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Chemical Engineering Journal 121 (2006) 37–43

Chemical Engineering Journal

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Performance, kinetics and equilibrium in biosorption of anionic dye Reactive Black 5 by the waste biomass of *Corynebacterium glutamicum* as a low-cost biosorbent

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Received 19 December 2005; received in revised form 10 March 2006; accepted 21 April 2006

Abstract

The protonated biomass of *Corynebacterium glutamicum* was used for the removal of Reactive Black 5 (RB 5). In batch experiments, the parameters studied included the effect of the dye concentration, pH, contact time, salt concentration and temperature. In the range of pH 1–3, the removal of RB 5 was kept at near 100%. The maximum uptakes estimated by using the Langmuir model were 169.5 and 185.2 mg/g at 20 and 40 °C, respectively. Kinetic studies showed a pseudo second-order rate of biosorption with respect to the solution. The uptake of RB 5 was not significantly affected by the high concentration of salts. Various thermodynamic parameters such as ΔG°, ΔH°, and ΔS° were evaluated with results indicating that this system was a spontaneous and endothermic process. In addition, the biomass could be repeatedly reused up to five times of sorption/desorption cycle, confirming that the biomass wastes can be a potential regenerable biosorbent for RB 5 removal.

Keywords: Biosorption; Reactive Black 5; *Corynebacterium glutamicum*; Isotherm; Desorption; Thermodynamics

1. Introduction

Textile industries consume large volumes of water and chemicals for the wet processing of textiles. The presence of very low concentrations of dyes in effluent discharged from these industries is highly visible and undesirable [1]. Brightly colored, water-soluble reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment systems unaffected [2]. Due to their chemical structure, dyes are resistant to fading when exposed to light, water and many chemicals [3,4]. Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade.

Various physical, chemical, and biological methods have been used for the treatment of dye-containing wastewater. Some chemical oxidation by Fenton reagent, ozone, UV plus H_2O_2 or NaOCl results in aromatic ring cleavage and may generate chemical sludge or by-products that are likely to be more toxic [5]. Aerobic biological treatment is known to be ineffective for dye removal but anaerobic bioremediation enables water-soluble dyes to be decolorized [6]. Physical adsorption technology, i.e., by activated carbons, has gained favor recently because it has a high efficiency in the removal of highly stable dyes, and is economically feasible when compared to other methods [7]. However, activated carbons are expensive and not easily regenerated [5]. Although ion exchange resins can be regenerated easily, the high cost hinders their wide application for the treatment of dye-bearing wastewater. Consequently, low-cost sorbents able to bind dye molecules and to be easily regenerated have been extensively researched and tested [5,8].

Many studies have been undertaken to find low-cost sorbents, which include peat, bentonite, steel-plant slag, fly ash, China clay, maize cob, wood shavings, and silica [9–13]. However, these low-cost sorbents generally have low uptake, which means that large amounts of sorbents are needed. Although good sorption capacities for reactive dyes (60–420 mg/g) are found for quaternized organic materials such as cellulose, sugarcane bagasse, rice husk, and coconut husk, successful regeneration

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doi:10.1016/j.cej.2006.04.005

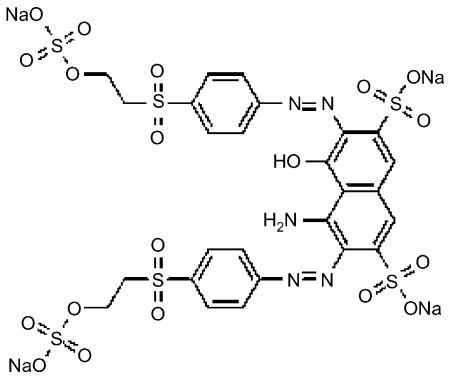

Fig. 1. Chemical structure of Reactive Black 5.

has not been reported [14]. Therefore, new, economical, easily available and highly effective sorbents still need to be found.

In this study, the waste biomass of *Corynebacterium glutamicum* was used and evaluated as a possible biosorbent for the treatment of an anionic dye, Reactive Black 5 (RB 5). This biomass is generated in great quantity from the full-scale fermentation process for amino acid production. Amino acid fermentation industries have been plagued with a huge amount of biological solid waste, mostly consisting of *C. glutamicum* biomass. Although this fermentation byproduct is potentially recyclable, until now most of it has been dumped at sea. Therefore, the feasibility of reusing this solid waste as a value-added biosorbent deserves to be assessed.

2. Materials and methods

2.1. Materials

The fermentation wastes (*C. glutamicum* biomass) were obtained in a dried powder form from a lysine fermentation industry (BASF-Korea, Kunsan, Korea). The protonated biomass was prepared by treating the raw biomass with a 1N HNO_3 solution for 24 h, thereby replacing the natural mix of ionic species with protons. The acid-treated biomass, designated as protonated biomass, was washed with deionized distilled water several times and thereafter dried at 60 °C in an oven for 24 h. The resulting dried *C. glutamicum* biomass was stored in a desiccator and used as a biosorbent in the sorption experiments.

All chemicals used in this study were of analytical grade. RB 5 was purchased from Sigma-Aldrich Korea Ltd. (CI 20505, Yongin, Korea). As shown in Fig. 1, RB 5 has two sulfonate groups and two sulfatoethylsulfon groups that have negative charges in an aqueous solution. The general characteristics of RB 5 are summarized in Table 1.

Table 1
General characteristics of Reactive Black 5 (RB 5)

Chemical formula	Molar mass	Color index number	λ_{max}
$C_{26}H_{21}N_5Na_4O_{19}S_6$	991.82	20505	597 nm

2.2. pH edge experiments

The pH edge experiments were carried out to investigate the equilibrium relationship between the dye uptake and the final pH, which is helpful in understanding the pH dependence of biosorption [15]. The pH edge experiments were conducted with 500 mg/l of initial RB 5 concentration and 10 g/l of the biomass. The pH was intentionally altered by adding 1N NaOH or 1N HNO_3 to the bottles. The suspension was agitated at 160 rpm in a shaker at a room temperature of 25 ± 2 °C. The contact time of 24 h was enough for sorption system to equilibrate. After the system reached the equilibrium state, the final pH was measured and the samples were taken and centrifuged for liquid–solid separation. The supernatant portion was used for the analysis of the concentration of residual RB 5 after proper dilution.

2.3. Effect of the salt concentration

To evaluate the effect of the salt concentration in the biosorption of RB 5 by *C. glutamicum* biomass, experiments were conducted with the addition of sodium chloride to the solution which contained with 40 ml of 500 mg/l dye solution and 0.4 g of the biomass. The concentration of NaCl used ranged from 0 to 0.3 M. The solution pH was maintained at pH 2 using 1N NaOH or HNO_3 during the experiment.

2.4. Kinetic experiments

Kinetic experiments were carried out by agitating 80 ml of dye solution of 500 mg/l of initial RB 5 concentration with 0.4 g of the biomass in a vessel maintained at 25 ± 2 °C, pH 3 and a constant agitation speed of 160 rpm. After shaking the vessel for predetermined time intervals, the samples were taken and centrifuged for liquid–solid separation and measured.

2.5. Isotherm experiments

To evaluate the sorption capacity of the biomass and the temperature effect, the isotherm experiments of RB 5 were conducted with 0.4 g of the biomass in 40 ml of working solution volume at pH 2 at three different temperatures (20, 30, and 40 °C). The initial concentration was altered from 100 to 4000 mg/l, which resulted in different final dye concentrations after the sorption equilibrium was achieved. Following the addition of the biomass into the dye-containing solutions, the solution pH was controlled at a desired value using 1N HNO_3, because the pH tended to increase while the RB 5 was binding to the biomass. Other conditions were the same as those used in the pH edge experiments.

2.6. Desorption and repeated reuse experiments

To evaluate the desorption efficiency, the RB 5-loaded biomass was centrifuged at 3000 rpm and the supernatant was removed. Thereafter, the settled biomass was resuspended with 40 ml of deionized distilled water, and the pH of the suspension was adjusted to the desired pH. The suspension was shaken at

160 rpm for 24 h to allow the dye to be released from the biomass. Thereafter, the desorbed dye was analyzed and the desorption efficiency was calculated as follows:

$$\text{Desorption efficiency (\%)} = \frac{\text{Released RB 5 (mg)}}{\text{Initially sorbed RB 5 (mg)}} \times 100 \quad (1)$$

After desorption, the biomass was again reused for subsequent sorption experiments. The sorption/desorption cycle was performed up to five times to evaluate the possibility of repeated reuse of the biosorbent. The sorption efficiency of each cycle was calculated as a percentage of the uptake at the first sorption.

2.7. Measurements of dye uptake

The dissolved dye concentration of samples was analyzed using a spectrophotometer (UVmini-1240, Shimadzu, Kyoto, Japan) at 517 nm, where the maximum absorption peak exists. Before analysis of RB 5 concentration, the samples were centrifuged at 3000 rpm for solid–liquid separation using a centrifuge (VS-21SMTI, Vision science, Bucheon, Korea). In order to allow for the change of working volume (up to 5%) resulting from the additions of HNO_3 solution, the dye uptake (q) was calculated from the mass balance as follows:

$$q = \frac{V_o C_o - V_f C_f}{M} \quad (2)$$

where V_o and V_f are the initial and final (initial plus added acid solution) volumes (l), respectively, C_o and C_f are the initial and final concentrations of RB 5 (mg/l), respectively, and M stands for the weight of biomass used (g).

3. Results and discussion

3.1. pH edge

The pH of the dye solution plays an important role in the whole biosorption process and particularly on the biosorption capacity. The variation in the biosorption of RB 5 was studied in the range of pH 1–11, and the results are shown in Fig. 2. Biosorption of RB 5 by *C. glutamicum* biomass was extremely dependent on the pH of the dye solution. The uptake of RB 5 showed the maximum value at pH $\leq$ 3, where 500 mg/l of RB 5 was completely removed by using the biomass of *C. glutamicum*. However, the uptake decreased with increasing pH up to pH 7, above which the uptake slightly increased. Hence, the sorption process for RB 5 removal needs to be operated at pH $\leq$ 3 on the basis of the results of pH edge. In addition, good performance of desorption process will be expected at pH around 7 at this was the point of lowest uptake.

The higher uptakes that were obtained at acidic pH may be explained in terms of electrostatic interactions between the biomass and the RB5 molecules. Two sulfonate groups of RB 5 are easily dissociated and have negative charges in the aquatic environment. In a previous study, it was found that the surface of *C. glutamicum* biomass has three functional groups: carboxyl, phosphonate, and amine [8,16]. Therefore, the negative sites

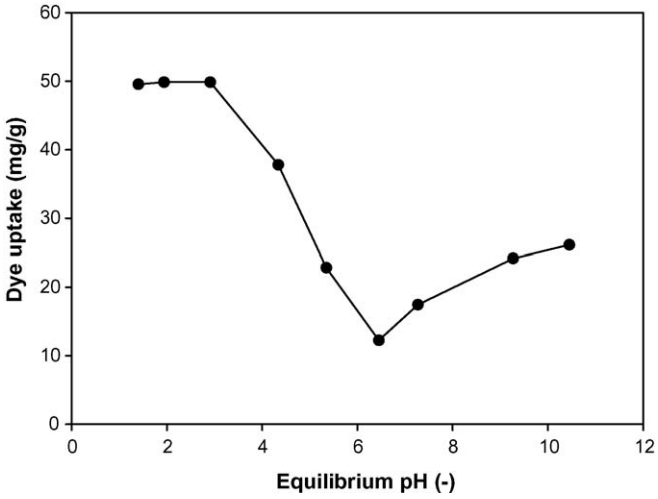

Fig. 2. pH edge on biosorption of RB 5.

of the biomass such as carboxyl and phosphonate groups do not favor the biosorption of dye anions due to the electrostatic repulsion, whereas the amine group ($-NH_2$) mainly found in protein molecules in the biomass can be protonated as a form of $-NH_3^+$ [17]. Such positively charged groups are likely to be the binding sites for negatively charged RB 5. Similar observations were also shown at dye biosorption by *Rhizopus arrhizus* biomass [18] and chemically cross-linked chitosan beads [19].

3.2. Effect of the salt concentration

In general, reactive dyes are applied to fabric in a high salt concentration in order to lower the dye solubility [20]. NaCl is mainly used as a salt to enhance the bath dye exhaustion. Therefore, unfixed dye in wastewater is accompanied by a high concentration of salts that are likely to interfere with dye biosorption. The effect of the salt concentration in the synthetic wastewater on the uptake of RB 5 was investigated (Fig. 3). At an initial RB 5 concentration of 500 mg/l, the effect of the salt concentra-

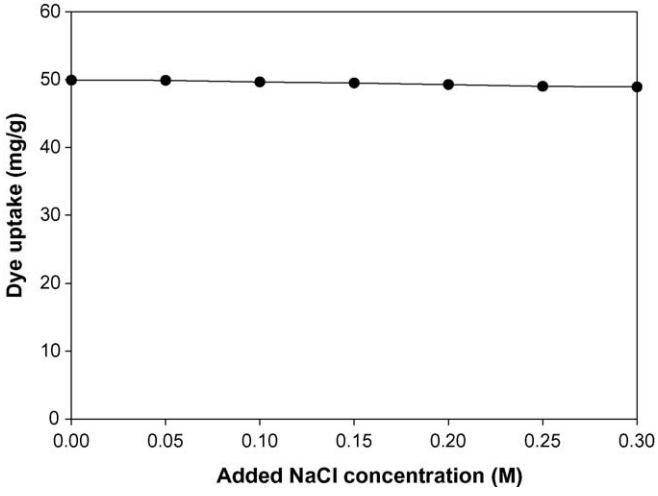

Fig. 3. Effect of the salt concentration on RB 5 uptake at initial dye concentration of 500 mg/l.

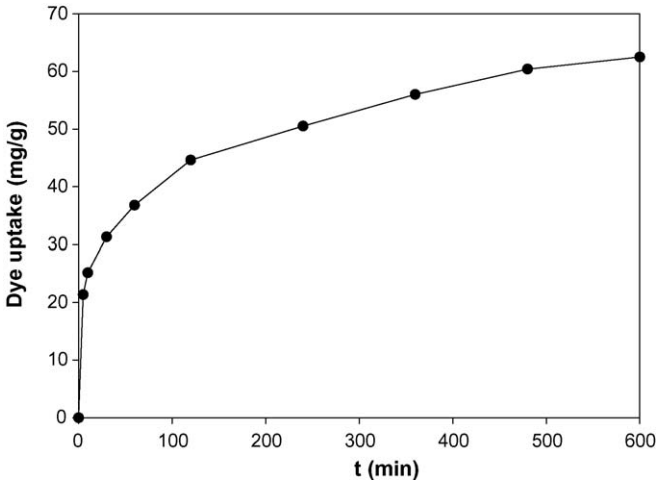

Fig. 4. Effect of the time contact on RB 5 biosorption rate by *C. glutamicum* biomass.

tion on the dye uptake was negligible, indicating that Cl^- ions do not compete with the sulfonate group of RB 5 molecules for amine sites of biomass. In addition, it can be noted that an elevated ionic strength with NaCl does not electrostatically interfere with the binding of RB 5 to the biomass significantly. From a practical point of view, this result implies that the waste biomass of *C. glutamicum* can be used for the removal of RB 5 from salt-containing wastewaters.

3.3. Biosorption kinetics

The kinetic study is important as it controls the overall process efficiency. Fig. 4 shows the biosorption kinetics of RB 5 on the biomass. The initial phase of biosorption was rapid such that almost 50% of RB 5 was adsorbed within 2 h.

Lagergren [21] suggested a rate equation for the sorption of solutes from a liquid solution. This pseudo first-order rate equation is:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \tag{3}$$

Integrating Eq. (3) for the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = 1$, gives:

$$\log(q_1 - q_t) = \log q_1 - \frac{k_1 t}{2.303} \tag{4}$$

where q_t and q_1 are the grams of solute sorbed per gram of sorbent at any time and at equilibrium (mg/g), respectively, and k_1 is the rate constant of first-order sorption (l/min). The pseudo

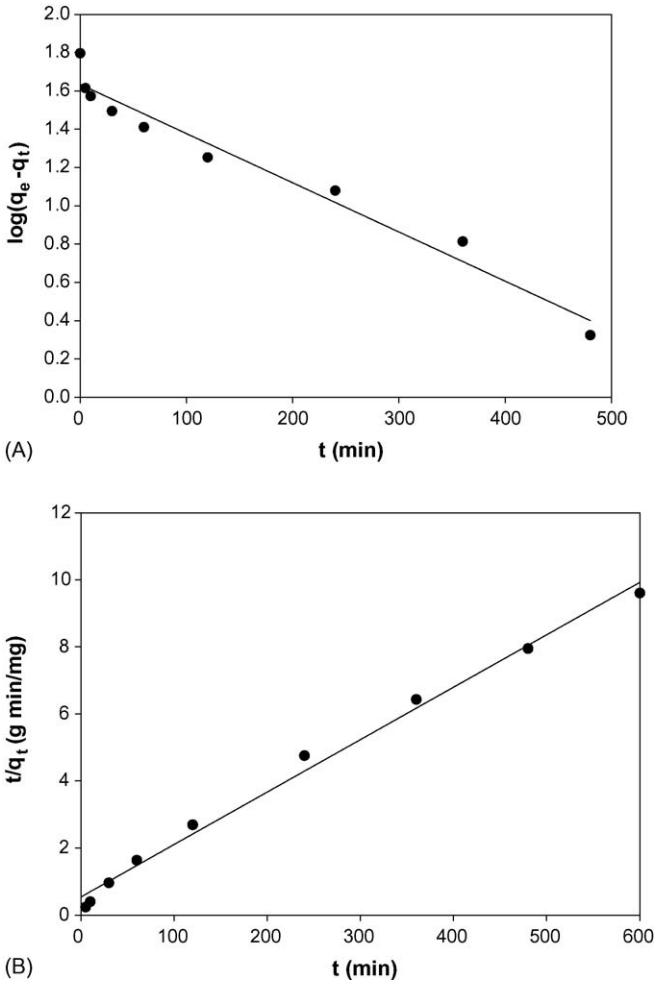

Fig. 5. Plots of sorption kinetic equations for RB 5 sorption by *C. glutamicum* biomass. (A) Pseudo first-order kinetic, (B) pseudo second-order kinetic.

first-order equation has been extensively used to describe the sorption kinetics.

The value of the sorption rate constant (k_1) for RB 5 biosorption by *C. glutamicum* biomass was determined from the plot of $\log(q_1 - q_t)$ against t (Fig. 5(A)). Although the correlation coefficient value was higher than 0.96, the experimental q_e value did not agree with the calculated one, obtained from the linear plot (Table 2). It is probable, therefore, that this biosorption system was not a first-order reaction.

Another model for the analysis of sorption kinetics is pseudo second-order. The rate law for this system is expressed as:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \tag{5}$$

Table 2
Kinetic parameters for RB 5 biosorption by *C. glutamicum* biomass

First-order kinetic				Second-order kinetic			
q_e (mg/g)	q_1 (mg/g)	k_1 (l/min)	r^2	q_2 (mg/g)	k_2 (g/(mg min))	h (mg/(g min))	r^2
62.5	43.1 (1.1)	5.99E-3	0.963	64.1 (2.1)	4.52E-4	1.86 (0.53)	0.992

Standard errors are present in the parentheses.

Integrating Eq. (5) for the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives:

$$\frac{1}{q_2 - q_t} = \frac{1}{q_2} + k_2 t \tag{6}$$

where q_2 is the grams of solute sorbed per gram of sorbent at equilibrium (mg/g), and k_2 the pseudo second-order rate constant of sorption (g/(mg min)). Eq. (6), can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \tag{7}$$

The initial sorption rate, h (mg/(g min)), at $t \to 0$ is defined as:

$$h = k_2 q_2^2 \tag{8}$$

The plot of t/q versus t gives a straight line with slope of $1/q_2$ and intercept of $1/k_2 q_2^2$ (Fig. 5(B)). There is no need to know any parameter beforehand and the grams of solute sorbed per gram of sorbent at equilibrium (q_2) and sorption rate constant (k_2) can be evaluated from the slope and intercept, respectively. The values of the parameters k_2, calculated q_2, experimental q_e and initial sorption rate h, together with the correlation coefficients, are presented in Table 2. The theoretical q_2 value also agreed very well with the experimental q_e value in the case of pseudo second-order kinetics. In addition, the correlation coefficient for the second-order kinetic model was greater than 0.992, indicating the applicability of this kinetic equation and the second-order nature of the sorption process of RB 5 on biomass. Similar phenomena have been observed in the biosorption of methylene blue on perlite [22] and Remazol Blue reactive dye on some yeasts [23].

3.4. Biosorption isotherms and thermodynamic parameters

The Langmuir isotherm assumes that sorption takes place at specific homogeneous sites within the adsorbent [24] and has been successfully applied to many sorption processes. The linear form of Langmuir isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{9}$$

where q_e is the adsorbed amount of the dye, C_e, the equilibrium concentration of the dye in solution, q_m, the monolayer biosorption capacity and b is the sorption constant related to the free energy of biosorption. The plots of C_e/q_e versus C_e for RB 5 biosorption on the biomass at different temperatures (20, 30, and 40 °C) were found to be linear over the whole concentration range studied (Fig. 6) and the linear correlation coefficient had a high value (>0.994), as shown in Table 3. The isotherm constants

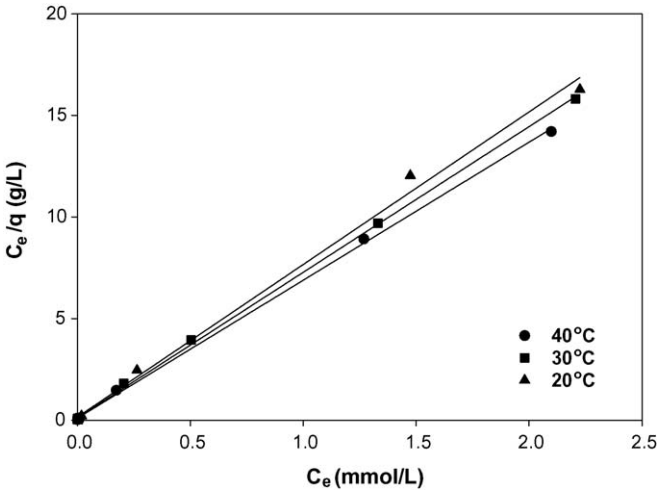

Fig. 6. Langmuir plots for RB 5 sorption by *C. glutamicum* biomass at different temperatures.

q_m and b of RB 5, listed in Table 3, increased with increasing temperature. The results revealed that the biosorption capacity increased from 0.13 (169.5) to 0.15 (185.2) mmol/g (mg/g) as the temperature increased from 293 to 313 K. Since the sorption increased when temperature rose, this system was endothermic.

The effect of isotherm shape can be used to predict whether a sorption system is 'favorable' or 'unfavorable' in batch processes. The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L [25]:

$$R_L = \frac{1}{1 + bC_0} \tag{10}$$

where R_L is a dimensionless separation factor, C_0, the initial concentration (mmol/l) and b is the Langmuir constant (l/mmol). The parameter R_L indicated the shape of the isotherm as follows:

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The calculated R_L values at different initial RB 5 concentration are shown in Fig. 7. The fact that the value of R_L was maintained within the range of 0–1 at all initial dye concentration confirmed the favorable uptake of the RB 5 process. In addition, the higher R_L values at lower dye concentrations showed that the biosorption was more favorable at lower dye concentrations. Nevertheless, referring to Fig. 7, it was obvious that *C. glutam-*

Table 3
Langmuir isotherm constants and thermodynamic parameters for RB 5 removal

Temperature (K)	q_m (mg/g)	q_m (mmol/g)	b (l/mmol)	r^2	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/(mol K))	r^2
293	169.5	0.133	49.3	0.994	−9.5			
303	175.4	0.139	66.3	0.999	−10.6	13.4	0.0787	0.963
313	185.2	0.147	70.9	0.999	−11.1			

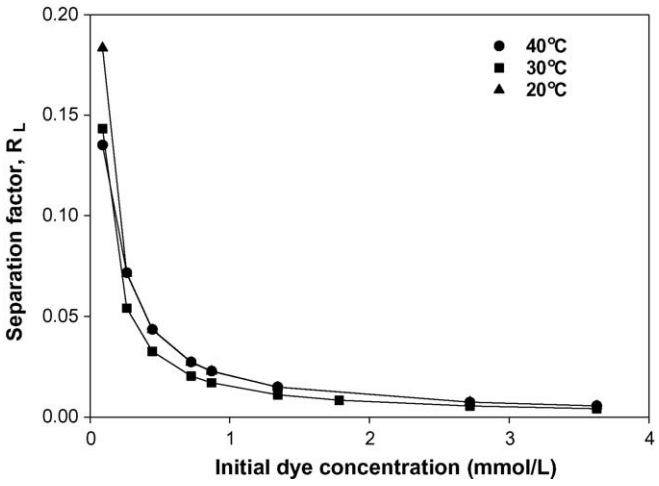

Fig. 7. Values of the separation factor, R_L, for RB 5 biosorption by *C. glutamicum* biomass at different temperatures.

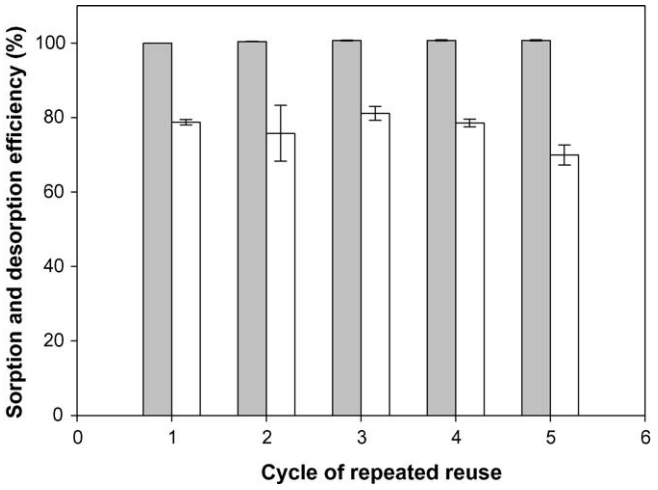

Fig. 8. Efficiencies of RB 5 sorption and desorption in repeated reuse experiments. The sorption was carried out at pH 2 and the desorption at pH > 7. Black and white bars represent the sorption and desorption efficiencies, respectively.

icum biomass is an effective biosorbent for removing reactive dye RB 5 from solution.

Based on fundamental thermodynamics concepts, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change, ΔG°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of the sorption reaction, considering the sorption equilibrium constant, b, is given by the following equation:

$$\Delta G^\circ = -RT \ln b \tag{11}$$

where ΔG° is the standard free energy change (kJ/mol), R, the universal gas constant, 8.314 J/K mol, and T is the solute temperature (K). The Gibbs free energy change, ΔG°, can be represented as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

A plot of ΔG° versus T was linear. Enthalpy change, ΔH° (kJ/mol), and entropy change, ΔS° (kJ/(mol K)), were determined from the slope and intercept of the plot, respectively (figure not shown). As shown in Table 3, the negative values of ΔG° confirmed the feasibility of the adsorption process at each temperature and the spontaneous nature of sorption with a high preference of RB 5 on the biomass. It was also observed that the value of ΔG° decreased with positive values of enthalpy change (ΔH°), suggesting the endothermic nature of the process, while the positive ΔS° values reflected the affinity of the biosorbent towards RB 5. In addition, the positive value of ΔS° also showed the increase of randomness at the solid-solution interface during the sorption of RB 5 on the biomass.

3.5. Repeated reuse

To be a good sorbent for dye removal, the dye-loaded sorbent should be regenerated; otherwise, the wastes have to be disposed of and fresh sorbents are required. In this study, after the protonated biomass of *C. glutamicum* was used for RB 5 sorption, RB 5 was eluted from the dye-loaded biomass by adjusting the solution at near pH 7, where the dye uptake was minimal (Fig. 2). Fig. 8 shows the results of repeated reuse experiments. The sorption/desorption cycle was continued up to five times and the sorption/desorption efficiencies were almost constant. However, the desorption efficiency was lower at almost 80%, compared to the 100% of the sorption efficiency. This result corresponded to that of the pH edge, which is shown in Fig. 2.

4. Conclusions

Considering that commercial sorbents such as activated carbons are hardly regenerated, this *C. glutamicum* waste biomass has a great potential as a reusable dye sorbent. Furthermore, it can be regenerated easily by adjusting the solution pH to a neutral condition. In other types of biomass, the desorption efficiency ranged from 30 to 80%, even though relatively expensive chemicals such as methanol, ethanol and organic surfactants such as Tween were used for regeneration [26].

In this study we achieved a desorption efficiency of almost 80%, and the sorption/desorption cycle was able to be maintained up to five times with almost constant sorption/desorption efficiencies. Therefore, the biomass waste of *C. glutamicum*, which is generated in great quantity from the full-scale fermentation process for amino acid production and is a potentially recyclable fermentation byproduct that is presently dumped at sea, shows great promise for the treatment of dye-containing wastewater as a new, low-cost, easily available and highly effective sorbent that is easily regenerated and can bind dye molecules with high uptake for repeated reuse.

Acknowledgements

This work was financially supported by KOSEF through AEBRC at POSTECH and partially by grant No. R08-

2003-000-10987-0 from the Basic Research Program of KOSEF.

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