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Immobilized citric acid-treated bacterial biosorbents for the removal of cationic pollutants

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ABSTRACT

Corynebacterium glutamicum, a full-scale fermentation process waste, showed good performance for the removal of a cationic dye, Basic Blue 3 (BB 3), after chemical modification using citric acid (CA) as an esterifying agent. This study investigated the potential use of immobilized biomass for dye biosorption in batch experiments. The powder form of CA-treated biomass (CAB) was immobilized in three polymer matrices: calcium alginate (CaA), polysulfone (PS) and polyurethane (PU). Three batch experiments were conducted: pH edge, isotherms and kinetics. As shown in the pH edge experiments, the BB 3 removal was favored at pH values greater than 7. The experimental equilibrium data were analyzed using two two-parameter (Langmuir and Freundlich models) and two three-parameter (Redlich–Peterson and Sips models) isotherm models. The experimental data were well described by the Redlich–Peterson isotherm model, followed by the Sips, Langmuir and Freundlich isotherm models. The kinetic data showed that immobilized CAB was slower than free CAB. Of the three diffusion models used to fit the kinetic data, pseudo-first order, pseudo-second order and intra-particle, the first fitted well for free CAB, and the second for immobilized CAB. Regeneration experiments of free and immobilized CAB were carried out for five sorption–desorption cycles, and immobilized CAB showed higher desorption efficiencies (>80%) than the powder form of free CAB, except for CaA-immobilized CAB which was dissolved in the second sorption cycle.

1. Introduction

Pollution caused by industrial wastewater has become a common problem in many countries. Especially, organic, inorganic and dye pollutions from industrial effluent disturb human health and ecological equilibrium [1]. Among various industries, the textile industry ranks first in the usage of dyes for fiber coloration. There are more than 100,000 commercially available dyes, most of which are difficult to decolorize due to their complex structure and synthetic origin [2]. Basic dyes are the brightest class of soluble dyes used in the textile industry [3]. Their tinctorial value is very high, with less than 1 mg/L of the dye producing an obvious coloration. Therefore, the color-bearing effluents require an economical treatment to remove the color/dye down to prescribed concentration levels prior to their discharge into water bodies. In terms of discharge volume and effluent combustion, wastewater from the textile industry is rated as the most polluting of all industrial sectors, which necessitates a suitable and cost effective dye/color-removal technology that works under the above circumstances [4].

Biosorption, the passive uptake of a pollutant from aqueous solutions by the use of non-living, microbial biomass, is a popular technique used for dye removal from wastewaters [5,6]. The main advantages of biosorption are lack of toxicity constraints, non-requirement of nutrient supply, high selectivity, cost effectiveness, high efficiency, and good performance [7]. Many microbial biomasses have been used as biosorbents for dye removal, including yeast, bacteria, and fungi that are generated in large quantities as waste byproducts from fermentation industries [8].

Some of the important biomasses used for the biosorption of basic dyes include *Citrus grandis* [9], baker yeast [10] and green alga [11]. The native biomass of *Corynebacterium glutamicum*, a gram-positive bacterium, has been studied as a potential biosorbent for dye removal in our previous reports [12–14]. Generally, the sorption capacity of native biosorbent is low, but surface chemical modification can greatly improve the sorption capacity of these biomaterials. As reported in previous literatures, citric acid can be employed as an esterifying agent to introduce net negatively charged carboxyl groups on the biomass surface, thereby, increasing its binding potential for cationic dye [15,16].

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Most batch sorption studies focused on the use of dead biomass/biological material in powder form. The use of non-living microbial biomass in its native form for large-scale process utilization is not practicable because of its small particle size, low mechanical strength, which may cause difficulty in the separation of biomass after biosorption, and significant mass loss after regeneration [17]. Therefore, for successful dye removal, the powder biomass needs to be immobilized to improve its mechanical strength and resistance to the various chemical constituents of aqueous waste.

Although the sorption performance of native biomass of *C. glutamicum* have been enhanced with surface modification using citric acid [15], they possess poor mechanical strength and little rigidity; which in turn limits its application under real conditions. In addition, the raw biomass of powder form cannot be used in a column system because of high pressure drop. Considering this, CA-treated *C. glutamicum* was immobilized using three different polymer matrices: calcium alginate (CaA), polysulfone (PS) and polyurethane (PU). The biosorption and regeneration potential of the free and immobilized biomasses were evaluated.

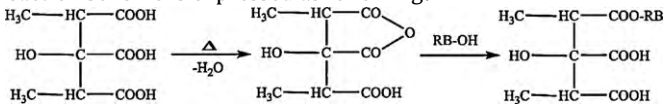
2. Materials and methods

2.1. Materials

Basic Blue 3 (BB 3), a model basic dye used as the adsorbate, with a purity of 25% and molecular weight of 359.89, was purchased from Sigma-Aldrich Korea Ltd. (Yongin, Korea). CA and other chemicals used in this study were of analytical grade and were also obtained from Sigma-Aldrich Korea Ltd. (Yongin, Korea).

2.2. Surface modification of biomass using citric acid

The biomass, *C. glutamicum*, which was obtained as a dried powder from a mono sodium glutamate fermentation industry (Deasang, Gunsan, Korea), was mixed with 0.8 M of CA solution at a ratio of 5.0 g biomass to 50 mL CA solution and stirred for 2 h at room temperature (25 ± 2 °C). The acid/biomass suspension was dehydrated at 60 °C for 24 h in a forced air oven, and then heated to 120 °C for 3.5 h. The CA-treated biomass (CAB) was removed, allowed to cool, and then washed several times with distilled water. The washed biomass was finally dried in the oven at 60 °C for 24 h, ground and sieved for uniform particle size (<0.25 mm) [15]. The reaction scheme is expressed as following:



2.3. Immobilization of citric acid-treated biomass

A 2% (w/v) alginate solution was prepared by dissolving 2 g of sodium alginate in 100 mL of distilled water with heating to accelerate dissolution. After cooling, 5 g of CAB was added and stirred. Then the alginate/biomass slurry was dropped into 0.1 M $CaCl_2$ solution with a syringe, with stirring to avoid aggregation of the beads. The resultant beads (CaA/CAB), of about 2–3 mm diameter, were cured in the $CaCl_2$ solution for 24 h at 4 °C, washed with distilled water twice, and then stored at 4 °C [18].

A 9% (w/v) PS slurry was prepared by dissolving 9 g of PS in 100 mL *N*,*N*-dimethyl formamide (DMF) solution by agitating for 2 h at 40 °C. Fourteen grams of powder CAB was mixed with the slurry for 2 h, and the resultant slurry was dripped in distilled water, where the beads were formed by a phase inversion process. The polymerized beads (PS/CAB) were cured for 24 h at 4 °C, rinsed with distilled water twice and then stored in a refrigerator at 4 °C [19].

PU/biomass, produced by kneading well with 6 g of CAB and 4 g of PU, was extruded into the distilled water and cured for 24 h. The immobilized biomass (PU/CAB) was then separated, washed twice with distilled water, dried in an oven at 60 °C for 24 h, ground and sieved for uniform particle size (0.6–1.0 mm in diameter).

2.4. Biosorption experiments

Biosorption experiments were carried out at room temperature (25 ± 2 °C) by contacting 0.1 g of dried biomass with 40 mL of BB 3 solution in 50 mL falcon tubes at the desired pH, and agitating in a shaker at 160 rpm and 25 ± 2 °C. The pH of the solution was controlled using 1 M HNO_3 and 1 M NaOH during the biosorption experiments. After equilibrium had been obtained, the dye-loaded biosorbent was separated from the dye solution by centrifugation at 9000 rpm for 5 min, and the remaining concentration in the supernatant was analyzed after appropriate dilution.

2.5. Desorption experiments

The BB 3-loaded biosorbent, which was exposed to 100 mg/L of dye solution at pH 7 and room temperature (25 ± 2 °C), was separated from the solution. The settled biomass was subsequently suspended with 40 mL of distilled water, and the pH values of the suspension were adjusted to the desired values (pH 3) using 1 M HNO_3 and 1 M NaOH, where the binding of BB 3 to each of biomass was the lowest. The remaining procedure was the same as that employed in the biosorption equilibrium experiments. These biosorption/elution cycles were repeated 5 times to evaluate the sorbent capacity.

2.6. Measurement of dye uptake

In this study, the dosages of the free and immobilized biomasses were all calculated based on 0.1 g dried biomass/40 mL dye solution to enable easier comparison of the biosorption capacities between the two biomasses. However, considering that the dried CaA could lock up the binding sites on the biomass surface, and also that the floatage of dried PS/CAB bead could be a problem for the batch biosorption experiments, CaA/CAB and PS/CAB were used in wet form. In order to better understand the amount of dried biomass per gram of wet beads, all calculations were based on the mass balance which was determined as 0.072 ± 0.001 g dried biomass/g wet CaA/CAB, 0.146 ± 0.004 g dried biomass/g wet PS/CAB and 0.600 ± 0.000 g biomass/g dried PU/CAB, respectively.

To account for the change in the working volume due to the additions of acidic or alkaline solution, the dye uptake (q) was calculated from the following mass balance:

$$q = \frac{V_0 C_0 - V_f C_f}{M} \quad (1)$$

where V_0 is the initial volume, V_f the final (initial plus added acid or alkaline solution) volume (L), C_0 and C_f the initial and final BB 3 concentrations (mg/L), respectively, and M is the mass of biosorbent used (g).

2.7. Analytical tools

The concentration of BB 3 in each samples was measured at 654 nm, the maximum absorption peak of BB 3, using a UV spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan).

The surface morphologies of the free and immobilized biomasses were examined with a scanning electron microscope (SEM, JEOL, JSM-5900, Japan). The beads were coated in an Auto Fine Coater fitted with Au target before the observation.

3. Results and discussion

3.1. Surface morphology of biosorbents

Fig. 1 shows SEM pictures of free and polymer matrix-immobilized CAB. The powder *C. glutamicum* (not shown) had been thermochemically modified with CA, which modified the surface morphology of *C. glutamicum* from rotundity to anomalous stereo. Comparing the magnified photo-micrograph of free CAB to polymer matrix-immobilized CAB, PS/CAB showed a very similar rough morphological surface to that of free CAB. The SEM image of CaA/CAB is not clear, but seems to show a rough appearance in some areas, indicating that free CAB was mostly entrapped with CaA, thereby blocking the biomass surface. As shown in Fig. 1(d′) the entrapment of free CAB within PU was well with loose form, which was considered helpful for mass transfer of dye molecules to the biosorbent.

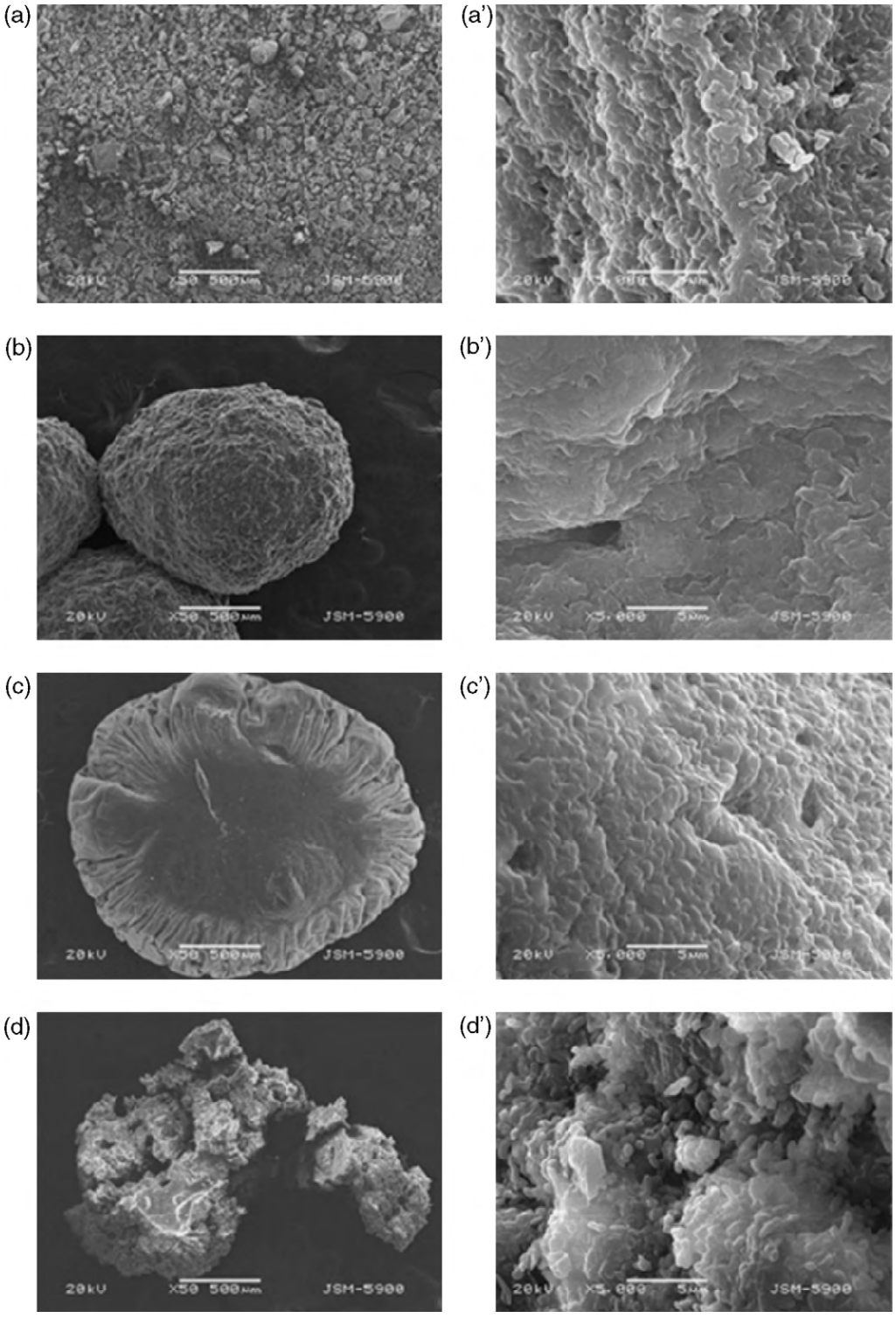


Fig. 1. Scanning electron micrographs of free CAB and polymer matrix-immobilized CAB biosorbents: (a) CAB (50×), (a′) CAB (5000×); (b) CaA/CAB bead (50×), (b′) CaA/CAB bead (5000×); (c) PS/CAB bead (50×), (c′) PS/CAB bead (5000×); (d) PU/CAB bead (50×), (d′) PU/CAB (5000×).

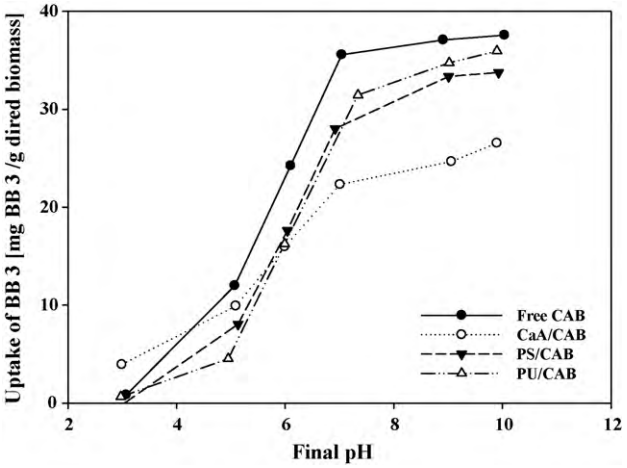


Fig. 2. Effect of pH on uptake of BB 3 by free and polymer matrix-immobilized CAB biosorbents (initial BB 3 concentration: 109.2 mg/L; biomass dosage: 2.5 g dried biomass/L BB 3; time: 24 h).

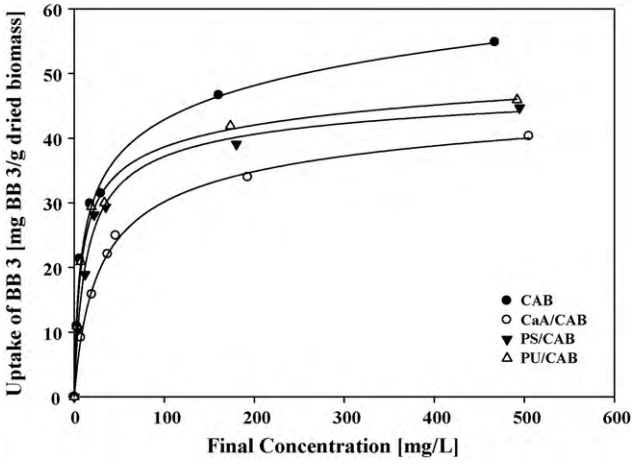


Fig. 3. BB 3 biosorption isotherms for free and polymer matrix-immobilized CAB biosorbents. The lines were predicted according to the Redlich–Peterson model (pH 7; biomass dosage: 2.5 g dried biomass/L BB 3; time: 24 h).

Both the CaA/CAB and PS/CAB beads were dried at 60 °C for analysis. The dried CaA/CAB bead exhibited a slight alternation in its shapes, as observed in Fig. 1(b). However, although the shape of the dried PS/CAB bead was not significantly changed (Fig. 1(c)), the dried bead showed a tendency to float, which is an undesirable feature for batch and column experiments. Therefore, both CaA/CAB and PS/CAB beads were used in wet form.

3.2. Effect of pH

The effect of pH, over the range from 3 to 10, on the biosorption of BB 3 by free CAB, CaA/CAB, PS/CAB and PU/CAB is shown in Fig. 2. The uptake of BB 3 on free CAB increased with increasing pH, which showed a similar trend to that on the raw *C. glutamicum* (data not shown). In our previous study, CA, containing three carboxyl groups per molecule, was successfully introduced onto the biomass surface via thermochemical reaction, thereby doubling the sorption capacity compared to that on the raw biomass [15]. The Fourier transform infrared (FT-IR) results revealed that the cell wall of *C. glutamicum* was comprised of carboxyl and amino groups. The carboxyl group, which is the mainly binding sites for adsorbing basic dye, has a pK_H value ranging from 3.5 to 5.0 [20]. At pH less than 3.5, the non-ionic form of the carboxyl group (–COOH) is present, which reduced the BB 3 removal to a negligible level. At pH greater than 3.5, the carboxyl group (–COOH) changed to carboxylate anions ($–COO^-$). These negatively charged groups on the biomass induced electrostatic binding with the cationic dye molecules, which increased the BB 3 removal as pH was increased from 3 to 7. As seen in Fig. 2, the alkaline condition (pH ≥7) was favorable for binding basic dye, with a stable uptake of BB 3 (>35.5 mg BB 3/g dried biomass).

Simultaneously, immobilized CAB showed the same trends as free CAB. The highest BB 3 uptakes of 26.5, 33.7, and 35.9 mg BB 3/g dried biomass for CaA/CAB, PS/CAB and PU/CAB, respectively, were observed at pH 10. The BB 3 removal onto CaA/CAB was less than that onto the other two (PS and PU) immobilized CAB samples, especially in alkaline conditions. This was caused by free CAB becoming over entrapped with CaA, which blocked some binding sites for cationic dyes.

3.3. Isotherm studies

The biosorption isotherm is the basic requirement in the design of any sorption system, as it expresses the relation between the mass of dye adsorbed per unit mass of adsorbent and the liquid phase dye concentration. The adsorption isotherms of BB 3 onto free and immobilized CAB were evaluated by varying the initial BB 3 concentration within the range of 0–607.9 mg/L, with a constant biomass dosage of 2.5 g/L. The uptake of BB 3 increased with increasing equilibrium concentration to eventually reach to a constant saturated value (Fig. 3).

In order to investigate the biosorption isotherms, the following two types each of two- and three-parameter models were used in this study:

Langmuir model [21]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

Freundlich model [22]:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Redlich–Peterson model [23]:

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta_{RP}}} \quad (4)$$

Sips model [24]:

$$q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \quad (5)$$

where q_m is the maximum dye uptake (mg/g), K_L the Langmuir equilibrium constant (L/mg), which is related to the affinity between the sorbate and sorbent, K_F the Freundlich constant ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$), which corresponds to the binding capacity, n the Freundlich exponent, which characterizes the affinity between the sorbent and sorbate, K_{RP} the Redlich–Peterson model isotherm constant, a_{PR} and β_{RP} the Redlich–Peterson model constant and exponent, respectively, K_S the Sips model isotherm constant, and a_S and β_S the Sips model constant and exponent, respectively. The constants and correlation coefficients obtained from these four isotherm models are listed in Table 1.

The Langmuir adsorption isotherm has traditionally been used to quantify and contrast the performance of different biosorbents. The Langmuir constant "q_m" is often used to compare the biosorbent performance, while the other constant "K_L" characterizes the initial slope of the isotherm. Thus, for a good biosorbent, a high q_m and a steep initial isotherm slope (i.e., high K_L) are generally desirable [25]. The Langmuir constants shown in Table 1 indicated that PU/CAB and PS/CAB performed well, with BB 3 uptake and affinity constant values comparable to those of

Table 1
Isotherm parameters for BB 3 biosorption using free and polymer matrix-immobilized CAB as biosorbents.

Isotherm model	Parameter	Free CAB	CaA/CAB	PS/CAB	PU/CAB
Langmuir	q_m (mg/g)	52.38 ± 3.00	41.36 ± 1.07	44.22 ± 1.33	44.58 ± 1.86
	K_L (L/mg)	0.08 ± 0.02	0.03 ± 0.00	0.07 ± 0.01	0.10 ± 0.02
	R^2	0.969	0.995	0.991	0.982
Freundlich	K_F ($mg^{1-1/n}\ L^{1/n}\ g^{-1}$)	13.52 ± 1.83	7.54 ± 1.28	11.93 ± 2.10	13.89 ± 2.16
	n	4.27 ± 0.49	3.62 ± 0.43	4.52 ± 0.72	4.94 ± 0.77
	R^2	0.970	0.967	0.948	0.952
Redlich–Peterson	K_{RP} (L/g)	8.12 ± 2.49	1.75 ± 0.22	3.67 ± 0.75	6.60 ± 1.61
	a_{RP} $(L/mg)^{\beta_{RP}}$	0.33 ± 0.16	0.07 ± 0.02	0.12 ± 0.05	0.23 ± 0.10
	β_{RP}	0.87 ± 0.03	0.92 ± 0.03	0.94 ± 0.04	0.92 ± 0.03
	R^2	0.993	0.998	0.994	0.993
Sips	K_S ($L^{\beta_S}\ mg^{1-\beta_S}/g$)	9.22 ± 2.41	2.26 ± 0.56	3.96 ± 1.38	7.62 ± 2.23
	a_S $(L/mg)^{\beta_S}$	0.14 ± 0.03	0.05 ± 0.01	0.09 ± 0.03	0.16 ± 0.04
	β_S	0.59 ± 0.13	0.82 ± 0.08	0.88 ± 0.14	0.72 ± 0.14
	R^2	0.990	0.997	0.993	0.990

free CAB. The q_m values decreased in the following order: free CAB > PU/CAB > PS/CAB > CaA/CAB.

The Freundlich isotherm was originally empirical in nature, but was later interpreted as the sorption to heterogeneous surfaces or surfaces supporting sites with various affinities. As shown in Table 1, free CAB and PU/CAB presented high values of the Freundlich isotherm constant, K_F, which corresponds to the binding capacity, followed by PS/CAB, while CaA/CAB presented the lowest value. The experimental n values were greater than unity for all biosorbents, indicating favorable biosorption and repulsive forces between the sorbed molecules [26].

To improve the fitness of the biosorption isotherm data, two three-parameter isotherm models were employed. The Redlich–Peterson model, which incorporated features of both the Langmuir and Freundlich isotherms, described the BB 3 biosorption data with a very high correlation coefficient (Table 1). Two limiting behaviors were apparent: the Langmuir form for $\beta_{RP} = 1$ and Henry's law form for $\beta_{RP} = 0$ [27]. It is worth noting that the β_{RP} values were close to unity, revealing the superior data fit afforded by the Langmuir model. The Sips model, under low sorbate concentrations, effectively reduced to the Freundlich isotherm and, therefore, did not obey Henry's law. For high sorbate concentrations, the Sips model predicted a monolayer sorption capacity, which was characteristic of the Langmuir isotherm [28]. The exponent β_S values found in Table 1 were all over 0.5, implying the BB 3 biosorption data obtained in this study were better represented by the Langmuir form than by the Freundlich form, as confirmed in Table 1. To summarize, on the basis of the correlation coefficient values and the predicted isotherm curves, the Redlich–Peterson model better described the BB 3 biosorption in all cases.

3.4. Kinetic studies

Biosorption kinetic study is important in the treatment of aqueous effluents as it provides valuable information on the reaction pathway and in the mechanism of adsorption reactions [29]. As shown in Fig. 4, the sorption equilibrium of free CAB was quickly reached within 10 min, but was considerably delayed for immobilized CAB to approximately 300 min for CaA/CAB, 600 min for PS/CAB and 780 min for PU/CAB. This relatively slow attainment of equilibrium by immobilized CAB was due to the entrapment of biomass by polymer matrices, which hampered the free attraction of BB 3 on the biomass, whereas the binding sites on free CAB were freely exposed to BB 3.

Table 2 summarizes the pseudo-first and pseudo-second order kinetic and intra-particle diffusion models, which were used to describe the biosorption of BB 3 on free and polymer matrix-immobilized CAB. The kinetic parameters of the fitted models are presented in Table 3. For free CAB, the pseudo-first order model described the kinetics better than the other two kinetic models, whereas the pseudo-second order model described the kinetics of immobilized CAB better than the pseudo-first order model. In addition, the theoretical values of q_e calculated from the pseudo-second order model were similar to the experimental uptake values (q_{ex}). The parameters obtained from the intra-particle diffusion model are also shown in Table 3. The correlation coefficients obtained by applying the intra-particle diffusion model to the kinetic experimental data were lower than those of the pseudo-first and pseudo-second order models. This suggested that the intra-particle diffusion did not control the rate.

3.5. Desorption studies

Repeated usability is an important factor for a good biosorbent. Such a biosorbent should not only possess higher adsorption capacity, but also show better desorption efficiency, which will significantly reduce the overall biosorbent cost. Five consecutive cycles of sorption/desorption experiments for free CAB and immobilized CAB were conducted (Fig. 5). The sorption/desorption experiments cycles were performed up to 5 times, except for CaA/CAB. Since the CaA/CAB beads were broken after one sorption/desorption cycle because of their insufficient mechanical stability, the experiments were not continued beyond the first cycle. Showing a similar trend to that of free CAB, the sorp-

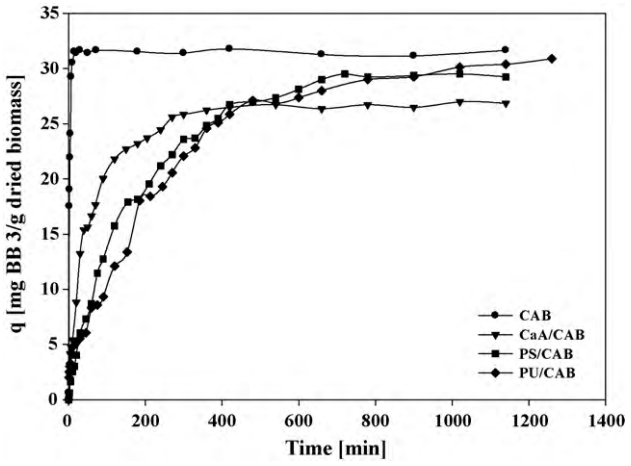


Fig. 4. Biosorption kinetics of BB 3 removal for free and polymer matrix CAB biosorbents (initial BB 3 concentration: 108.6 mg/L; biomass dosage: 2.5 g dried biomass/L BB 3; time: 24 h; pH 7).

Table 2
Three kinetic models.

Kinetic model	Different equation	Integrate. equation	Non-linear equation	Ref.
Pseudo-first order	$\frac{dq}{dt} = k_f(q_e - q_t)$	$\ln(q_e - q_t) = \ln(q_e) - k_f t$	$q_t = q_e[1 - \exp(-k_f t)]$	[30]
Pseudo-second order	$\frac{dq}{dt} = k_s(q_e - q_t)^2$	$q_t = \frac{k_s q_e^2 t}{1+q_e k_s t}$	$q_t = \frac{k_s q_e^2 t}{1+q_e k_s t}$ $h_0 = k_s q_e^2$	[29]
Intra-particle diffusion			$q_t = k_{id} t^{1/2} + C$	[31]

Table 3
Kinetic parameters for BB 3 biosorption using free and immobilized CAB as biosorbents.

Kinetic model	Parameter	Free CAB	CaA/CAB	PS/CAB	PU/CAB
Pseudo-first order	k_1 (min^{-1})	0.317 ± 0.019	0.019 ± 0.001	0.006 ± 0.000	0.005 ± 0.000
	q_e (mg/g)	31.57 ± 0.37	25.80 ± 0.36	29.09 ± 0.27	30.08 ± 0.60
	R^2	0.985	0.981	0.996	0.984
Pseudo-second order	k_2 (g/mg min)	0.017 ± 0.003	0.001 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
	q_e (mg/g)	32.75 ± 0.72	28.24 ± 0.25	34.90 ± 0.38	36.75 ± 1.04
	h_0 (mg/g min)	17.70 ± 0.00	0.80 ± 0.000	0.24 ± 0.000	0.14 ± 0.000
	R^2	0.957	0.995	0.997	0.984
Intra-particle diffusion	k_{id} (mg/g $min^{0.5}$)	0.463 ± 0.200	0.763 ± 0.092	1.046 ± 0.055	0.986 ± 0.044
	C (mg/g)	21.28 ± 2.84	8.22 ± 1.56	1.76 ± 0.97	1.89 ± 0.79
	R^2	0.239	0.732	0.924	0.923

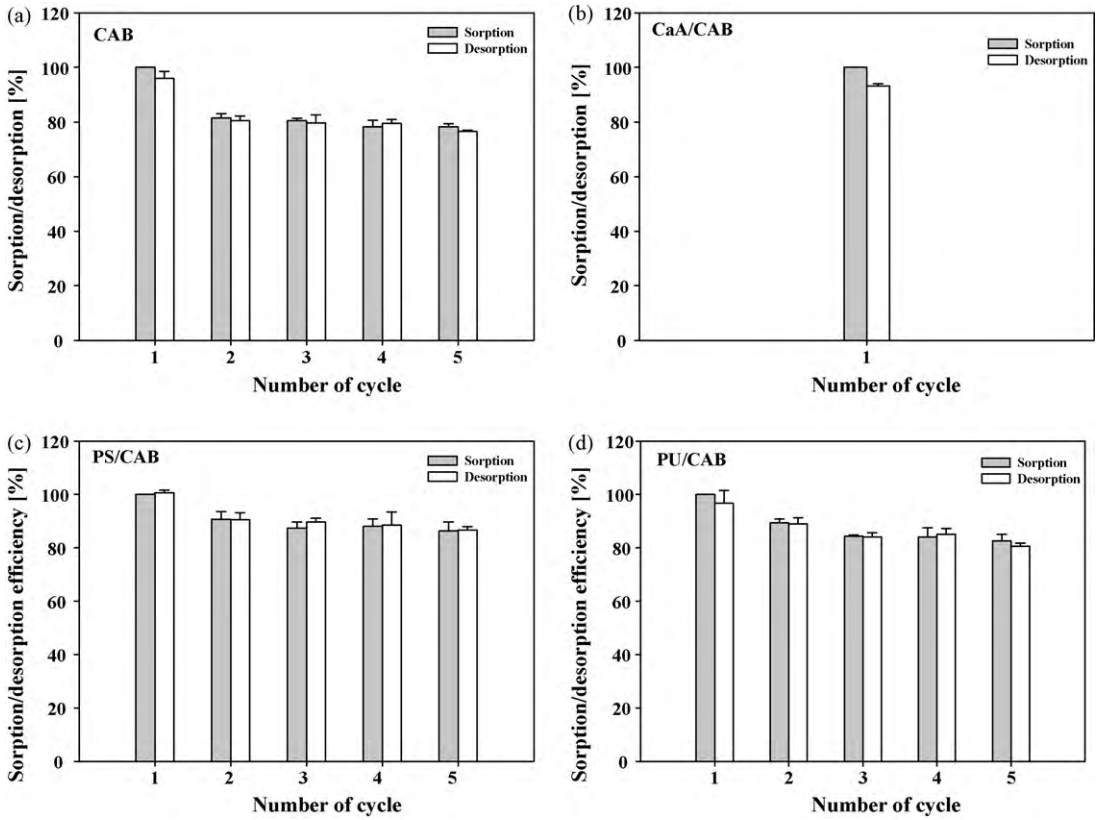


Fig. 5. Sorption/desorption cycles for free CAB (a), CaA/CAB (b), PS/CAB (c) and PU/CAB (d) (sorption: initial BB 3concentration = 108.9 mg/L, biomass dosage = 2.5 g dried biomass/L BB 3, time = 24 h, pH 7; desorption: biomass dosage = 2.5 dried biomass/L D.I. water, time = 24 h; pH 3).

tion/desorption efficiencies of PS/CAB and PU/CAB decreased a little from the first to the fifth cycle. At the end of the fifth cycle, the sorption efficiencies of PS/CAB and PU/CAB were decreased to 86.7% and 80.6%, respectively, but nevertheless remained higher than that of free CAB (76.5%). Centrifugation and filtration are important during the separation of the biomass from the final effluent solution, but for the powdered CAB, biomass separation was a little difficult. The PS/CAB and PU/CAB immobilized biomasses exhibited relative ease of separation along with high sorption/desorption efficiencies.

4. Conclusions

The fermentation waste, *C. glutamicum*, was thermochemically modified using CA to enhance the binding sites for BB 3 biosorption. To increase the reusability, CA-modified *C. glutamicum* was immobilized in three polymer matrices: CaA, PS and PU. An alkaline condition (pH ≥7) favored the BB 3 removal. All forms of CAB (free or immobilized) exhibited good BB 3 biosorption performance at pH 7, with the isotherm obtained under this condition being

described by using the Langmuir, Freundlich, Redlich–Peterson and Sips models. The Redlich–Peterson isotherm model described the experimental data best, followed in order by the Sips, Langmuir and Freundlich isotherm models. Kinetic experiments showed that attainment of equilibrium was slower for immobilized CAB than for free CAB, because of the entrapment of biomass in the polymer matrices which cloaked some binding sites for BB 3. Of the three models used to fit the kinetic data, pseudo-first order, pseudo-second order and intra-particle diffusion, the second fitted well for all forms of immobilized CAB. Desorption and subsequent reuse were successful with PS/CAB and PU/CAB, which gave good performance with BB 3 removal efficiencies of greater than 80% in all five subsequent cycles examined.

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