg
q_0 = maximum dye adsorption capacity of the beads, mg/g
M = mass of the beads, g
V = throughput volume of the dye solution, mℓ
Q = flow rate, mℓ/min.

Equation (2) can be converted to the simple format as follows:

$$\frac{C}{C_0} \approx \frac{1}{1+\exp(b - aV)} \quad (3)$$

where:

$$a = \frac{kC_0}{Q} \quad (4)$$

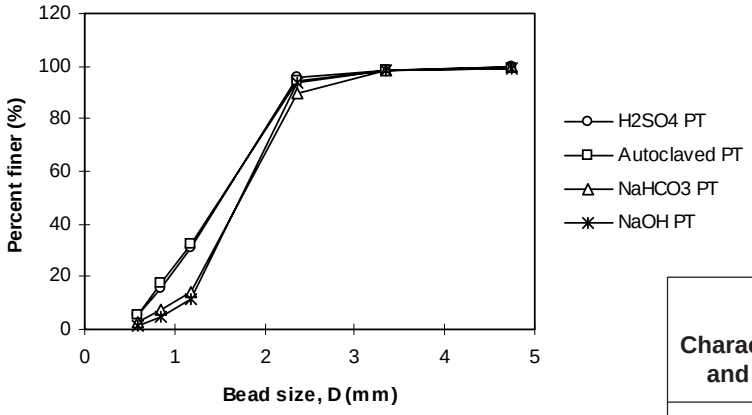

Figure 1
Sieve analysis for the beads made of different pretreated (PT) biomass

$$b = \frac{kq_0M}{Q} \quad (5)$$

Therefore, if Q, M and C_0 are constants, C/C_0 is the function of V. Once a and b are determined, k and q_0 can be calculated by the following formula derived from Eqs. (4) and (5):

$$k = \frac{aQ}{C_0} \quad (6)$$

$$q_0 = \frac{bQ}{kM} \quad (7)$$

The Thomas model was analysed by non-linear estimation included in STATISTICA software (Release 5, 1997 edition) for WINDOWS by the Quasi-Newton method.

Results and discussion

Bead production

The beads produced by the methods described above were spherical in shape and greyish white in color. In the experiment, it was observed that the flow rates of slurry of DMF-polysulphone-biomass and air were important factors affecting the bead size distribution. As expected, increasing the flow rate of slurry caused the bigger beads to be formed, while increasing the flow rate of air resulted in smaller beads being produced. Finally, the air flow rate was fixed at about 22.65 ℓ/min and the needle valve in the fabrication unit was used to control the flow rate of the slurry.

Sieve analysis

Figure 1 shows the results of the sieve analysis for the four kinds of beads developed from the different pretreated biomasses. They had a similar size distribution. The curves of percent finer versus sieve opening almost overlapped each other. About 60 to 80% of beads were in the size range of 1.18 to 2.36 mm, 61.5% for beads developed from autoclaved pretreated biomass (corresponding to Basic Blue 9 removal) and 82.4% for beads containing NaOH plus autoclaved pretreated biomass (corresponding to Disperse Red 1 removal), respectively. The effective sizes and uniformity coefficients for the four different beads are given in Table 4.

Kapoor and Viraraghavan (1998) observed that the beads developed from the NaOH pretreated *A. niger* biomass and polysulphone had an effective size of 0.718 mm and a uniformity coefficient of 2.17, which were comparable with the results obtained in this study. The size distribution of the four kinds of beads used in the column studies is given in Table 5.

TABLE 4
Characteristics of beads used in the column studies and adsorption capacity of polysulphone beads

Dye removed by beads	Effective size(D_{10}) (mm)	Uniformity coefficient (C_u)	Specific surface area (m^2/g)	Adsorption capacity of polysulfone bead(mg/g)
Acid Blue 29	0.7	2.43	2.40	0.63
Basic Blue 9	1.1	1.68	3.16	1.70
Congo Red	0.9	2.06	2.86	0
Disperse Red 1	0.7	2.43	2.54	0.44

TABLE 5
Size distribution of the beads used in the column studies

Size of beads (mm)	Per cent (%)			
	Acid Blue 29	Basic Blue 9	Congo Red	Disperse Red1
3.35-4.75	1.2	1.0	1.3	0.5
2.36-3.35	3.1	4.5	8.9	4.5
1.18-2.36	68.6	65.6	78.0	84.4
0.85-1.18	16.4	16.2	7.1	6.8
0.60-0.85	10.7	12.6	4.7	3.8
Total (%)	100	100	100	100

Surface area

The porous structure is very important for dye molecules to be adsorbed on the biomass present inside the beads. The surface areas of the four kinds of beads in the size range of 1.18 to 2.36 mm are given in Table 4. The beads containing autoclaved biomass had the highest value of 3.16 m^2/g. The other three kinds of beads had similar values from 2.40 to 2.86 m^2/g. Kapoor and Viraraghavan (1998) reported that the beads containing NaOH pretreated *A. niger* biomass and polysulphone had a surface area of 3.40 m^2/g, while the beads made from sphagnum peat biomass and polysulphone possessed a surface area in the range of 3.27 to 3.90 m^2/g, corresponding to the size range of 1.44 to 2.03 mm (Spinti et al., 1995). Therefore, the data on surface area are comparable with other studies.

Dye removal by polysulphone beads

The studies showed that polysulphone beads with a diameter less than 0.6 mm had some dye removal effects, depending on the dye structures. The adsorption capacities of polysulphone beads for the

four dyes are given in Table 4. The polysulphone beads had the highest adsorption capacity for Basic Blue 9 (1.70 mg/g), while they had no removal effect on Congo Red.

Column studies

Adsorption

Figures 2 to 5 show the observed breakthrough points and the effluent pH for the adsorption of Acid Blue 29, Basic Blue 9, Congo Red and Disperse Red 1, vs. throughput volume, respectively. In the studies, the allowable breakthrough concentration was considered to be 0.15 C_0.

For Acid Blue 29, the value of C/C_0 increased gradually. When C/C_0 reached 0.15, the throughput volume of the dye solution was approximately 1400 mℓ (50 bed volumes); when C/C_0 reached 0.5, the throughput volume increased to approximately 5000 mℓ (170 bed volume); when the beads in the column were exhausted (C/C_0 = 0.8), the throughput volume was approximately 12600 mℓ (420 bed volumes). The results indicated that the beads had a high adsorption capacity, but the adsorption capacity increased gradually. It took a long time for the beads to be saturated by the dye molecules of Acid Blue 29.

For Basic Blue 9, the value of C/C_0 increased faster than that of Acid Blue 29. When C/C_0 reached 0.15, the throughput volume was approximately 240 mℓ (8 bed volumes); when C/C_0 increased to 0.5, the throughput volume was approximately 660 mℓ (20 bed volumes); when the column was exhausted (C/C_0 = 0.8), the throughput volume was approximately 1360 mℓ (40 bed volumes).

For Congo Red, the values of C/C_0 increased drastically under the two flow rates (3 and 6 mℓ/min). The column reached breakthrough very quickly. When C/C_0 reached 0.15, the throughput volume was only about 5 mℓ (0.2 bed volume); when C/C_0 reached 0.5, the throughput volume was approximately 30 to 40 mℓ (1 bed volume) for the two flow rates; when the beads in the column were exhausted (C/C_0 = 0.8), the throughput volumes were approximately 380 mℓ (10 bed volumes) and 730 mℓ (20 bed volumes) for the two flow rates of 6 and 3 mℓ/min, respectively. The lower flow rate increased the throughput volume at exhaustion.

For Disperse Red 1, the situation was similar to that of Congo Red. The column reached the breakthrough almost at the beginning. When C/C_0 reached 0.5, the throughput volume was about 5 mℓ (0.2 bed volume) for the two flow rates; when the column was exhausted (C/C_0 = 0.8), the throughput volumes were approximately 60 mℓ (2 bed volumes) and 45 mℓ (1.5 bed volumes) for the two flow rates of 6 and 3 mℓ/min, respectively, which were very low values.

For Acid Blue 29, the pH of effluent at the beginning was about 6.0, which was higher than the initial pH (4.0) of the dye solution. It then decreased gradually to a value of 4.2 and remained constant until the column was exhausted. This pH value was close to the initial pH of the dye solution. For Basic Blue 9, the pH of effluent at the beginning was about 7.0 which was higher than the initial pH (6.0) of the dye solution. It then decreased gradually

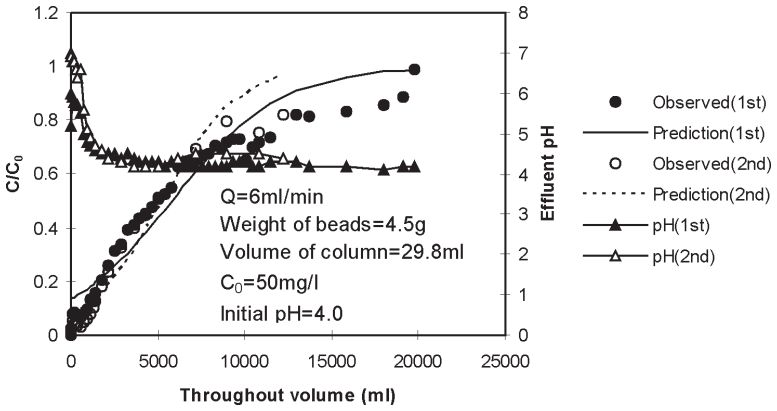

Figure 2
The observed breakthrough points and prediction curves by the Thomas model as well as effluent pH for Acid Blue 29

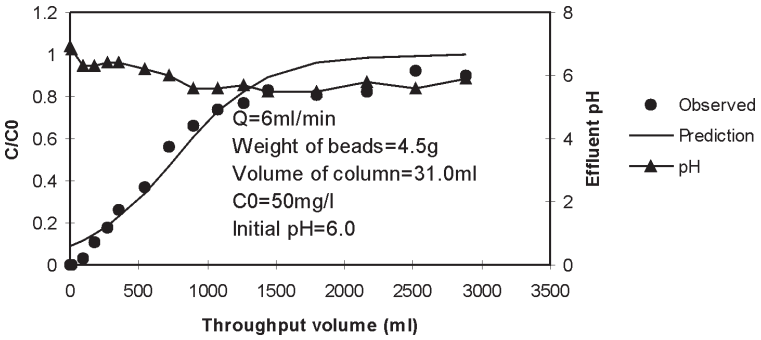

Figure 3
The observed breakthrough points and prediction curves by the Thomas model as well as effluent pH for Basic Blue 9

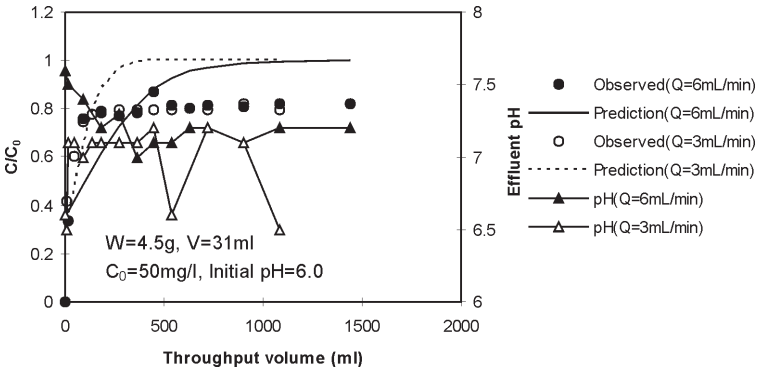

Figure 4
The observed breakthrough points and prediction curves as well as effluent pH for Congo Red

to a value of approximately 5.6 and maintained this value until the column was exhausted. For Congo Red, the pH of effluent at the beginning was 7.6 at the higher flow rate. It then decreased gradually to a value of approximately 7.2 and was constant until the column was exhausted. At the lower flow rate, the pH of effluent at the beginning was 6.6 and then increased to a value of 7.1. There were some fluctuations of pH close to the exhaustion of the column. For Disperse Red 1, the values of effluent pH at the beginning were almost the same (approximately 7.0) at the two flow rates. All then decreased gradually to a value of approximately 4.2, and this value remained constant

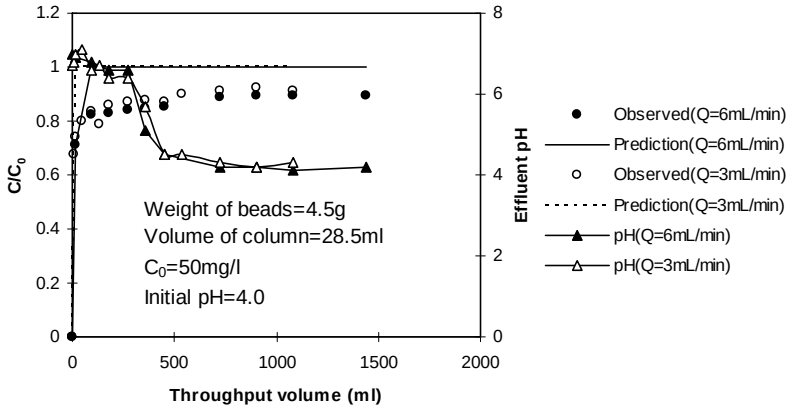

Figure 5
Observed breakthrough points and prediction curves by the Thomas model as well as effluent pH for Disperse Red 1

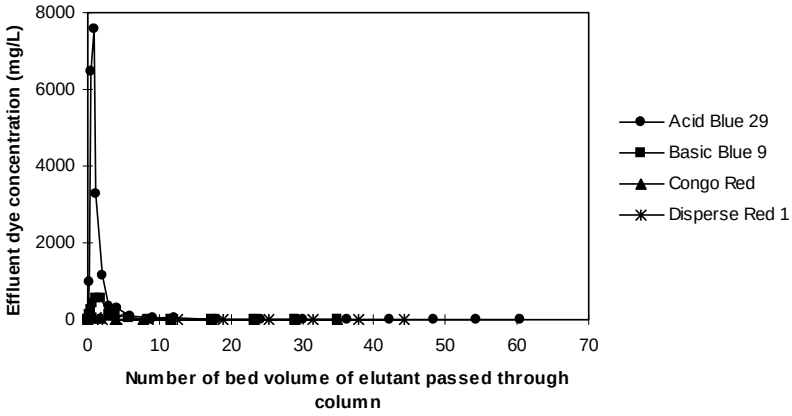

Figure 6
Elution curve for dye desorbed from beads in column

until the exhaustion of the column, which was close to the initial pH of the dye solution.

The breakthrough data from column studies for Acid blue 29, Basic Blue 9, Congo Red and Disperse Red1 adsorption were fitted to the Thomas model shown in Eq. (3) and the constants of a and b were obtained after regression analysis. These constants and related statistical parameters are given in Table 6. The Thomas model constants, k and q_0 were calculated according to Eqs. (6) and (7) and are given in Table 6. Figures 2 to 5 also show the prediction curves by the Thomas model for these four dyes' adsorption, respectively. Table 6 shows that the beads had the highest adsorption capacity for Acid Blue 29 (64.7 mg/g), while the beads had a much lower value for Basic Blue 9 (8.3 mg/g). The beads had a very low adsorption capacity for Congo Red and Disperse Red 1, and the lower flow rate corresponded to the lower adsorption capacity. The t-test showed that all the constants for Acid Blue 29 and Basic Blue 9 estimated by the Thomas model were statistically significant at the 95% confidence level, while the constants for Congo Red were not. The t-test was not available for the constants of Disperse Red 1 even though the correlation coefficient R was not low. Because the two columns for Congo Red and Disperse Red 1 reached the breakthrough point in very short time, it resulted in limited data being obtained before the breakthrough point and caused unsatisfactory t-test results. When the flow rate for these two dyes was reduced to half, the situation was still the same as before.

The beads consisted of two-third fungal biomass and one-third polysulphone by weight. In this study, the adsorption capacity contributed from polysulphone in the biomass-polysulphone beads was assumed zero. Therefore, the adsorption capacity contributed by the biomass in the biomass-polysulphone beads was 1.5 times of the adsorption capacity of the biomass-polysulphone beads and given in Table 6. Table 6 also gives the values of adsorption capacities (Q^0) for the four dyes obtained in batch studies, using the powdered *A. niger* fungal biomass. For Acid Blue 29, the biosorption capacity of the biomass in the beads increased by approximately 8% ,compared to that of the powdered biomass while it decreased to approximately 25% for Basic Blue 9. In the case of Congo Red and Disperse Red 1, the biomass in the beads adsorbed much less, compared to that of the powdered biomass. These results seem to indicate that the immobilisation of biomass into the polysulphone matrix might influence dye adsorption on the biomass in the beads negatively. This may be due to the organic solvent, DMF, which might cause chemical modifications to fungal biomass. This requires further detailed study.

Elution

When the beads in the column became exhausted with dyes, the dyes were eluted by their corresponding elutants (Table 2). Figure 6 shows the concentration of the four dyes in the elutants vs. the volume of elutants (in bed volumes), respectively. The majority of the adsorbed dyes in the beads were eluted in approximately 10 bed volumes. Due to the high adsorption capacity of the beads for Acid Blue 29, the peak dye concentration in the elutant was very high, approximately 7 500 mg/ℓ, which indicated that this dye could be recovered. The total amounts of dyes adsorbed on and desorbed from the beads were calculated by integrating the breakthrough data and elution data, respectively and the desorption rates for the four dyes were thus obtained. They were 69.6% for Acid Blue 29, 90.7% for Basic blue 9, 43.9% for Congo Red and 59.7% for Disperse Red 1, respectively, which were consistent with the results in batch elution studies (data not shown). The performance of elution for Acid Blue 29 and Basic Blue 9 from the beads was acceptable while for Congo Red and Disperse Red 1 it was poor. In the elution studies, it was observed that the biomass-ploysulfone beads were stable after elution with HCl and NaOH.

Reuse of the regenerated beads for Acid Blue 29

After regeneration by deionised water, the beads were reused in the column for Acid Blue 29 removal. Figure 3 shows the observed breakthrough points and the effluent pH vs. throughput volume in the second column adsorption cycle for Acid Blue 29. The observed breakthrough points in the second adsorption cycle were close to those in the first. The value of C/C_0 also increased gradually. When C/C_0 reached 0.15, the throughput volume was approximately 1 600 mℓ (55 bed volumes), which was higher than that in the first cycle (1400 mℓ, 50 bed volumes). When C/C_0 reached 0.5, the throughput volume increased to approximately

TABLE 6
The Thomas model constants obtained by non-linear regression analysis for the column studies

Dye	Statistical parameter	a(1/mℓ)	b	R	k (mℓ/min. mg beads)	q_0 (mg/g beads)	$q_0$mg/g biomass in beads	Q^0mg/g powdered biomass
Acid Blue 29 (1st cycle) (Q = 6 mℓ/min)	N = 45 Std. Err. t(43) p-level	0.00032 0.00002 12.87 0.000	1.86 0.14 13.53 0.000	0.96	0.04	64.7	97.1	89.7
Acid Blue 29 (2nd cycle) (Q = 6 mℓ/min)	N = 23 Std. Err. t(21) p-level	0.00047 0.00005 9.48 0.000	2.48 0.20 12.33 0.000	0.97	0.06	59.1	88.7	NA
Basic Blue 9 (Q = 6 mℓ/min)	N = 16 Std. Err. t(14) p-level	0.00305 0.00050 6.07 0.000	2.31 0.34 6.78 0.000	0.97	0.4	8.3	12.5	15.5
Congo Red (Q = 6 mℓ/min)	N = 13 Std. Err. t(11) p-level	0.00577 0.00822 0.70 0.498	0.58 0.89 0.65 0.530	0.69	0.7	1.1	1.7	8.2
Congo Red (Q = 3 mℓ/min)	N = 45 Std. Err. t(43) p-level	0.01584 0.01314 1.20614 0.251	0.86 0.60 1.44 0.18	0.70	1.0	0.6	0.9	8.2
Disperse Red 1 (Q = 6 mℓ/min)	N = 11 Std. Err. t(9) p-level	1.33689 NA NA NA	15.13 NA NA NA	0.86	160.4	0.1	0.2	6.3
Disperse Red 1 (Q = 3 mℓ/min)	N = 45 Std. Err. t(43) p-level	1.05637 NA NA NA	5.59 NA NA NA	0.78	63.4	0.1	0.2	6.3

Note: NA = not applicable; the adsorption capacity contributed from polysulphone in the biomass - polysulphone beads was assumed zero. A control with polysulphone beads only in a column is necessary to account for any adsorption by polysulphone beads only.

5 000 mℓ (170 bed volumes) almost the same as that in the first cycle. When the column was exhausted ($C/C_0 = 0.8$), the throughput volume was approximately 12 000mℓ (400 bed volumes) lower than that in the first cycle (12 600 mℓ, 420 bed volumes). The change of the effluent pH in the second adsorption cycle was nearly the same as that in the first cycle.

The breakthrough data in the second adsorption cycle for Acid Blue 29 was also fitted to the Thomas model and the results are given in Table 6. Figure 3 also shows the prediction curve by the Thomas model for the second adsorption cycle. The t-test showed that the Thomas constants were also statistically significant at the 95% confidence level, like those in the first cycle. In the second cycle, the adsorption capacity of the biomass-polysulphone beads was over 91% of that in the first cycle, which showed a good potential to develop a system using immobilised *A. niger* biomass for the removal of certain dyes from aqueous solutions.

Conclusions

A. niger fungal biomass can be immobilised into polysulphone solid matrix to form spherical biomass-polysulphone beads. The beads had a porous structure with a specific surface area in the range of 2.40 to 3.16 m^2/g (diameter of the beads: 1.18 to 2.36 mm). The effective size of beads was in a range of 0.7 to 1.1 mm and 60 to 80% of the beads ranged between 1.18 and 2.36 mm in size. The biomass-polysulphone beads exhibited excellent handling characteristics in columns and were stable in acid and base solutions.

Column studies for the removal of four dyes from aqueous

solutions indicated different performances, dependent upon the dye structure. For Acid Blue 29, the beads in the column possessed the highest adsorption capacity. At column exhaustion, the throughput volume was as high as 420 bed volumes. For Basic Blue 9, the adsorption capacity of the bead was much lower than that for Acid Blue 29, its throughput volume at exhaustion was 40 bed volumes. In contrast, the columns reached breakthrough point and exhaustion in a shorter time for Congo Red and Disperse Red 1.

The breakthrough data from the column studies can be described by the Thomas model. The t-test showed that all the constants for adsorption of Acid Blue 29 and Basic Blue 9 were statistically significant at 95% confidence level, but not for Congo Red adsorption. The t-test was not available for the constants of Disperse Red 1 adsorption.

The elution studies showed that Acid Blue 29 and Basic Blue 9 could be easily eluted from the beads with desorption rates of approximately 70% and 90%, respectively, while Congo Red and Disperse Red 1 were difficult to be eluted with desorption rates of approximately 40% and 60%, respectively.

The regeneration and reuse studies indicated that the beads for Acid Blue 29 could be regenerated by deionised water and the reused beads could retain over 90% of the original adsorption capacity of the beads. These results suggest that treatment systems using the beads of immobilised *A. niger* biomass in polysulphone could be developed for the removal of some dyes from aqueous solutions.

Further research

The ratio of the amount of biomass to polysulphone in the slurry used for the beads production would affect the pore structure and dye removal capacity of the beads. Therefore, the optimal ratio should be studied to produce the beads with a proper pore structure and high dye removal capacity.

In the slurry preparation, the organic solvent, DMF, dissolves polysulphone. This might cause some chemical modifications to the fungal biomass, which could cause some influence on the adsorption capacity of the biomass in the beads. These effects should be studied further.

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