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Chemical modification of *Corynebacterium glutamicum* to improve methylene blue biosorption

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ABSTRACT

This research examines the possibility of enhancing the biosorption potential of a fermentation industry waste (*Corynebacterium glutamicum*) towards methylene blue (MB). The biosorption capacity was enhanced via succination, which chemically modified the amine groups to carboxyl. Experiments at different pH conditions demonstrated that both raw and succinated *C. glutamicum* performed well in MB biosorption at neutral or basic conditions. Biosorption isotherm experiments revealed that the succinated biomass outperformed raw biomass in MB biosorption but underperformed compared to two commercial activated carbons (SPC-100 and SPS-200). The MB sorption capacities were 207.3, 337.5, 457.4 and 500.6 mg/g for raw biomass, succinated biomass, SPC-100 and SPS-200, respectively. Kinetic experiments revealed that almost complete biosorption equilibrium was attained within 5 min, followed by complete saturation in 30 min, for both forms of *C. glutamicum*. Desorption experiments were optimized at a solution pH of 2, to attain an approximate elution efficiency of 99.7% for MB-loaded *C. glutamicum*. Conversely, desorption was difficult with MB-loaded activated carbons, with elution efficiencies of only 5–6.1% being achieved. Regeneration experiments were only possible with succinated *C. glutamicum*, which performed well in five repeated cycles with high MB-removal efficiencies.

1. Introduction

A dye can generally be described as a colored substance that has an affinity to an applied substrate. Dyes are widely used in industries such as textiles, paper, plastics, leather, etc., for coloring of their products. The effluents emanating from these industries often contain high concentrations of dye wastes. Two percent of dyes that are produced are discharged directly in aqueous effluent, and 10% are subsequently lost during the textile coloration process [1]. To clarify the scope of the situation, over 100,000 dyes are commercially available with a combined annual production of over 7×10^5 t [2]. The various techniques that have been employed for the treatment of dye and heavy metal bearing industrial effluents can be categorized into two broad divisions: physico-chemical and biological methods. The former include precipitation, adsorption, ion-exchange, membrane and electrochemical technologies. Much has been discussed about their downside aspects in recent years [3,4], which can be summarized as they are costly, not environment friendly and usually depend on the concentration of the waste. Therefore, a search is on for efficient, eco-friendly and cost-effective remedies for wastewater treatment.

The biological removal of dyes, termed biosorption, has been suggested as a cheaper and more effective alternative to existing treatment techniques [5]. Biosorption utilizes the ability of dead/inactive biomass to remove dyes from solutions. Many bacteria and fungi have been found to bind a variety of dye classes [2]. However, most of these have been cultivated and explored for their biosorption potential. Producing biomass solely for transformation into biosorbents has been shown to be too expensive [6]. Furthermore, the continuous supply of biomass cannot be assured, which will severely limit any successful application in industrial biosorption applications. Hence, an ideal approach to the production of practical biosorbents is to employ industrial wastes. *Corynebacterium glutamicum*, an industrial waste biomass originating from the lysine fermentation industry, has shown good reactive dye biosorption capacity [7]. The current annual production of amino acids from fermentative processes using *C. glutamicum* is 1,500,000 t of L-glutamate and 550,000 t of L-lysine [8]. Hence the quantity of waste *C. glutamicum* generated after fermentation is usually high, which adds interest to the potential utilization of this waste.

Thus, this research focuses on employing *C. glutamicum* wastes for the removal of methylene blue (MB) from aqueous solution. Efforts were also made to enhance the carboxyl groups via

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succination. Two forms of commercially activated carbons, prepared from coal and sawdust, were compared with *C. glutamicum* on the basis of MB biosorption.

2. Materials and methods

2.1. Solute, sorbents and preparation

Methylene blue, $C_{16}H_{18}ClN_3S{\cdot}3H_2O$, was purchased from Sigma–Aldrich Korea Ltd. (Yongin, Korea); it was 82% pure, and had a molecular weight of 373.9.

The fermentation wastes (*C. glutamicum* biomass) were obtained in a dried powder form from a nucleic acid-related, fermentation industry (Deasang, Gunsan, Korea). The biomass was dried by spray drying for 24 h, referred to as raw biomass, and subsequently used in the biosorption experiments.

For succination, 10 g of the raw biomass were treated with 1000 ml of 0.1 M sodium carbonate, maintained at pH 8.0 at room temperature. An additional 16 g of succinic anhydride were added every 15 min for the next 2 h (eight additions of 16 g succinic anhydride to the biomass; total 128 g), thereby inducing amino succination of the available amino groups. The modified biomass was centrifuged, washed with distilled water, and suspended in 1.0 M hydroxylamine (pH 8.0). Finally, the succinated biomass was washed with distilled water and freeze-dried.

The commercial activated carbons, SPS-200 (sawdust-based) and SPC-100 (coal-based), were obtained in a dried powder form from Samchully Activated Carbon Co., Ltd. (Yeongi-gun, Korea). The various properties of the two activated carbons are summarized in Table 1.

2.2. FT-IR analysis

Infrared spectra of the biomass samples were obtained using a Fourier transform infrared spectrometer (FT-IR-8900, ABB Bomem, Quebec, Canada). The sample, prepared as KBr disc, was examined within the range 400–4000 cm^{-1} to identify the functional groups responsible for the biosorption.

2.3. Biosorption experimental procedure

The biosorption experiments were conducted by bringing 0.1 g of sorbent into contact with 40 ml dye solution, at the desired pH, in 50 ml plastic bottles (high-density polyethylene), which were maintained in a incubated rotary shaker at 160 rpm and 25 °C. The pH of the solution was initially adjusted using either 0.1 M HNO_3 or 0.1 M NaOH, which were subsequently used to control the pH during the experiments. After 12 h of contact with the dye solution, the biosorbent was separated by centrifugation at 3000 rpm for 5 min. The dye (MB) concentration in the supernatant was determined using a spectrophotometer (UV-2450, Shimadzu, Kyoto, Japan) at 660 nm, after appropriate dilution. Kinetic experiments were conducted using the same method as above, except that the samples were collected at different time intervals to determine the time point at which biosorption equilibrium was attained.

Table 1
General characteristics of the activated carbons

Properties		SPS-200	SPC-100
Raw material	–	Saw dust	Coal
Type	–	Powder	Powder
Mesh size (through 200 mesh)	(%)	90 (minimum)	90 (minimum)
Moisture	(%)	10	10
pH	–	6–10	6–10
Specific surface area	(m^2/g)	900	900
Total pore volume	(cc/g)	0.5–0.7	0.5–0.7
Average pore diameter	(Å)	16–30	15–18
Fe_2O_3	(%)	0.03	0.05
Chloride	(%)	0.05	0.05

The amount of MB sorbed by the sorbent was calculated from the differences between the concentrations of MB added to that in the supernatant using the following equation:

$$Q = \frac{V(C_0 - C_f)}{M} \quad (1)$$

where Q is the MB uptake (mg/g), C_0 and C_f the initial and equilibrium MB concentrations in the solution (mg/l), respectively, V the solution volume (l) and M the mass of biosorbent (g).

2.4. Desorption experimental procedure

The MB-loaded biomass, which was exposed to 50 mg MB/l at pH 9 and 25 °C, was separated from the biosorbent–water slurry by centrifugation. The biosorbent was then brought into contact with 40 ml of different desorbents for 3 h in a rotary shaker at 160 rpm. The remaining procedure was the same as that employed in the biosorption equilibrium experiments. After desorption, the biosorbent was washed several times with deionized water and the regenerated biosorbent was reused for the next cycle. These cycles of biosorption followed by elution were performed five times to evaluate the sorbent capacity.

Both isotherm and kinetic data modeling were performed by non-linear regression using the Sigma Plot (version 4.0, SPSS, USA) software. The average percentage error between the experimental and predicted values was calculated using:

$$\varepsilon(\%) = \frac{\sum_{i=1}^{N}(Q_{exp,i} - Q_{cal,i}/Q_{exp,i})}{N} \times 100 \quad (2)$$

where Q_{exp} and Q_{cal} represent the experimental and calculated dye uptake values, respectively, and N is the number of measurements.

3. Results and discussion

3.1. FT-IR analysis

For the detail investigation on the intensity and nature of functional groups on the biomass surface, FT-IR spectra of the raw and succinated biomass were analyzed. As shown in Fig. 1, the FT-IR spectra of raw and succinated biomasses showed characteristic absorption bands. The absorption peaks around 3500–3000

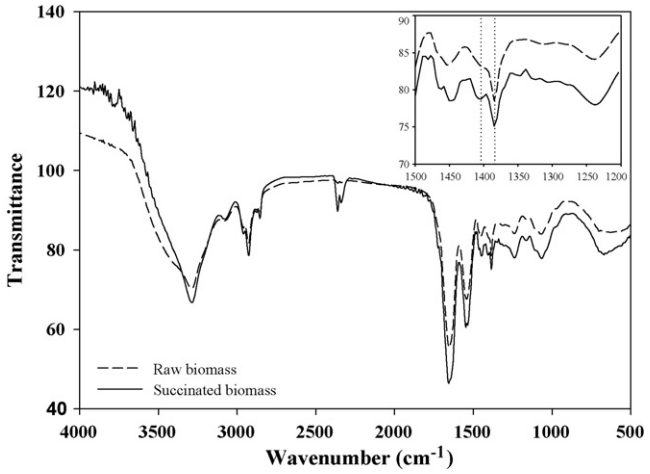
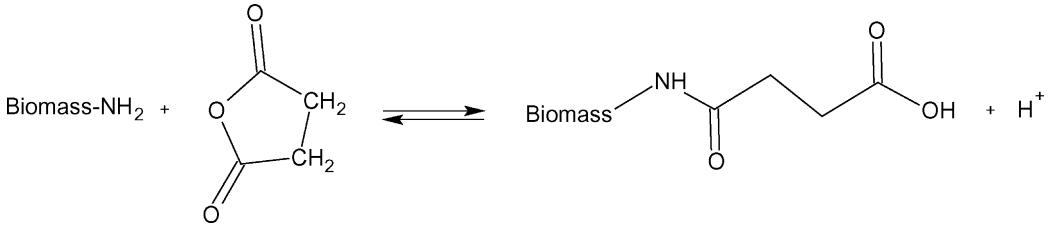


Fig. 1. FT-IR spectra of raw and succinated *C. glutamicum* biomass.

and 1538 cm^{-1} are indicative of the existence of amine groups [9]. The broad absorption band at 3500–3000 cm^{-1} became relatively narrow in the case of succinated biomass. It infers the transformation of amine to carboxyl group according to the chemical reaction mechanism used in this study. The spectrum also displays absorption peaks at 1652 and 1233 cm^{-1}, corresponding to carboxyl groups [10]. In particular, the peaks of 1384 and 1404 cm^{-1} are indicative of protonated carboxylic acid and carboxylate anion on the biomass surface, respectively. The marked change of the carboxylate anion band in succinated biomass was considered to be due to the increased carboxyl groups. The phosphonate groups showed some characteristic absorption peaks around 1157 cm^{-1} (P=O stretching) and 1078 cm^{-1} (P–OH stretching).



3.2. pH edge experiments

In the initial stages of the experiments, the influence of equilibrium pH on MB biosorption was examined (Fig. 2). The solution equilibrium pH severely affected the MB biosorption capacity of *C. glutamicum*, with maximum uptake being achieved at pH 6 and above. The cell wall of the Gram-positive bacterium is mainly comprised of a peptidoglycan layer connected by amino acid bridges [11]. Imbedded in the Gram-positive cell wall are polyalcohols called teichoic acids, which give an overall negative charge to the bacterial cell wall due to the presence of phosphodiester bonds between teichoic acid monomers [12]. In near neutral or alkaline pH conditions, the biomass will have net negative charge. On the other hand, basic dyes release colored, positively charged dye ions in solution, which are electrostatically attracted towards the negatively charged cell surface. In particular, the carboxyl groups present in *C. glutamicum* were mainly responsible for MB biosorption. The pK_a value of the carboxylic group usually lies in the range of 3.6–4.5 [13,14]. Therefore, the carboxyl group has a negative charge at a pH approximately higher than 5 and electrostatically binds MB to the bacterial biomass. At pH values below 5, the carboxyl groups exist in protonated form which gives the biomass an overall positive charge. Under this situation, the occupation of MB onto carboxyl groups will be difficult and hence low uptake was observed at acidic pH values (Fig. 2).

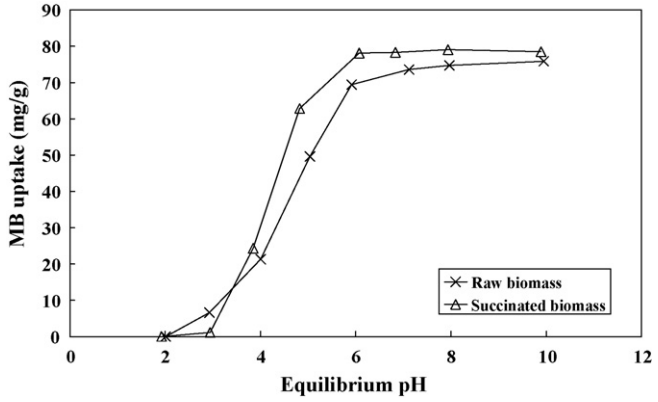


Fig. 2. Effect of pH on MB uptake by raw and succinated *C. glutamicum* biomass (C_0 = 200 mg/l; temperature = 25 ± 1 °C, agitation speed = 160 rpm).

Efforts were also made to chemically modify the amine groups via succination and the reaction step can be expressed as follows:

The modification of amine groups to carboxyl enhanced the biosorption capacity of *C. glutamicum*, which further confirmed the importance of carboxyl groups in the binding of MB (Fig. 2).

3.3. Biosorption isotherm and modeling

In this section, the MB adsorption capacity of raw and succinated *C. glutamicum* was compared with different activated carbons. Experimental MB sorption isotherms of different sorbents are presented in Fig. 3. Typical H-shaped sorption isotherms [15] were observed for all cases of sorbents. The ratio between the MB concentration remaining in solution and that sorbed on the solid decreased with increasing MB concentration, providing a concave curve with a strict plateau. In comparison, both activated carbons outperformed both raw and succinated *C. glutamicum* biomasses. The sorption capacity of activated carbon is usually dependent on its specific surface area, pore volume and porosity. In addition, increasing solution pH increases the number of hydroxyl groups, which thereby increases the number of negatively charge sites and strengthens the attraction between MB and the adsorbent surface. Thus, the surface functional groups were deprotonated with increasing pH, which decreased the surface charge density. This implies that the

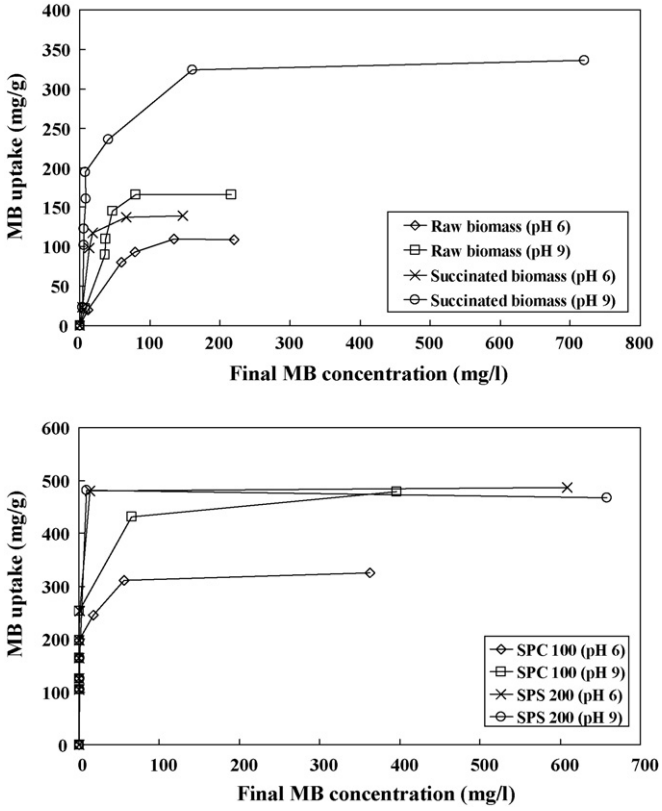


Fig. 3. MB biosorption isotherms for the four different sorbents (temperature = 25 ± 1 °C, agitation speed = 160 rpm).

adsorption of cationic dye could be enhanced at higher pH conditions. However, between the two activated carbons, the sorption performance of SPS-200 was least affected by pH.

Modeling of the MB isotherm data was attempted using the Langmuir, Freundlich and Toth models, which can be represented as follows:

$$\text{Langmuir model} : Q = \frac{Q_{max} b C_f}{1 + bC_f} \quad (3)$$

$$\text{Freundlich model} : Q = K_F C_f^{1/n} \quad (4)$$

$$\text{Toth model} : Q = \frac{Q_{max} b_T C_f}{[1 + (b_T C_f)^{1/n_T}]^{n_T}} \quad (5)$$

where Q_{max} is the maximum dye uptake (mg/g), b the Langmuir equilibrium constant (l/mg), K_F the Freundlich constant ((mg/g)(mg/l)$^{-1/n}$), n the Freundlich constant, b_T the Toth model constant and n_T the Toth model exponent. The main reason for the extended use of these isotherm models is that they incorporate easily interpretable constants. The constants and correlation coefficients obtained from the three isotherm models are listed in Table 2. The Langmuir adsorption isotherm has traditionally been used to quantify and contrast the performance of different sorbents. It served to estimate the maximum dye uptake values where they could not be reached in the experiments [16]. The constant b represents the affinity between the sorbent and sorbate. The Langmuir constant values confirmed the superior performance of both activated carbons, followed by that of the succinated biomass and raw *C. glutamicum*. The Q_{max} and b values decreased in the following order: SPS-200 > SPC-100 > succinated biomass > raw biomass. For favorable biosorption, high Q_{max} and a steep initial isotherm slope (i.e., high b) are desirable.

The Freundlich isotherm was originally empirical in nature, but was later interpreted as the sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. Table 2 clearly demonstrated the poor description of the isotherm data provided by the Freundlich model in all cases. High values of K_F and n were observed for both forms of activated carbon, suggesting that the binding capacity was maximized and the affinity between the carbon and dye molecules was also raised.

To improve the fitness of the biosorption isotherm data, a three-parameter isotherm model, i.e., the Toth model was also used. The Toth isotherm, derived from potential theory, has proven to be useful in describing the sorption in heterogeneous systems, such as phenolic compounds onto carbon. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, i.e., most sites have sorption energy less than the mean value [17]. As expected, the Toth model described the isotherm data well with high R^2 and low percentage error vales (Table 2). The successful application of the Toth model to the present data supports the heterogeneous nature of the biosorbent surfaces and the presence of different functional groups. On the basis of the correlation coefficient, percentage error values and predicted isotherm curves, the Toth model better described the MB adsorption in all the cases than the Langmuir and Freundlich models.

3.4. Biosorption kinetics and modeling

For any practical applications, the process design, operation control and sorption kinetics are very important [18]. The sorption kinetics in a wastewater treatment is significant, as it provides valuable insights into the reaction pathways and the mechanism of a sorption reaction [19]. In addition, the kinetics describes the solute uptake, which in turn controls the residence time of a sorbate at the solid–solution interface. Fig. 4 shows the plot of MB uptake versus contact time at different initial MB concentrations at pH 9. The MB uptake increased with increasing initial MB concentration. Initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence the dye uptake increased with increasing initial dye concentration. For instance, the amount biosorbed by succinated *C. glutamicum* increased from 107.2 to 312.9 mg/g as the initial MB concentration was increased from 273 to 858 mg/l, whereas the MB-removal efficiency decreased from 98.1 to 91.1% over this concentration increase range. This is because at lower concentrations, the ratio of the initial moles of dye to the available surface area is low which causes the fractional sorption to become independent of the initial concentration [20]. However, at higher concentration the available sorption sites are decreased compared to the moles of dye present and hence the MB percentage removal is dependent upon the initial dye concentration. Furthermore, the equilibrium was attained completely independent of the initial dye concentration. For both raw and succinated biomasses, almost complete biosorption equilibrium was attained within 5 min, followed by complete saturation in 30 min. The very fast kinetics observed with different forms of *C. glutamicum* biomass represents a significant advantage for application to wastewater treatment systems and suggests the suitability of the material for continuous flow systems [21].

The experimental biosorption kinetic data were modeled using pseudo-first and -second order kinetics, which can be represented in their non-linear forms as follows:

$$\text{pseudo-first order model} \quad q_t = q_e(1 - \exp(-k_1 t)) \quad (6)$$

$$\text{pseudo-second order model} \quad q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (7)$$

Table 2
Biosorption isotherm constants during MB biosorption by the four different sorbents

Isotherm models		Raw biomass		Succinated biomass		SPC-100		SPS-200	
		pH 6	pH 9	pH 6	pH 9	pH 6	pH 9	pH 6	pH 9
Langmuir	Q_{max} (mg/g)	117.4	207.3	147.5	337.5	295.6	457.4	493.6	500.6
	b (l/mg)	0.035	0.031	0.072	0.090	0.78	0.55	1.97	0.694
	R^2	0.930	0.936	0.949	0.923	0.901	0.953	0.990	0.916
	ε (%)	11.1	14.1	14.3	31.1	4.03	5.78	3.57	5.52
Freundlich	K_F (l/g)	28.1	31.1	54.3	90.6	182.0	213.8	230.8	206.8
	n	2.23	2.97	4.52	4.63	9.32	6.98	7.58	7.17
	R^2	0.802	0.842	0.805	0.831	0.924	0.923	0.817	0.733
	ε (%)	21.3	27.6	26.8	48.3	4.29	15.0	8.45	23.9
Toth	Q_{max} (mg/g)	103.1	165.7	135.7	338.1	319.7	457.4	483.7	510.0
	b_T (l/mg)	0.014	0.018	0.053	0.091	1.00	2.55	1.38	2.01
	n_T	0.179	0.013	0.182	1.01	0.9	1.15	0.50	1.67
	R^2	0.978	0.989	0.997	0.922	0.971	0.957	0.991	0.919
	ε (%)	1.86	1.59	2.67	31.2	33.4	5.78	1.57	17.7

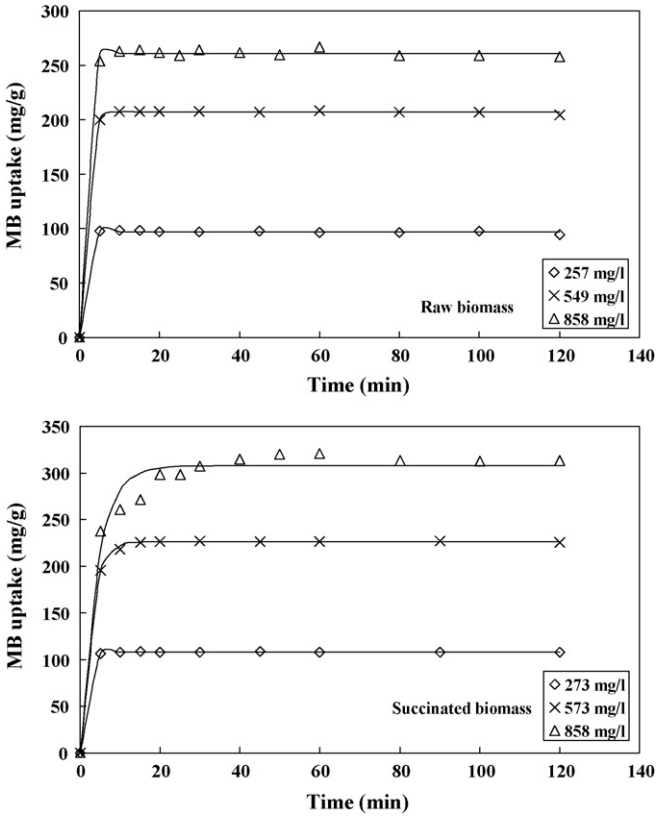


Fig. 4. Biosorption kinetics for raw and succinated *C. glutamicum* biomass (temperature = 25 ± 1 °C, agitation speed = 160 rpm). Curves are predicted by the non-linear, pseudo-first order model.

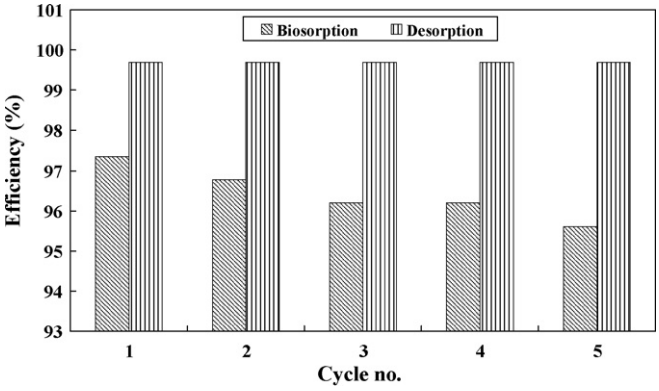


Fig. 5. Regeneration and reuse of succinated *C. glutamicum* in five sorption–desorption cycles (sorption pH 9, desorption pH 2).

where q_e is the amount of dye sorbed at equilibrium (mg/g), q_t the amount of dye sorbed at time t (mg/g), k_1 the pseudo-first order rate constant (1/min) and k_2 the pseudo-second order rate constant (g/mg min). The rate constants, predicted equilibrium uptakes, corresponding correlation coefficients and percentage error values for all concentrations tested were calculated and are summarized in Table 3.

In the case of the pseudo-first order model, the correlation coefficients were above 0.975 and the percentage error values less than 0.1%. In addition, the calculated q_e was very close to the experimental q_e, suggesting the applicability of the model to fit the kinetic data for the initial concentrations examined. The rate constant decreased with increasing initial concentration. The pseudo-second order model is based on the sorption capacity of the solid phase and predicts the sorption behavior over the entire study range [22]. This was consistent with the better results obtained with the pseudo-second order model (Table 3). The correlation coefficients were always greater than 0.993 with percentage error values less than 0.9%. However, the model slightly over predicted q_e values compared to that of the pseudo-first order model. Considering the correlation coefficient, percentage error and predicted uptake values, the biosorption of MB onto raw and succinated biomasses was considered to have followed the pseudo-first order model.

3.5. Desorption

Desorption is of the utmost importance for inexpensive biomass preparation/generation. It may decrease the process cost and also the dependency of the process on a continuous biosorbent supply. A successful desorption process requires proper selection of elutants and this strongly depends on the type and mechanism of the biosorption. The sorption experiments revealed the necessity of neutral or basic conditions for MB binding to the sorbent, suggesting that the sorbed dye molecules can only be recovered under acidic conditions. Therefore, MB-loaded sorbents were exposed to three different elutants: 0.1 M HCl, 0.1 M HNO_3 and deionized water (pH 2). All elutants performed well in the desorption of MB from MB-loaded *C. glutamicum*, with elution efficiencies of over 99.7%. However, they exhibited very poor performances on MB-loaded activated carbons, with elution efficiencies of around 1.5–6.1%. Therefore, only succinated *C. glutamicum* was used in regeneration experiments, since it exhibited both good MB uptake capacity and easy desorption.

3.6. Regeneration and reuse of biomass

The regeneration experiments explored the biosorption potential of succinated biomass for MB over five sorption–desorption cycles (Fig. 5). The biomass almost completely retained its first cycle MB-removal efficiency (97.3%) throughout the five cycles examined, aided by a consistently high elution efficiency of around 99.7%

Table 3
Biosorption kinetic constants for MB biosorption by raw and succinated *C. glutamicum* biomass

Kinetic models		Raw biomass			Succinated biomass		
		257 (mg/l)	549 (mg/l)	858 (mg/l)	273 (mg/l)	573 (mg/l)	858 (mg/l)
Pseudo-first order	q_e (mg/g)	98.1	207.7	263.6	108.2	226.3	307.7
	k_1 (1/min)	0.965	0.648	0.621	0.861	0.394	0.244
	R^2	0.999	1.00	0.998	1	0.999	0.975
	ε (%)	0.02	0	0.1	0	0	0
Pseudo-second order	q_e (mg/g)	98.6	211.8	270.5	108.3	229.8	324.2
	k_2 (g/mg min)	0.162	0.016	0.011	0.161	0.006	0.002
	R^2	0.999	0.997	0.998	0.999	0.997	0.993
	ε (%)	0.01	0.9	0.1	0	0.03	0.04

by deionized water (pH 2, 0.1 M HCl). The biomass weight loss was also minimal with only 9.8% loss was observed at the end of fifth cycle.

4. Conclusions

The following conclusions were drawn from the present study on the biosorption of MB from aqueous solution using raw and succinated *C. glutamicum*:

- The FT-IR spectra confirmed the presence of carboxyl, phosphonate and amine groups. The carboxyl group of *C. glutamicum* was found to be responsible for electrostatic binding of MB cations. Thus, chemical modification of amine groups to carboxyl via succination enhanced MB biosorption capacity.
- The pH edge experiments revealed that neutral or basic conditions were required to optimize the MB biosorption.
- Biosorption isotherms obtained at pH 6 and 9 were modeled using the Langmuir, Freundlich and Toth models. At pH 9, the succinated biomass exhibited a biomass uptake capacity of 337.5 mg MB/g, compared to 207.3 mg MB/g for the raw biomass, according to the Langmuir model. However, both of the activated carbons outperformed the succinated biomass in MB uptake.
- The pseudo-first order model described the biomass-MB kinetic data with a higher correlation coefficient, lower percentage error values and better prediction of uptake values than the pseudo-second order model.
- Desorption and subsequent reuse was only possible with the succinated biomass, which performed well with MB-removal efficiencies of greater than 97.3% in all five subsequent cycles examined.
- With the advantages of being an inexpensive and easily available waste product, *C. glutamicum* biomass shows promising potential for the development of a practical biosorbent. In addition, via succination, it was shown that MB biosorption capacity can be enhanced 1.6 times than pristine biomass. Even though its MB sorption capacity was slightly inferior to that of activated carbon, the ability of this biomass to be reused over several subsequent cycles is an important additional advantage for full-scale industrial application.

Acknowledgements

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References

[1] J.R. Easton, The dye makers' view, in: P. Copper (Ed.), Colour in Dyehouse Effluent, The Society of Dyers and Colorists, Alden Press, Oxford, 1995, pp. 6–21.
[2] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, Proc. Biochem. 40 (2005) 997–1026.
[3] B.W. Atkinson, F. Bux, H.C. Kasan, Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents, Water SA 24 (1998) 129–135.
[4] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Biores. Technol. 97 (2006) 1061–1085.
[5] A. Kapoor, T. Viraraghavan, Fungal biosorption—an alternative treatment option for heavy metal bearing wastewaters: a review, Biores. Technol. 53 (1995) 195–206.
[6] M. Tsezos, Biosorption of metals. The experience accumulated and the outlook for technology development, Hydrometallurgy 59 (2001) 241–243.
[7] K. Vijayaraghavan, Y.-S. Yun, Utilization of fermentation waste (*Corynebacterium glutamicum*) for biosorption of Reactive Black 5 from aqueous solution, J. Hazard. Mater. 141 (2007) 45–52.
[8] T. Hermann, Industrial production of amino acids by coryneform bacteria, J. Biotechnol. 104 (2003) 155–172.
[9] D.L. Pavia, G.M. Lampman, G.S. Kriz, Introduction to Spectroscopy (Third edition), Harcourt college publishers, Philadelphia, 2001, p72.
[10] S.W. Won, S.B. Choi, Y.-S. Yun, Interaction between protonated waste biomass of *Corynebacterium glutamicum* and anionic dye Reactive Red 4, Colloids Surface A: Physicochem. Eng. Aspects 262 (2005) 175–180.
[11] M.U. Mera, M. Kemper, R. Doyle, T.J. Beveridge, The membrane-induced proton motive forces influences the metal binding ability of *Bacillus subtilis* cell walls, Appl. Environ. Microbiol. 58 (1992) 3837–3844.
[12] T.J. Beveridge, C.W. Forsberg, R.J. Doyle, Major sites of meal binding in *Bacillus licheniformis* walls, J. Bacteriol. 150 (1982) 1438–1448.
[13] M.E. Romero-Gonzalez, C.J. Williams, P.H.E. Gardiner, Study of the mechanisms of cadmium biosorption by dealginated seaweed waste, Environ. Sci. Technol. 35 (2001) 3025–3030.
[14] K. Vijayaraghavan, K. Palanivelu, M. Velan, Treatment of nickel containing electroplating effluents with *Sargassum wightii* biomass, Proc. Biochem. 41 (2006) 853–859.
[15] G. Limousin, J.P. Gaudet, L. Charlet, S. Szenknect, V. Barthes, M. Krimissa, Sorption isotherms: a review on physical bases, modeling and measurement, Appl. Geochem. 22 (2007) 249–275.
[16] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Res. 37 (2003) 4311–4330.
[17] Y.S. Ho, J.F. Porter, G. McKay, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, Water Air Soil Pollut. 141 (2002) 1–33.
[18] S. Azizian, Kinetic models of sorption: a theoretical analysis, J. Colloid Interface Sci. 276 (2004) 47–52.
[19] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.
[20] K. Vijayaraghavan, K. Palanivelu, M. Velan, Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles, Biores. Technol. 97 (2006) 1411–1419.
[21] Z. Reddad, C. Gerente, Y. Andres, P.L. Cloirec, Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.
[22] G. McKay, Y.S. Ho, J.C.Y. Ng, Biosorption of copper from wastewaters: a review, Sep. Purif. Meth. 28 (1999) 87–125.