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Research Article

Bed depth service time model for the biosorption of reactive red dye using the *Portunus sanguinolentus* shell

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ABSTRACT: Biosorption is an efficient and regenerative technique that often uses low-cost adsorbent materials, particularly for the treatment of wastewaters containing dyes and heavy metals. This study investigates the ability of crab shell (*Portunus sanguinolentus*) to remove reactive red dye in a packed bed up-flow column (internal diameter 2 cm; height 35 cm). Crab shell has high surface area (after proper size reduction) and high regenerative capacity. The experiments were performed with different bed heights (20 and 30 cm) and using different flow rates (12 and 17 ml/min) in order to obtain experimental breakthrough curves. The bed depth service time (BDST) model was used to analyze the experimental data and the model parameters were evaluated. The column regeneration studies were carried out for five different sorption–desorption cycles. The elutant used for the regeneration of the sorbent was 0.01 M EDTA (disodium) solution at pH 9.8 adjusted using NH_4OH. This solution was found to have the best bed regeneration capacity and could be reused for several sorption–desorption cycles. The elution efficiency was greater than 99.1% in all seven cycles. Continuous use of the crab shell leads to a decrease in the adsorptive performance, as observed by the breakthrough curves becoming flatter and also because of a broader mass transfer zone. © 2009 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: biosorption; BDST model; crab shell adsorbent; reactive red dye; adsorbent regeneration

INTRODUCTION

Biosorption is a new technique that emerged in the 1980s and has gained a considerable amount of attention because of its higher efficiency and regenerative capacity, particularly in the adsorption of contaminants like dyes and heavy metals. Biosorption is a multidisciplinary process, which includes chemisorptions, surface and pore adsorption, ion exchange, microprecipitation, hydroxide condensation over bio-surface and surface adsorption.[1] Most of the available materials on the earth are naturally biodegradable, which are generally called *biomass*. Among the available biomasses, only a few exhibit the property of surface adsorption, which are sensitive to the operating variables like temperature, pressure, concentration of the effluent and the pH of the effluent. Therefore, the choice of the biomass for the removal of pollutant (dye or heavy metal) present in the effluent should have higher resistance toward these operating variables and should also have high regenerative capacity.

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In most of the biomasses, the surface characteristics play a major role in immobilizing the dye molecules, which further depend on the native biomass mechanical strength, particle size and resistance toward chemicals that could be either present in the aqueous effluent or that might be used for dye adsorption.[2,3] In the dying industries, most of the effluents contain large amount of dye molecules and the remaining are the undesirable chemicals. Removal of these dye substance from the dye-bearing effluent is a complex problem because of the difficulty in treating these effluents by conventional methods.[4,5]

In this present study, the *Portunus sanguinolentus* shell (crab shell) was used as biosorbent crab shells are generally inexpensive because of their easy availability in the form of waste in all fish-processing industries or in fish markets. It has high surface area (after proper size reduction) and has high regenerative capacity.[6,7] In the costal areas of Tamil Nadu, India, approximately 4000 t of live crabs are caught per month, from which 2000 t of crab shells are disposed as waste. The aim of this article is to use the waste crab shell as suitable biomass for the removal of reactive red 198. In most of the earlier investigations, it was restricted to

batch equilibrium studies. The probable reason for this restriction is mainly due to the unavailability of bulk quantities of biomass.[8] The rigidity of the biomass and its ability to withstand extreme pH conditions employed during regeneration (desorption) are the other important factors, which limit the biosorbent usage in column studies.[8,9] In this present article, a continuous up-flow packed bed bioadsorber column was used, where the breakthrough profiles for the sorption of dye were analyzed using bed depth service time (BDST) model.

MATERIALS AND METHODS

Preparation of adsorbent

The shells of the *Portunus sanguinolentus* were collected from fish-processing industries along the coastal areas of Elliot's beach, Chennai, India. The shells were initially deskinned properly and washed with 0.1 N hydrochloric acid, and further washed with distilled water until the solution reached a neutral pH (pH of 7). After complete washing, the shells were dried in a hot air oven at 40 °C for about 1 h to completely remove the moisture content. The shells were then crushed into small particles using a ball mill. The crushed *Portunus sanguinolentus* shell particles were then shaken in a sieve shaker to get uniformly sized particles (0.767 mm). The uniform-sized particles were then collected and stored for the further experimental use. Before using these uniform-sized particles for adsorption study, particles were soaked in 0.1 N hydrochloric acid for about 30 min to remove the top layer of the shell. After the removal of the top layer, the particles were washed with distilled water and then sun dried; significantly, a 3–5% difference was found in the weight.

Dye solution

The reactive red 198 is an acid dye, which is widely used in the textile and paper industries, was purchased from Sigma Aldrich. Reactive red 198 (Melting Point of the Dye = 138 °C and $\lambda_{max} = 517$ nm) has a chemical formula of $C_{25}H_{15}ClN_7Na_3O_{10}S_3$, and a chemical name of 2,7-naphthalenedisulfonic acid, 5-((4-chloro-6-(phenyl amino)-1, 3, 5-triazin-2-yl) amino)-4- hydroxy-3-((2-sulfophenyl) azo)-, trisodium salt. The structure of reactive red 198 is shown in Fig. 1. An accurately weighed quantity of the dye was dissolved in double-distilled water to prepare the stock solution (1000 mg/l). Experimental solutions of the desired concentration were obtained by successive dilutions of the stock solution.

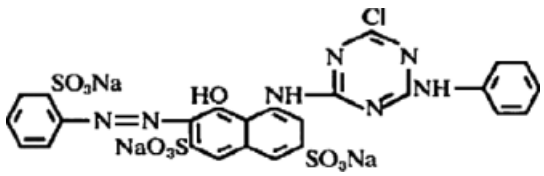

Figure 1. Chemical structure of reactive red 198.

Method

A continuous packed glass column of diameter 2 cm and height 35 cm was used in this present adsorption study. The schematic view of the experimental setup is shown in Fig. 2. The column was initially filled with processed crab shell particles of size 0.6 mm to a height of 30 cm. The 30-cm filled crab shell initially weighed around 30 g. At the bottom of the column, glass wool was placed over a perforated plate as a supporting material for the crab particles. The initial dye concentration of about 50 ppm was prepared and pumped through the column at a flow rate of 12 ml/min using a peristaltic pump. The outlet samples were collected periodically and the optical density and the pH of the samples were observed using a spectrophotometer and a pH meter respectively. During operation, the column was said to be exhausted or saturated when the optical density of the outlet sample was equal to that of the original optical density of the inlet dye solution. After the column attained saturation, the column was regenerated for the consecutive adsorption cycle by washing the total column with 10 pH distilled water, which was prepared by adding sodium hydroxide pellets to distilled water. The optical density of the outlet

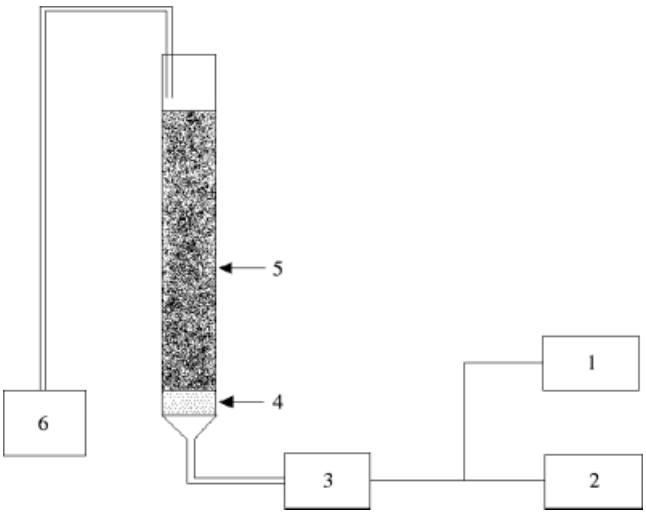

Figure 2. Experimental set-up of up-flow packed column. (1. Dye solution, 2. 10 pH distilled water, 3. Peristaltic pump, 4. Glass wool, 5. Crab shell particles, 6. Effluent storage).

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under desorption process was noted periodically to evaluate the performance of the desorption process. The elution process was stopped when the optical density of the out coming elutant was same as the inlet value. Adsorption–desorption cycles were carried out five times and the percentage of dye removed in each cycle was evaluated. The experiments were further extended for different column heights and for different flow rates. For each experiment, the same above-mentioned sorption process was followed.

Modeling and analysis of column data

The analysis of the breakthrough curve was done by using the BDST model. BDST is a simple model for predicting the relationship between bed height, Z, and service time, t, in terms of process concentration and adsorption parameters,[10] as shown in the following equation:

$$\ln\left(\frac{C_o}{C_b - 1}\right) = \ln(e^{K_a N_o Z/v} - 1) - K_a C_o t \qquad (1)$$

Hutchins[11] proposed a linear relationship between the bed height and service time given by the following equation (Eqn 2):

$$t = \frac{N_o Z}{C_o v} - \frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_b} - 1\right) \qquad (2)$$

where C_o is the initial dye concentration (mg/l), C_b is the breakthrough dye concentration (mg/l), N_o is the sorption capacity of the bed (mg/l), v is the linear velocity (cm/min) and K_a is the rate constant (l/mg/min). The quantity of the dye retained in the column is represented by the area above the breakthrough curve (C *vs* t) that is obtained through numerical integration.[8] Dividing the dye mass (m_{ad}) by the sorbent mass (M) leads to the dye uptake capacity (Q) of the crab shell particles. The breakthrough time (t_b) is the time at which the dye concentration reaches 1 mg/l. The bed exhaustion time (t_e) is the time at which the dye concentration reaches 49 mg/l. These two times are used to evaluate the overall sorption zone (Δt) given by Volesky *et al*.[8];

$$\Delta t = t_e - t_b \qquad (3)$$

The length of the column in each cycle is used to calculate the length of the mass transfer zone (Z_m), where it can be effectively calculated by the following equation:

$$Z_m = Z\left(1 - \frac{t_b}{t_e}\right) \qquad (4)$$

The effluent volume is calculated by multiplying the volumetric flow rate with the bed exhaustion time t_e.[12]

$$V_{eff} = F t_e \qquad (5)$$

where F is the volumetric flow rate (ml/min).

The total amount of dye passed through the column (m_{total}) can be calculated by the following equation[12]:

$$m_{total} = \frac{C_o F t_e}{1000} \qquad (6)$$

Total dye removal is the ratio of the mass of dye retained in the column (m_{ad}) to the total amount of dye passed through the column (m_{total}). Its percentage is obtained by Aksu and Gonen[12]:

$$\text{Total dye removal } (\%) = (m_{ad}/m_{total}) \times 100 \qquad (7)$$

The mass of the dye desorbed (m_d) in each cycle is obtained from the elution curve (C *vs* t). The area under the elution curve gives the amount of dye desorbed. The elution efficiency is the ratio of the mass of dye desorbed to the mass of dye adsorbed.[8]

$$E(\%) = \frac{m_d}{m_{ad}} \times 100 \qquad (8)$$

RESULTS AND DISCUSSION

Effect of bed height

The sorption performance of crab shell particles was done for two different bed heights of 20 and 30 cm and at a flow rate of 12 ml/min. The column was so designed that the amount of the crab shell after filling the column, with a height of 20 and 30 cm, was

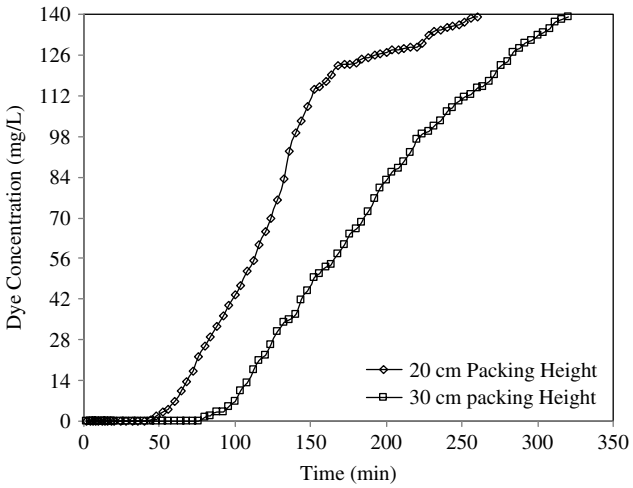

Figure 3. Breakthrough curves for different bed heights.

Table 1. Parameters obtained at different bed heights.

Bed height (cm)	Uptake (mg/g)	t_b (min)	t_e (min)	Δt (min)	t_s (min)	V_{eff} (ml)	% removal	dC/dt (mg/l/min)
20	3.09	48	260	212	122.8	3120	72.31	0.683
30	3.15	80	320	240	179.6	3840	73.12	0.512

exactly 20 and 30 g respectively. Figure 3 shows the breakthrough profile of dye sorption at different bed heights and it was observed that the sorption behavior is similar for both the cases, which is irrespective of the bed height. This could be because the uptake capacity strongly depends on the amount of sorbent available for the sorption. Further, it was observed that the breakthrough time (t_b) and the exhaustion time (t_e) increased with increase in bed height (Table 1). The stoichiometric time (t_s) reflects the time at which complete saturation of the sorption capacity of the bed occurs.[13] By plotting C/C_o *versus* time, the stoichiometric time can be calculated from the area above the curve, which is shown in Table 1. The slope of the S-shaped-curve from t_b to t_e decreased as the bed height increased from 20 to 30 cm, indicating that the breakthrough curve becomes steeper as the bed height decreases. The uptake capacity was calculated by the area above the breakthrough curve. The breakthrough curves flattened as the column height increased. As expected, an increase in the bed height results in the high volume of the dye solution treated, which results in higher percentage of dye removal. The effluent volume, the mass of dye adsorbed and the percentage removal of the dye increased with increase in the bed height. At greater bed heights, the time taken to attain saturation increased, and the overall sorption zone (Δt) increased with increase in the bed height.

The BDST model was used to physically measure the capacity of the bed at different breakthrough values. The column service time was fixed at a particular time, i.e. the effluent dye concentration reached 1 mg/l. The plot of service time against bed height at a flow rate of 12 ml/min was linear, indicating the validity of the BDST model for the present system (graph not included). The sorption capacity of the bed per unit bed volume, N_o, was calculated from the slope of the BDST plot, assuming the initial concentration and the linear velocity, v, as constant during the column operation. The rate constant, K_a, calculated from the intercept of the BDST plot, characterizes the rate of solute transfer from the fluid phase to the solid phase.[13] The computed N_o and K_a were 167.125 mg/l and 0.00705 l/mg/min respectively. If K_a is large, even a short bed avoids breakthrough, but as K_a decreases a progressively longer bed is required to avoid breakthrough.[13] The BDST model parameters can be useful to scale up the process for other flow rates without further experimental data and analysis.

Effect of flow rate

The effect of flow rate on dye sorption by crab shell particles was studied by varying the flow rate from 12 to 17 ml/min under constant bed height and constant initial concentration of the dye solution (30 cm and 50 mg/l respectively). Figure 4 shows the effect of effluent dye concentration with time at different flow rates of dye solution. From the figure, it was observed that, as the flow rate increases, the breakthrough curve becomes steeper and also resembles the same S-shaped-curve nature. Further, the breakthrough time, exhaustion time,

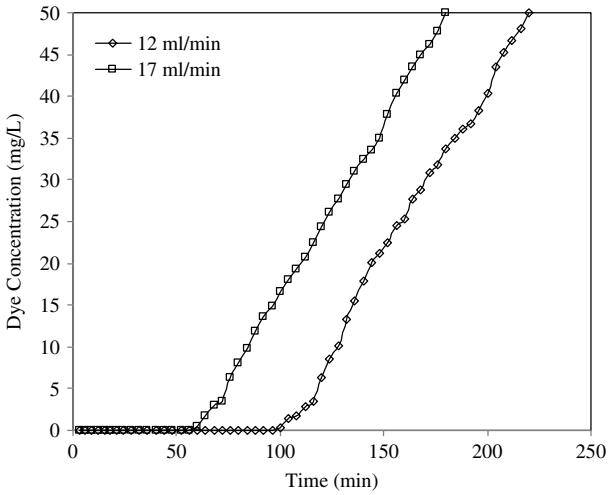

Figure 4. Breakthrough curves for different flow rates.

Table 2. Parameters obtained at different flow rates.

Flow rate (ml/min)	Uptake (mg/g)	t_b (min)	t_e (min)	Δt (min)	t_s (min)	V_{eff} (ml)	% removal	dC/dt (mg/l/min)
12	3.23	104	220	116	158	2640	73.41	0.42
17	3.13	68	180	112	122	3060	61.37	0.412

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stoichiometric time and uptake capacity decrease as the flow rate increases; these values are listed in Table 2. The reason for this behavior could be that, as the flow rate increases, the residence time of the solute in the column decreases, which causes the dye solution to leave the column before saturation occurs; further, the process is intraparticle mass transfer controlled, hence a slower flow rate favors the sorption and, when the process is subjected to external mass transfer control, a higher flow rate decreases the film resistance.[14] Even though the volume of dye solution treated is higher at flow rates of 12 and 17 ml/min, the lowest flow rate displays a high dye removal percentage. At a lower flow rate, we notice that the breakthrough time and the exhaustion time decrease with increase in flow rate along with the stoichiometric time.

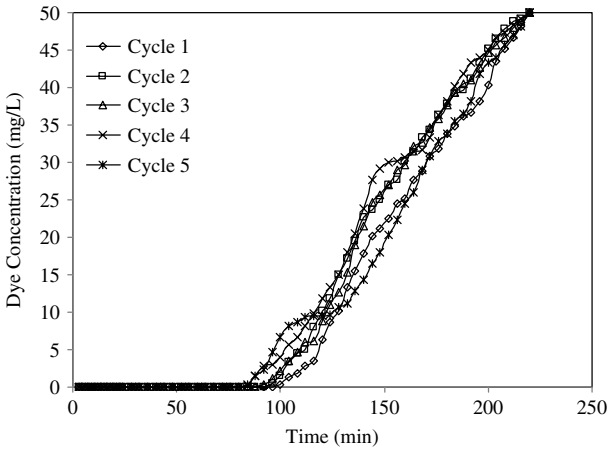

Figure 5. Breakthrough curves for all the five cycles.

Regeneration

Regeneration of the column plays a major role in deciding the versatility of the adsorbent. In this present study, the regeneration cycle was carried out for five sorption–desorption cycles. Initially, the column was packed with 30 g of crab shell particles yielding an initial bed height of 30 cm. The flow rate was adjusted to 12 ml/min using a peristaltic pump. The breakthrough time, the exhaustion time, stoichiometric time and dye uptake capacity for all five cycles are summarized in Table 3. The breakthrough time steadily decreased from 108 to 80 min as the cycle progressed from 1 to 5. A similar trend was observed for the case of stoichiometric time, where the exhaustion time increased as the cycle progressed. Further, the bed exhaustive limit was selected at 49 mg of dye per liter in order to avoid time delay that occurs for full bed saturation. The overall sorption zone (Δt) tends to increase as the cycle progresses, indicating that the sorption sites were not easily accessible as they were still occupied by the dye or destroyed by the previous elution step.

Figure 5 shows the breakthrough curves for all the cycles. From the figure, it is observed that the breakthrough curve tends to flatten as the number of cycles increases, which can be interpreted from the slope of the breakthrough curve. The slope of the breakthrough curves decreased as the number of cycles increased. Further, the bed length decreased from 30 to 27.9 cm after the fifth sorption–desorption cycle. This could be because of some soluble constituents of the sorbent being dissolved in the strong alkaline environment due to the elution step. Figure 6 shows the elution curves for all the five desorption cycles. This deterioration is also reflected in the dye uptake capacity of the crab shell particles, where the dye uptake obtained in the first sorption cycle was never reached again in any of the subsequent cycles, even though the uptake was slightly increased in the last cycle, where the uptake strongly depends on the previous elution step. The prolonged elution process for the regeneration cycle could have destroyed the binding sites or inadequate elution may have allowed dyes to be retained in the site. The minimum bed length (Z_m) required to obtain the breakthrough time (t_b) at $t = 0$ (also called critical bed length) was uniformly increased as the cycle progressed, indicating the broadening of the mass transfer zone.

For a system of continuous operation to work successfully, the desorption process and agents must be effective and should not cause much damage to the sorbent. Furthermore, the understanding of the mechanism responsible for dye sorption would be very helpful in selection of eluting agents. The crab shell comprises mainly calcium carbonate and chitin along with some proteins. Chitin has been postulated as being the main constituent responsible for dye coordination.[4,15]

Table 3. Sorption parameters for all cycles.

Cycle	Uptake (mg/g)	t_b (min)	t_e (min)	Δt (min)	t_s (min)	Z (cm)	Z_m (cm)	V_{eff} (ml)	% Removal
1	3.16	108	210	102	159	30	14.57	2520	75.23
2	3.02	100	212	112	150.5	29.8	15.74	2544	71.22
3	3.05	96	216	120	151.5	29.6	16.44	2592	70.60
4	2.92	88	218	130	145.5	29.5	17.59	2616	66.97
5	3.13	80	220	140	159.5	29.2	18.58	2640	71.13

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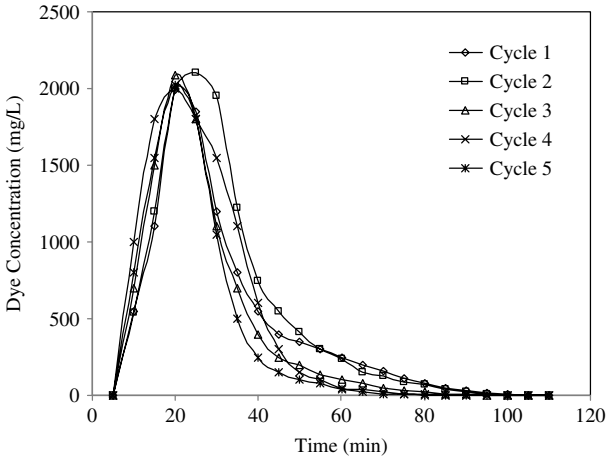

Figure 6. Elution curves for all the five cycles.

The mechanism involved is usually complex formation between dissolved dye species and chitin. In order to retrieve the cations, which are physicochemically sequestered to the cell surface, a strong complexing agent might be helpful. A preliminary examination revealed that, among several complexing agents (results not presented), 0.01 M EDTA (disodium) solution at pH 9.8 adjusted using concentrated NH_4OH was found to be suitable for the present system. Also, Chui *et al*.[16,17] reported that 0.1 M EDTA recovered 80–100% of Cu(II) and Ni(II) from shrimp chitin in column experiments.

From Fig. 5, it is observed that the all the cycles exhibit a similar trend: a sharp increase in the beginning followed by a gradual decrease. Further, the flow rate in the elution process is maintained at 12 ml/min to avoid the over contact of the elutant with the sorbent and also to obtain maximum dye concentration in a shorter time. The elution efficiency is found to be greater than 97% in all the five cycles. The elution efficiencies for all the cycles are presented in the Table 4.

CONCLUSION

This study identifies crab shell as a suitable biosorbent to be utilized for continuous removal of dye from aqueous solution. An up-flow packed bed column was employed in the present study, as it allows a large volume of waste water from textile industries to be continuously treated using a defined quantity of sorbent in the column. The experimental data confirmed that the bed height influence was not pronounced in dye uptake by crab shell, as it remained relatively constant for all bed heights investigated. The increase in the flow rate resulted in decreased dye uptake, probably due to insufficient residence time of the solute in the column. A successful biosorption process operation required the multiple reuses of the sorbent, which greatly reduced the process caused as well as decreased the dependency of the process on continuous supply of the sorbent. The sorption performances of the crab shell were evaluated in five sorption–desorption cycles. A loss in sorption performance was observed as the cycles progressed, which was also indicated by a decrease in breakthrough time, broadening of mass transfer zone, loss in sorbent weight, decrease in dye uptake and decline in percentage dye removal at the end of the fifth cycle. It is always desirable to select an elutant, which neither affects the physical condition of the sorbent nor alters the dye uptake. The process of identifying an efficient elutant for a particular sorbent is rather complicated and requires a complete understanding of the mechanism responsible. For the present system, 10 pH distilled water adjusted using sodium hydroxide pellets works well, exhibiting elution efficiencies of greater than 97% for all the five sorption–desorption cycles. The economic and environmental advantages of reusing the shell particles and good sorption capacity makes crab shell an attractive treatment for effluents that contain dye.

Table 4. Elution efficiency for all cycles.

Sorption cycle no.	Elution efficiency (%)	dC/dt (mg/l/min)
1	98.5	0.442
2	97.2	0.418
3	98.9	0.419
4	98.4	0.394
5	99.2	0.352

NOMENCLATURE AND UNITS

C	out let dye concentration (mg/l)
C_o	initial dye concentration(mg/l)
C_b	breakthrough dye concentration (mg/l)
E	elution efficiency (%)
F	volumetric flow rate (ml/min)
K_a	rate constant (l/mg/h)
M	sorbent mass (g)
m_d	mass of the dye desorbed
m_{ad}	dye mass (mg)
m_{total}	total dye sent to the column (mg)
N_o	sorption capacity of the bed (mg/l)
t	service time (s)
t_b	time at which dye concentration in the effluent reaches 1 mg/l
t_e	time at which dye concentration in the effluent exceeds 49 mg/l
Δt	over all sorption zone (s)
V	linear velocity (cm/h)
V_{eff}	effluent volume

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Z_m mass transfer zone
Z bed height (cm)

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