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Biosorption of Lead, Copper, and Cadmium with Continuous Hollow-Fiber Microfiltration Processes

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ABSTRACT

A hollow-fiber crossflow microfiltration membrane was utilized to retain a biomass of *Pseudomonas aeruginosa* PU21 for continuous biosorption of lead (Pb), copper (Cu), and cadmium (Cd) ions in single or ternary metal systems. The results obtained from the microfiltration systems showed that in both single and ternary biosorption, the metal removal efficiency based on a molar basis was clearly Pb > Cu > Cd. For a single-membrane process with an influent metal concentration of 200 μM and a flow rate of 350 mL/h, the effluent concentration of Pb and Cu satisfied the national regulations for an influent volume of 6.3 L. With a three-metal influent, the adsorption capacity of the biomass for Pb, Cu, and Cd was reduced 4, 50, and 74% compared to that for single-metal adsorption. Selective biosorption with a three-column sequential microfiltration operation exhibited an enhancement of 40 and 57% of total metal removal for Cu and Cd, respectively, over the results from single-membrane operation. The multimembrane operation also enabled locally optimal accumulation of Pb, Cu, and Cd at the first, second, and third stage, respectively. The regeneration efficiency of the biomass was 70% after three repetitive adsorption/desorption cycles, whereas the Pb recovery efficiency was maintained at nearly 90%. A rapid-equilibrium model (Model A) and a mass-transfer model (Model B) were used to describe the results of single- and multimetal biosorption with the microfiltration processes. Model A exhibited excellent prediction for the results of single-metal biosorption, while Model B was more applicable to interpret the multimetal biosorption data.

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Key Words. Biosorption; Microfiltration; Hollow fiber; Heavy metals; Multimetal adsorption

INTRODUCTION

Much effort has been devoted over past decades to research on the adsorption and accumulation of heavy metals by a biomass of microorganisms (1–4) in an effort to develop biosorption as an alternative means for the treatment of heavy-metal-contaminated water. Some key factors which seem to limit the practical implications of the biosorption process for the removal of heavy metals from aquatic systems have been encountered. The major challenges associated with the biosorption of heavy metals include competition of coexisting ions, recovery and regeneration of loaded biomass, and process design for continuous biosorption. However, the literature about those topics is relatively rare. It is the objective of this study to attempt to deal with those limiting factors by developing effective continuous biosorption processes able to remediate wastewater contaminated by multiple metal ions, and also to be able to operate them repetitively.

Although a suspended biomass offers good contact with the adsorbates during adsorption, it is normally not used directly in a biosorption process; instead, the biomass is often immobilized to enhance its stability, mechanical strength, reusability, and the ease of handling. Gel entrapment, which utilizes natural or artificial gel materials as the support matrix, is one of the most popular immobilization techniques (5). In general, the increase of mass transfer resistance in gel immobilization is a major drawback which may severely hinder the adsorbate/adsorbent interaction. In addition, biosorption with immobilized cells has frequently been designed as a fixed-bed reactor (6, 7), which could further aggravate the mass transfer problem due to the poor mixing in a fixed-bed reactor. To prevent the disadvantages raised from fixed-bed biosorption, Brady et al. (8) utilized a hollow-fiber microfiltration membrane to confine the cells inside the membrane for continuous biosorption. The process allows continual separation of biosorbent and the treated solution, and provides an excellent environment for contact of the biomass and the adsorbates, thereby leading to improved adsorption efficiency. In addition, the membrane reactor is easy to operate and to regenerate, thus making it a potential alternative to conventional biosorption processes.

Our previous work (9, 10) demonstrated that a biomass of *Pseudomonas aeruginosa* PU21 (Rip64) can effectively adsorb heavy metals, including mercury (Hg), lead (Pb), copper (Cu), and cadmium (Cd). Batch biosorption experiments also indicated that the biomass exhibited its highest adsorption preference for Pb, whereas adsorption of Cd was the least favorable (11). In this

study, resting cells of a biomass of *P. aeruginosa* PU21 (Rip64) were entrapped with a hollow-fiber microfiltration (HFMF) membrane for heavy metal biosorption in single- and multimetal systems. The behavior of the selective adsorption of Pb, Cu, and Cd was monitored in a continuous mode. Up to three membranes were connected in series to enhance the metal-removal capacity and to allow selective separation of the three metals in each HFMF stage. Mathematical models were also derived to describe the behavior of continuous heavy metal biosorption with HFMF processes for single and ternary systems.

EXPERIMENTAL METHODS

Bacterial Strain and Cultivation

Pseudomonas aeruginosa PU21, an auxotrophic derivative of PAO1, was isolated from clinical sewage by Jacoby (12). The strain harbors a 142.5 Kb plasmid Rip64 which encodes for the narrow-spectrum mercury resistance (12). The strain was cultivated aerobically at 37°C in Luria-Bertani (LB) broth (Difco), which was amended with 25 mg Hg^{2+}/L to avoid contamination from other microorganisms and to induce the mercury resistance. Mass production of the biomass was achieved with a 5-L fermentor (Eyela Jar Fermentor MDF) equipped with devices that measure and control temperature, dissolved oxygen level (DO), pH, and agitation speed.

Preparation of Biosorbent

Biosorbent for Batch Biosorption

Cells of *P. aeruginosa* PU21 were harvested by centrifugation (15,000*g*, 8 min) from early-stationary cultures with a cell density of approximately 1.5–2 g/L. After being rinsed twice with deionized, reverse osmotically treated water, the cells were prepared at designated concentrations with phosphate-buffered saline (PBS) for the use in biosorption experiments. The PBS consists of KH_2PO_4 (0.2 g/L), Na_2HPO_4 (1.15 g/L), KCl (0.2 g/L), and NaCl (8 g/L).

Biosorbent for Continuous Biosorption

Cells of *P. aeruginosa* PU21 from early-stationary cultures (1.5–2 g/L) with a volume of approximately 5 L were stored in a biosorbent reservoir (Fig. 1) where the cells were concentrated to a final cell mass concentration of 7.3 g/L by circulating the cell solution through a conventional crossflow HFMF membrane (Asahi Chemical Synthesis Industry; MF Lab Module, PMP-102, pore size 0.25 μm). This procedure is a preparatory step for the continuous

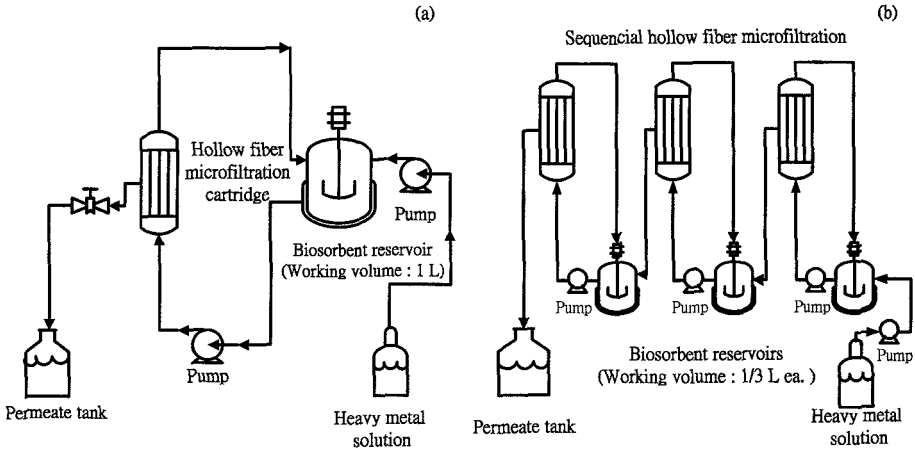

FIG. 1 Schematic description of a hollow-fiber crossflow microfiltration device for continuous biosorption of heavy metals. (a) Single-membrane microfitration system; (b) multimembrane microfiltration system.

metal-removal operation. The concentrated biosorbent was rinsed by introducing sterile deionized water into the reservoir to remove residual growth medium. The microfiltration (MF) device is described schematically in Fig. 1. The cell concentration and rinse were performed at 4°C to prevent further cell proliferation.

Measurement of Heavy Metals

The heavy metal adsorbates used in this study, $Pb(NO_3)_2$, $CuCl_2$, and $CdCl_2$, were obtained from Riedel-de Haen, Inc. Heavy metal contents in solutions were measured with a Polarized Zeeman Atomic Absorption Spectrometer (Hitachi Model-Z-6100).

Time Course of Biosorption

The biosorbent with a final concentration of 1.5–2 g cell/L was suspended in 12 mL of heavy metal solution (200 μM) in a glass container which was gently agitated at room temperature. Samples were taken from the solution at desired intervals and were subsequently centrifuged at 15,000*g* for 8 minutes. The heavy metal concentration in the resulting supernatant was determined. The centrifuge tubes and containers used in this study were all made of glass and were treated with 30% HNO_3 prior to being applied in the metal biosorption experiments. The acid-wash treatment was found to be effective for avoiding metal sorption to the containers.

Procedures of Biosorption of Heavy Metals with the HFMF Processes

The layout of a single-membrane HFMF process is illustrated in Fig. 1(a). Heavy metal solutions containing single-component or ternary mixtures of Pb^{2+}, Cu^{2+}, and Cd^{2+} (each at 200 μM, pH 5.0) were pumped into a 5-L biosorbent reservoir and mixed with 7.3 g of the biomass. The metal/biomass mixture with a working volume of 1 L was introduced into the cartridge, allowing entrapment of the biosorbent inside the membrane. To avoid a high initial effluent metal concentration, the reject flow was restricted initially, and a batch-mode biosorption was carried out for the first 1.5 hours of operation, during which the mixture was circulated inside the membrane. After 1.5 hours the permeates were released and collected in the permeate tank where samples were taken to measure the residual metal concentration. The batch-pretreatment procedures ensured decrease of metal concentration to a desired level prior to the release of the effluent. In general, the metal influent rate and the permeate flow rate were maintained constant at 350 mL/h, reflecting a retention time of approximately 2.86 hours. Control experiments were also performed to determine possible metal loss due to the MF device alone. With identical operation conditions as described above, but without the biosorbent, the deviation between metal concentrations in the permeates and in the influents was always less than 5%.

Continuous biosorption was also performed with a serial combination of three MF membranes (Fig. 1b). The operation conditions for each membrane, including the feeding rate, permeate flow rate, retention time, and the biosorbent concentration, were identical to those used for the single-membrane process. However, since 7.3 g of the biomass was evenly distributed to the three membrane systems, the working volume in the biosorbent reservoir for each subsystem was adjusted to 1/3 L to maintain the same biomass concentration (7.3 g/L) as that used for the single-membrane system. The sequential microfiltration was utilized solely to investigate the selective biosorption with ternary mixtures of Pb, Cu, and Cd.

Procedures for Metal Recovery and Biosorbent Regeneration with the HFMF Processes

Typical strategies for the recovery of biomass-associated metal and for the regeneration of the biomass were demonstrated with a single-membrane process using Pb as the adsorbate. The Pb solution at the concentration of 200 μM was continuously fed into the HFMF system with a flow rate of 350 mL/h and a total biomass weight of 7.3 g. The Pb feeding was terminated when the effluent Pb concentration exceeded 5 μM (about 18 hours of feeding), after which the effluent concentration rose abruptly. This timing is normally de-

fined as the breakthrough time (t_b). The cartridge was then washed with HCl solution at pH 2.0 (10) with the restriction of effluent stream to recover the metal adsorbed on the biomass. The acid washing was employed for approximately 5 hours, and the metal concentration in the bulk was measured. The regenerated biosorbent was rinsed thoroughly with deionized water before being used for the next adsorption run. The adsorption/desorption (A/D) cycle was repeated three times. It should be emphasized that the adsorption operation was terminated before saturation of biomass was reached to ensure a low bulk Pb concentration, which is beneficial to metal recovery with acid treatment. Besides, the adsorption of Pb after the breakthrough time was very limited since at that time the biosorbent was very close to saturation.

RESULTS AND DISCUSSION

Variations of Bulk Biomass Concentration during HFMF Operations

Figure 2 exhibits time-course measurements of bulk biomass concentration during biosorption of Pb with the HFMF process. The time scale in Fig. 2 can

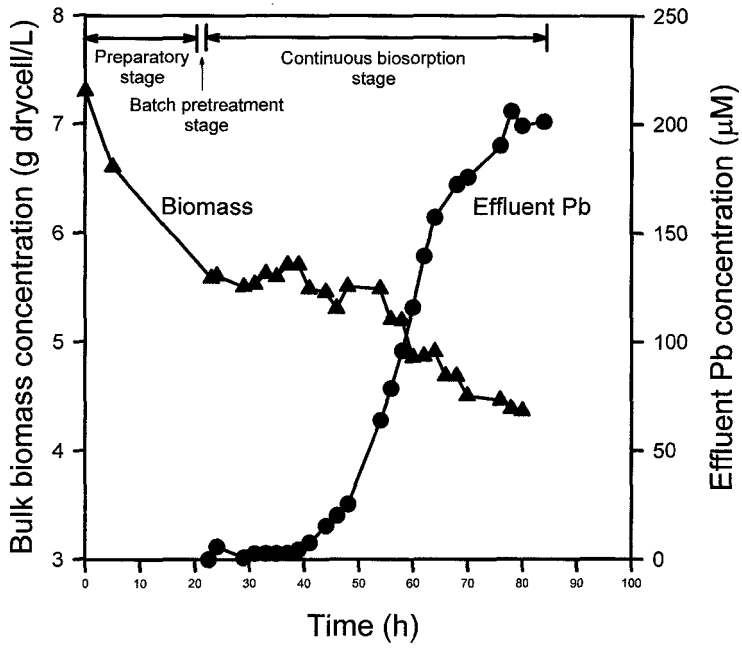

FIG. 2 Bulk biomass concentration (▲) and effluent Pb concentration (●) profiles in the course of hollow-fiber microfiltration operation.

be divided into three stages. The first 20.5 hours was the preparatory stage during which the cell solution was concentrated to a desired concentration and rinsed with deionized water. Between 20.5 and 22 hours was the batch-pretreatment stage, during which the biomass/metal mixture was circulated inside the MF membrane with restriction of the effluent stream. The rest of the time scale belonged to the continuous biosorption stage, during which 200 μM of Pb solution was fed into the HFMF system at a constant rate of 350 mL/h and the permeates were released at the same rate. The effluent Pb concentration profile during the third stage is also demonstrated in Fig. 2.

It is clearly seen from Fig. 2 that the bulk biomass concentration decreased approximately 20% during the preparatory stage, suggesting that a portion of cells may stick to the membrane surface or even enter the porous structure of the MF membrane due to the employment of side pressure. Using a MF membrane biosorption process similar to this work, Brady et al. (8) also observed that during filtration the biomass (yeast) tended to pack onto the membranes, causing a decrease in bulk cell concentration. The biomass concentration remained nearly constant from 22 to 52 hours (the first 30 hours of continuous biosorption), until another drop of biomass concentration occurred after 52 hours. These results seem to indicate that the membrane surface or pores were essentially saturated during the cell-concentration stage, after which the bulk biomass concentration was unchanged despite continuous operation of the membrane for 30 hours.

It is noticed that in the constant-biomass region the effluent Pb concentration was also nearly constant and remained at a very low level until the effluent Pb concentration increased sharply after around 40 hours due to saturation of the biosorbent (Fig. 2). The decrease in bulk biomass concentration after 52 hours was accompanied by an increase in the effluent Pb concentration, suggesting that the decrease of biomass concentration may be correlated to the accumulation of Pb in the bulk. One of the possibilities is that an osmotic pressure shock caused by a rapid increase of metal concentration caused disruption of cells into finer cell fragments which may be able to diffuse further into membrane pores, resulting in the loss of biomass from the bulk in the final period of continuous biosorption (Fig. 2). Cell disintegration at a Pb^{2+} concentration of 200 μM was indirectly evidenced by a threefold increase of total protein content in the supernatant of the cell solution. Although cell disintegration may occur during continuous HFMF operation, the loss of biomass due to leakage of the MF membrane was negligible since the cell concentration in the permeates was undetectable.

Biosorption of Single Metals with the HFMF Processes

The concentration profiles of Pb, Cu, and Cd in the effluents resulting from the HFMF process loaded with single metals are presented in Fig. 3. It shows

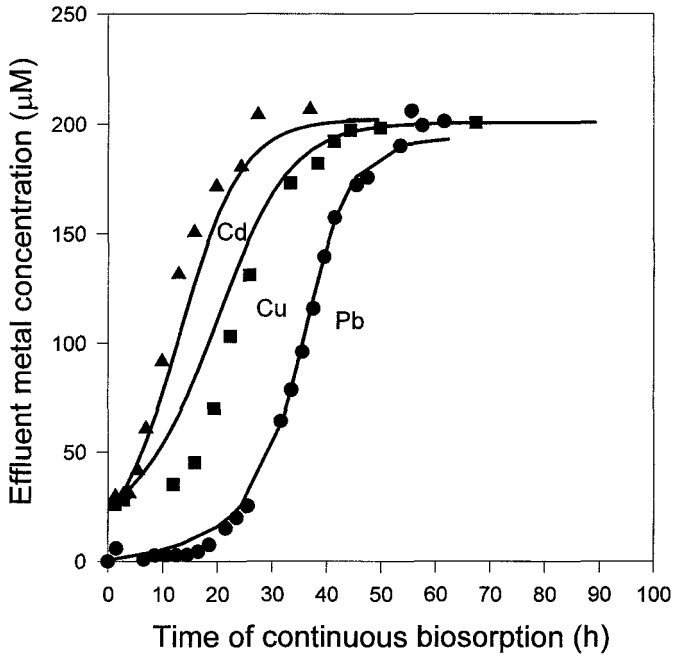

FIG. 3 Effluent concentration profiles of Pb (●), Cu (■), and Cd (▲) for single-component biosorption with the continuous hollow-fiber microfiltration process (symbols: experimental data; solid lines: prediction by Model A).

that with the same influent metal concentration (200 μM) and the same biosorbent concentration (7.3 g/L), the HFMF process exhibited the highest capacity for Pb, while adsorption of Cd was the least efficient. This trend is consistent with what was observed from batch biosorption in our previous studies (10, 11), which reported that on a molar basis the saturation capacity of *P. aeruginosa* PU21 decreased in the order of Pb > Cu > Cd. Figure 3 also shows that for the first 18 hours (6.3 L influent volume), the effluent Pb and Cu concentrations were able to meet the national regulation requirements of Taiwan, which are 5 μM for Pb and 47 μM for Cu. However, the Cd effluent from HFMF operation could not satisfy the nation's requirement of 0.9 μM, whereas for the first 6.5 hours the effluent Cd concentration was lower than 27 μM, significantly lower than the feeding concentration of 200 μM (Fig. 3).

With the operation strategy the total amount of Pb adsorption was 2360 μmol, corresponding to an adsorption capacity of approximately 324 μmol/g dry cell. The Cu and Cd adsorptions resulting from the data shown in Fig. 3 were 1550 μmol of Cu (212 μmol Cu/g dry cell) and 752 μmol of Cd (103

μmol Cd/g dry cell). The maximal metal adsorption capacity obtained from single-membrane HFMF biosorption operations was compared with the batch adsorption capacity at an equilibrium metal concentration of 200 μM, equal to the influent metal concentration in HFMF operations. According to our previous work (10), the batch biosorption capacities of *P. aeruginosa* PU21 cells at 200 μM for Pb, Cu, and Cd were 483, 281, and 338 μmol/g dry cell, respectively, which are higher than those obtained from the HFMF system. The lower adsorption capacity in the continuous processes may be attributed to the shorter retention time for the continuous operation and, more importantly, to the loss of bulk biomass concentration during HFMF operations (Fig. 2) because a portion of the initial amount of biomass may adsorb on the membrane surface or diffuse into the membrane pores. This biomass that was not in the bulk may be less efficient on metal sorption due to mass transfer restrictions or blocking of a portion of metal adsorption sites on the biomass surface. Besides, since the bulk metal concentration in the continuous process was always lower than the influent concentration (200 μM) except for the final stage of the operation when the biomass was fully saturated (Fig. 3), a lower adsorption capacity in the continuous process is to be expected.

Selective Biosorption of Heavy Metals with HFMF Processes

Single-Membrane Operation

Figure 4 presents effluent metal concentration profiles resulting from single-membrane HFMF biosorption with the influent comprising equal molar concentrations (200 μM) of Pb, Cu, and Cd. In Fig. 4(a–c) the multimetal biosorption data are compared with those from single-metal biosorption under the same operation conditions. Inspection of Fig. 4 shows that in the presence of competing ions the adsorption efficiency for each metal was generally lower than that observed when they were alone. The decrease in Cd adsorption due to coexisting ions was the most severe, while the co-ion effect on Pb adsorption was negligible. In ternary systems the net cumulative adsorption of Pb, Cu, and Cd at saturation, calculated from Fig. 4, was 96, 50, and 26% of that obtained from single-metal biosorption (Table 1). The results suggest that the adsorption preference of the biomass over the three metals was Pb > Cu > Cd, which is consistent with that observed from batch biosorption experiments (11).

The effluent Cd concentration profile for ternary systems, shown in Fig. 4(c), exhibits an overshoot region over the operation time of 15 to 50 hours, during which the effluent Cd concentration was higher than its influent concentration (Fig. 4c). Although less significant than that observed for the Cd profile, a slight overshoot of effluent Cu concentration was also observed be-

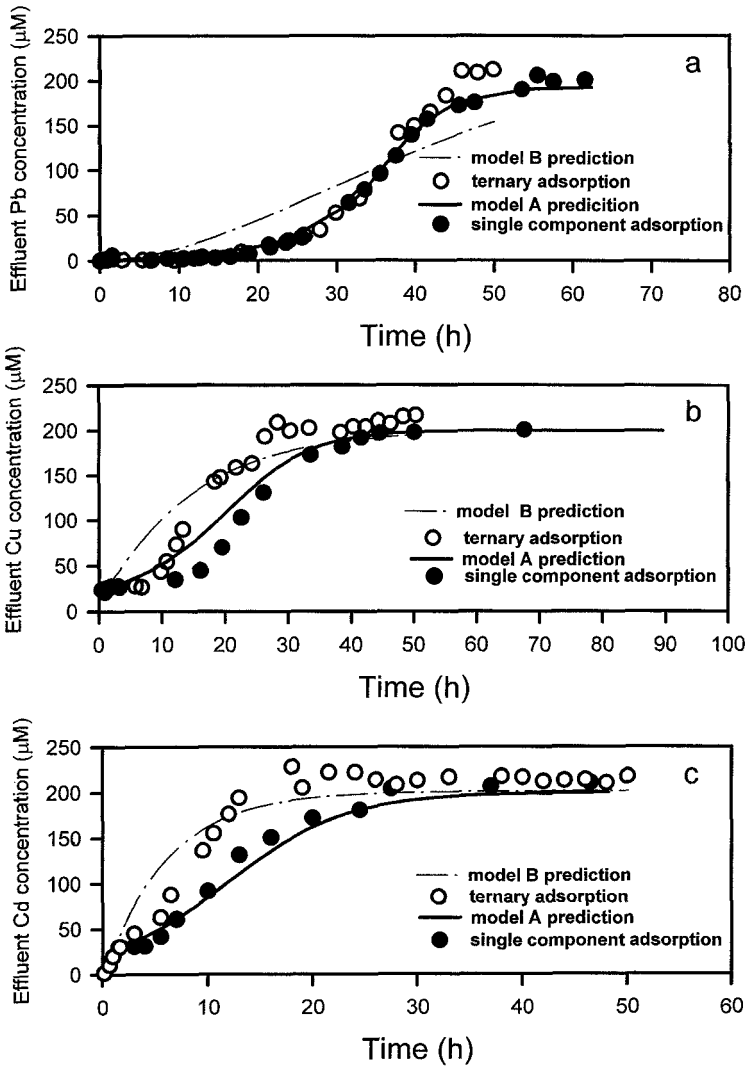

FIG. 4 Comparison of effluent concentration profiles of (a) Pb, (b) Cu, and (c) Cd for single-component and ternary biosorption with the hollow-fiber microfiltration process (●: experimental data for single-component biosorption; ○: experimental data for ternary biosorption; solid lines: Model A prediction for single-component biosorption results; dashed lines: Model B prediction for ternary biosorption results).

TABLE 1
The Quantity of Metal Adsorption by the Biomass of *P. aeruginosa* PU21 for Single- and Multimembrane HFMF Systems with One-Metal or Three-Metal Influents

	Total biomass (g)	Pb adsorption (μmol)	Cu adsorption (μmol)	Cd adsorption (μmol)	Subtotal (μmol)
Single-membrane system:					
One-metal influent	7.3	2360	1550	752	—
Three-metal influent	7.3	2266	775	188	3229
Multimembrane system (three-metal influent):					
Stage 1	2.43	762	257	65	1084
Stage 2	2.43	629	469	44	1142
Stage 3	2.43	591	356	186	1133
Subtotal (g or μmol)	7.3	1982	1082	295	3359

tween 28 and 50 hours (Fig. 4b). No overshoot occurred in the Pb concentration profile (Fig. 4a). It is thought that the overshoot in the effluent concentration of metals is a result of ion exchange when metal ions with higher selectivity (such as Pb) replace lower selectivity ones (such as Cd) from the adsorbed surface. It is most likely that the overshoot takes place when the adsorbent surface is nearly saturated and the adsorbates start to compete for the looser occupied sites. Since adsorption of Cd is the least preferable to the biomass, the overshoot of Cd occurs earlier than that of Cu. The net substitution of Pb by Cu or Cd is negligible because its effluent concentration was always below 200 μM. This observation provides further evidence to support the order of the metal selectivity of biomass of *P. aeruginosa* PU21 as Pb > Cu > Cd.

Multimembrane Operation

A sequential HFMF biosorption process was conducted by connecting three MF membranes in series (Fig. 1b) for two purposes. First, the multimembrane process may be able to improve the removal efficiency of the metals (e.g., Cd) which could not be reduced to a satisfactory level with a single-membrane process. Second, the multimembrane process may enable locally predominant uptake of the metals at different membrane stages by making use of the different selectivities of the biosorbent for Pb, Cu, and Cd. This may allow individual recovery of each metal from a contaminated ternary mixture.

Results for the biosorption of a ternary mixture of Pb, Cu, and Cd by a three-membrane process are demonstrated in Figs. 5 and 6. Figure 5 shows the effluent concentration profile results from each membrane stage. The metal

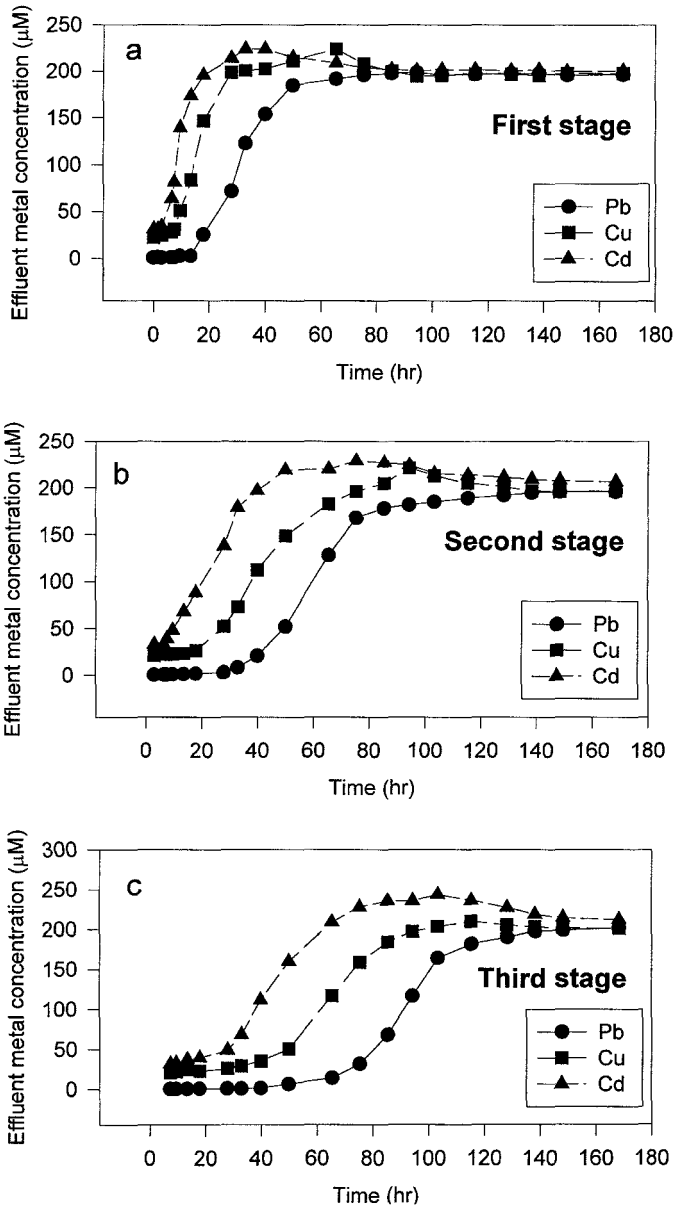

FIG. 5 Effluent concentration profiles of Pb (●), Cu (■), and Cd (▲) for ternary biosorption with multimembrane microfiltration processes. (a) First stage; (b) second stage; (c) third stage.

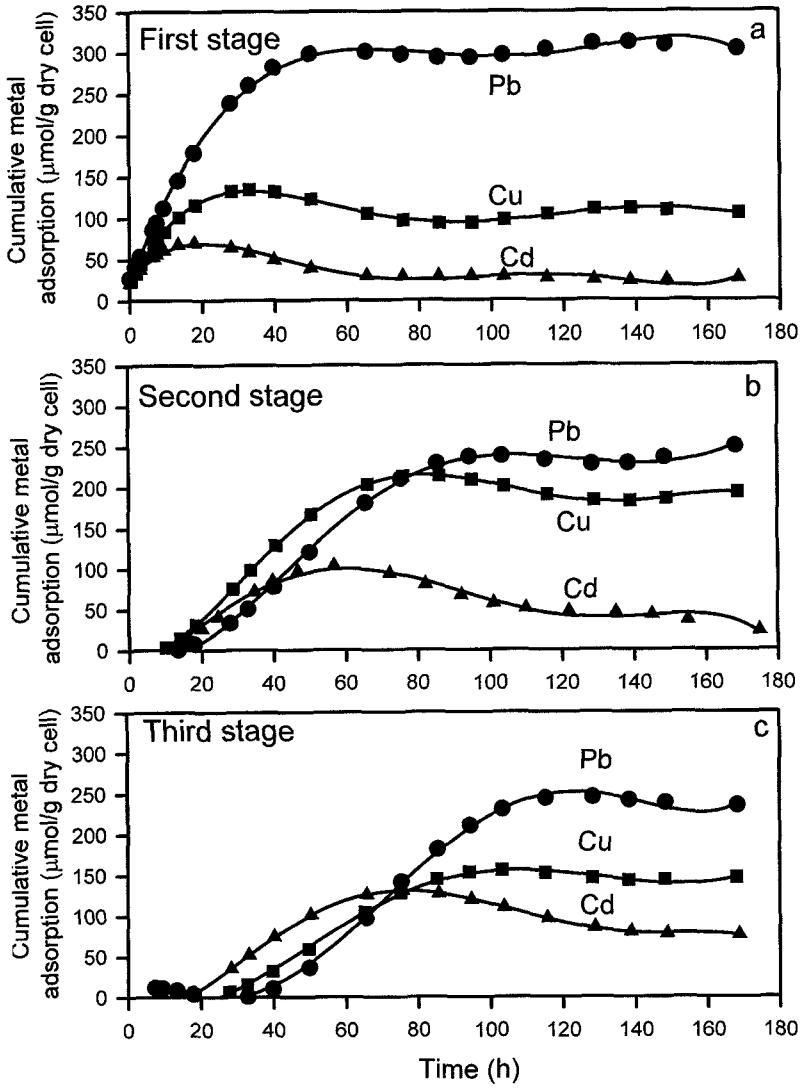

FIG. 6 Cumulative adsorption profiles of Pb (●), Cu (■), and Cd (▲) for ternary biosorption with multimembrane microfiltration processes. (a) First stage; (b) second stage; (c) third stage.

removal efficiency gradually improved from the first stage to the third stage. From comparison of the effluent profiles at the final (third) stage (Fig. 5c) with the single-membrane results (Fig. 4a–c), it appears that for the same total amount of biomass (7.3 g), the three-membrane operation exhibits better metal adsorption efficiency than does the single-membrane system. The conclusion drawn here can be further verified quantitatively from the data presented in Fig. 6, which compares the cumulative adsorption profiles of the three metals at each HFMF stage. As summarized in Table 1, metal adsorption in three membranes together was 1982 μmol for Pb, 1082 μmol for Cu, and 295 μmol for Cd, in contrast to 2266, 775, and 188 μmol for Pb, Cu, and Cd, respectively, in the single-membrane process. This indicates that multimembrane operation results in much better capacity for Cu and Cd than the single membrane system, with a 40 and 57% increase for Cu and Cd, respectively. Meanwhile, the biosorbent in the three-membrane system maintains nearly 90% of its Pb adsorption capacity for the single-membrane operation. Table 1 also shows that although the order of net cumulative adsorption in each stage is always Pb > Cu > Cd; the cumulative adsorption of Pb decreases with an increasing number of stages, whereas the maximal cumulative adsorption for Cu and Cd occurs at the second and third stage, respectively (Fig. 6, Table 1). These results seem reasonable because the multimembrane operation creates a local low-Pb environment at the second and the third stage, allowing better adsorption of the less favorable adsorbates (Cu and Cd) at those two stages.

On the other hand, the total amount of metal adsorption by the biomass for the three metals together (Table 1) also increase slightly from 3229 μmol (single-membrane system) to 3359 μmol (three-membrane system). However, the deviation in total metal adsorption (Pb + Cu + Cd) among the three stages (Table 1) is within 5%, with an average value of 1120 μmol (460 μmol/g). This suggests that during sequential HFMF operation, the total metal adsorption capacity of the biomass at each stage is essentially uniform and is not affected by variations in the influent composition.

It can be observed from Fig. 6 that the optimal cumulative adsorption of the three metals was 312 μmol/g for Pb (138 hours of Stage 1), 214 μmol/g for Cu (76 hours of Stage 2), and 130 μmol/g for Cd (75 hours of Stage 3). These values are comparable to the maximal capacity for each metal obtained when it was alone (Table 1), implying that the effect of competition of co-ions can be minimized locally with multimembrane operation. Consequently, separation of the three metals may be achievable. However, as shown in Fig. 6, the three-membrane process used in this study apparently was unable to obtain a clear-cut separation of the three metals. Nevertheless, the degree of separation may be improved by increasing the number of HFMF stages. Figure 6 also shows that after reaching a peak, the cumulative adsorption profiles for Cu and Cd gradually declined, reflecting the replacement of the adsorbed Cu and Cd

species by more preferable adsorbates (e.g., Pb). This can be related to the overshoot behavior demonstrated in Figs. 4 and 5.

Adsorption/Desorption (A/D) Cycles with HFMF Processes

Table 2 summarizes the efficiency of Pb recovery and biomass regeneration for each A/D cycle. It shows that after three A/D cycles, above 90% of biomass-laden Pb can be recovered while the biomass retains nearly 70% of its original capacity for Pb. The regeneration efficiency appears to decrease with increasing A/D cycles, and the decrease in the regeneration efficiency is more significant than that observed in the batch (resting-cell) system in which the biomass lost only 16% of its original capacity after three A/D cycles (10), in contrast to a 30% loss for the HFMF system.

It is worth noting that repetitive acid washing resulted in finer cell particles, probably because the acid treatment caused some damage on the cell wall structure. In a recent report, Kratochvil et al. (13) found that treatment with 0.1 M HCl caused considerably weight loss of biomass of *Sargassum fluitan*, which also suggests possible cell damages by acid washing. In the HFMF system, some of the smaller cell fragments could be pushed into the pore structure or even pass through the MF membrane, thereby causing a decrease in bulk biomass concentration. If the finer cell fragments resulting from acid washings do not penetrate across the membrane, they may be stacked in the membrane pores, and the surface area available for metal biosorption may be reduced due to overlapping of cell particles, leading to a decrease in overall adsorption efficiency. This may explain why the regeneration efficiency of the biomass in the HFMF system was lower than that in the resting-cell system after repetitive acid treatment.

TABLE 2
Efficiencies of Pb Recovery and Biomass Regeneration in Repetitive Adsorption and Desorption Cycles with the HFMF Process

Cycle No.	Pb recovery efficiency (%)[a]	Biomass regeneration efficiency (%)[b]
1	97	100
2	102	84
3	90	70

[a] Pb recovery efficiency $= \dfrac{\text{amount of Pb desorbed from the loaded biomass at cycle } N}{\text{amount of Pb adsorbed at cycle } N}$

[b] Biomass regeneration efficiency $= \dfrac{\text{amount of Pb adsorbed at cycle } N.}{\text{amount of Pb adsorbed at cycle 1}}$

Mathematical Models for Biosorption of Metals with HFMF Processes

The concentration profiles of Pb, Cu, and Cd resulted from HFMF processes with single- and three-metal influents can be described by mathematical models based upon a material balance for the adsorbate species in the system. By selecting an appropriate control volume, the material balance for an adsorbate i can be written as

$$V\frac{dC_{l,i}}{dt} = v(Cin_i - C_{l,i}) - WV\frac{dq_i}{dt} \tag{1}$$

where $C_{l,i}$ = the concentration of adsorbate i in the liquid phase (μM)
Cin_i = the influent concentration of adsorbate i (μM)
q_i = the amount of adsorbate i adsorbed per unit weight of biosorbent (μmol/g cell)
V = the working volume of the HFMF process (L)
v = the metal feeding rate and the effluent flow rate (L/h)
W = total biosorbent concentration in the HFMF system (g/L)
t = time of operation (h)

Since a portion of the initial amount of biomass added into a HFMF biosorption system may become less effective due to packing or diffusion of biomass to the MF membrane, the W value was therefore modified by an effectiveness coefficient θ to give a more precise expression ($W\theta$) for the representation of total "effective" biomass concentration in the system. The value of θ is in the $0 \leqq \theta \leqq 1$ range. Incorporation of θ into Eq. (1) gives

$$\frac{dC_{l,i}}{dt} = \frac{v}{V}(Cin_i - C_{l,i}) - W\theta\frac{dq_i}{dt} \tag{2}$$

Rapid-Equilibrium Model (Model A)

The adsorption kinetics of Pb, Cu, and Cd by biomass of *P. aeruginosa* PU21 was determined with batch operations in which the initial metal concentration was 200 μM and the biomass concentration was 7.3 g/L. The results, illustrated in Fig. 7, show that biosorption of the three metals reaches equilibrium in less than 10 minutes. The time is much shorter than what would normally be taken (about 30–70 hours) to saturate the same quantity of biosorbent in a continuous HFMF process (Fig. 3) with the influent metal concentration equal to the initial metal concentration used in batch operation. Therefore, it seems reasonable to assume that in HFMF operation the biosorbent reaches equilibrium instantaneously, and therefore the liquid-phase concentration ($C_{l,i}$) in Eq. (2) is replaced by the equilibrium concentration (Ce_i) to ob-

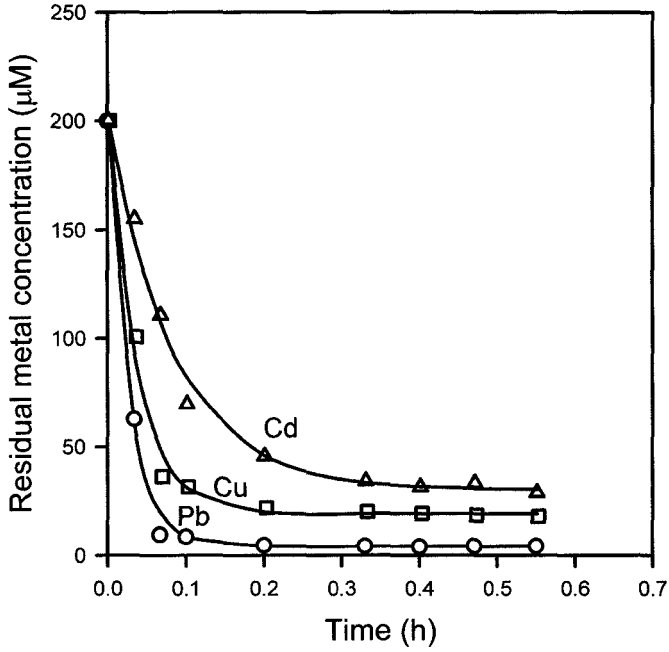

FIG. 7 Time course of residual concentrations of Pb (○), Cu (□), and Cd (△) for batch biosorption in a ternary system (biomass concentration: 7.3 g/L; initial concentration for Pb, Cu, and Cd: 200 μM each).

tain the following expression:

$$\frac{dCe_i}{dt} = \frac{v}{V}(Cin_i - Ce_i) - W\theta\frac{dq_i}{dt} \tag{3}$$

Since it is presumed that $C_{l,i} = Ce_i$, q_i can be estimated by a typical Langmuir isotherm as follows:

$$q_i = \frac{q_{\max,i}K_iCe_i}{1 + K_iCe_i} \tag{4}$$

where $q_{\max,i}$ is the maximal adsorption capacity of the biosorbent for adsorbate i (μmol/g) and K_i is the Langmuir constant (L/μmol), which is proportional to the affinity between the adsorbate and the adsorbent. Substitution of Eq. (4) into Eq. (3) results in Eq. (5):

$$\frac{dCe_i}{dt} = \frac{v(Cin_i - Ce_i)(1 + K_iCe_i)^2}{V[(1 + K_iCe_i)^2 + W\theta q_{\max,i}K_i]} \tag{5}$$

According to our previous work (11), the value of $q_{\max,i}$ for Pb, Cu, and Cd is 520, 632, and 327 μmol/g dry cell, and the K_i value is 0.0903, 0.0423, and 0.0242 L/μmol for Pb, Cu, and Cd, respectively. With those parameters, Eq. (5) was used to fit the experimental data presented in Fig. 3. The only unknown parameter, θ, was estimated with the model, and the optimal value of θ was 0.6045. The numerical software used for model simulations was Matlab (Version 4.0) and Mathematica (Version 2.2). The model prediction (solid curves) is compared with the experimental data (symbols) in Fig. 3. It is observed that Eq. (5) is able to predict the effluent Pb concentration profile fairly well, while the predictions for the Cu and Cd profiles were less accurate.

When Model A was used to describe biosorption for the three-metal system, the extended Langmuir isotherm may be used to represent q_i:

$$q_i = \frac{q_{\max,i} K_i Ce_i}{1 + \sum_{i=1}^{3} K_i Ce_i} \tag{6}$$

Since the expression of q_i becomes much more complicated than that for single-component adsorption, plugging Eq. (6) into Eq. (3) created significant nonlinearity and complexity, making calculation of the resulting equation very tedious and numerically unstable. As a result, Model A seems to have poor applicability for the estimation of multicomponent adsorption results.

Mass-Transfer Model (Model B)

For a better description of multicomponent biosorption data, a mass-transfer model was derived to resolve the difficulties associated with Model A. In this model the rapid-equilibrium assumption was not applied in order to avoid a complex expression of q_i. Instead, it was assumed that the adsorption of species i is closely related to the concentration gradient formed between the bulk and the biomass surface. Therefore, the rate of concentration changes of adsorbate i in the bulk can be described as (14):

$$-\frac{dC_{l,i}}{dt} = k_{l,i} W (C_{l,i} - C_{l,i,s}) \tag{7}$$

where $C_{l,i}$ is the concentration of metal i in the bulk (μM), $C_{l,i,s}$ is the concentration of metal i at the biomass surface (μM), and $k_{l,i}$ is the mass transfer coefficient (L/g/h). It was further considered that the metal concentration at the surface of the biosorbent is in linearly equilibrium with the solid-state metal concentration q_i (μmol i adsorbed/g adsorbent):

$$C_{l,i,s} = K_{l,i} q_i \tag{8}$$

where $K_{l,i}$ is the linear equilibrium constant (g/L).

For batch adsorption, the mass balance of metal i is

$$Ci_i = C_{l,i} + Wq_i \tag{9}$$

where Ci_i is the initial concentration of metal i (μM). Combining Eqs. (7)–(9) gives

$$-\frac{dC_{l,i}}{dt} = k_{l,i}\, W\left[C_{l,i} - \frac{K_{l,i}(Ci_i - C_{l,i})}{W}\right] \tag{10}$$

With the initial condition $C_{l,i}(0) = Ci_i$, Eq. (10) can be solved analytically, and the solution is

$$C_{l,i} = Ci_i\left\{1 - \frac{W\{1 - \exp[-k_{l,i}t(W + K_{l,i})]\}}{W + K_{l,i}}\right\} \tag{11}$$

As indicated in Fig. 7, Eq. (11) is able to describe the batch adsorption profile successfully, and the optimal values of parameters $k_{l,i}$ determined from model simulation are 5.19 L/g/h for Pb, 3.39 L/g/h for Cu, and 1.39 L/g/h for Cd. Thus, the $k_{l,i}$ values appear to increase as the adsorbate becomes more preferable to the biomass. On the other hand, the optimal estimation of $K_{l,i}$ values are 0.13, 0.75, and 1.26 g/L for Pb, Cu, and Cd, respectively.

By combining Eqs. (7) and (8), one obtains a new expression for q_i which represents the amount of metal i adsorbed per unit weight of biosorbent during the continuous biosorption operation:

$$q_i = \frac{C_{l,i}}{K_{l,i}} + \frac{1}{K_{l,i}k_{l,i}W}\frac{dC_{l,i}}{dt} \tag{12}$$

Substitution of Eq. (12) into Eq. (2) gives a final expression of Model B for continuous biosorption in ternary systems:

$$\frac{d^2 C_{l,i}}{dt^2} + k_{l,i}\,(K_{l,i} + W\theta)\frac{dC_{l,i}}{dt} = \frac{K_{l,i}k_{l,i}v}{V}\,(Cin_i - C_{l,i}) \tag{13}$$

In contrast to Model A, which required an intensively nonlinear differential equation to describe multimetal biosorption, Model B needed only a linear second-order differential equation (eq. 13), which is much easier to handle numerically. Equation (13) was thus used to fit the experimental data for multimetal biosorption with the following initial conditions:

$$C_{l,\mathrm{Pb}}(0) = 0.579\ \mu\mathrm{M}; \qquad C_{l,\mathrm{Cu}}(0) = 22.5\ \mu\mathrm{M}; \qquad C_{l,\mathrm{Cd}}(0) = 0.890\ \mu\mathrm{M}$$

$$\left.\frac{dC_{l,\mathrm{Pb}}}{dt}\right|_{t=0} = \left.\frac{dC_{l,\mathrm{Cu}}}{dt}\right|_{t=0} = \left.\frac{dC_{l,\mathrm{Cd}}}{dt}\right|_{t=0} = 0$$

The above initial conditions for $C_{l,i}$ are the measured bulk concentrations of each metal at the end of batch pretreatment, i.e., the onset of continuous biosorption.

The results of the fitting of Model B to the data from ternary biosorption are presented as dashed lines in Fig. 4(a–c). The optimal values for parameter $k_{l,i}$ estimated from Model B are 0.01, 0.10, and 0.96 L/g/h for adsorbates Pb, Cu, and Cd, respectively. The estimated $K_{l,i}$ values are 0.45, 0.95, and 3.92 g/L for Pb, Cu, and Cd, respectively. The $k_{l,i}$ and $K_{l,i}$ values determined from continuous biosorption are smaller than those obtained from batch experiments. In addition, the order of $K_{l,i}$ values was always Cd > Cu > Pb, for batch and continuous biosorption, whereas the trend of $k_{l,i}$ values with respect to the three metal adsorbates was inverted for the two operation modes. As indicated in Fig. 4, Model B predicts essentially correct trends of the selective biosorption data whereas it exhibits considerable deviations for the interpretation of Pb profiles. Therefore, the model needs to be improved to give better representation for Pb profiles resulting from continuous biosorption in the ternary system. One possible attempt is to modify the linear correlation between $C_{l,i,s}$ and $K_{l,i}q_i$ in Eq. (8).

CONCLUSIONS

A hollow-fiber microfiltration (HFMF) system was shown to be an effective tool for the development of a continuous biosorption process that enabled in-situ separation of biosorbent from the treated solution and also the regeneration of biomass for repetitive operations. Continuous biosorption of Pb, Cu, and Cd individually with the HFMF process resulted in slightly lowers biomass capacities than those obtained from batch experiments due to the loss of bulk biomass concentration during operation. Biosorption with a ternary mixture of the three metals demonstrated an adsorption preference of biomass of Pb > Cu > Cd. In the three-metal system, the metal adsorption capacity was lower than that obtained from a single-metal system except for Pb. With the same amount of biomass, the adsorption efficiency of Cu and Cd was significantly improved with a three-membrane sequential HFMF process as compared with the single membrane results. However, addition of membrane stages did not appreciably vary the final quantity of Pb adsorption. The models developed in this study were able to predict single- and multimetal biosorption reasonably well, whereas there is still room for improvement in the mathematical models to allow better fitting to the results for ternary biosorption.

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