# Removal of cationic dyes from aqueous solution using an anionic poly-γ-glutamic acid-based adsorbent

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## Abstract

Natural polymeric materials are gaining interest for application as adsorbents in wastewater treatment due to their biodegradable and non-toxic nature. In this study, a biopolymer, poly-γ-glutamic acid (γ-PGA) derived from bacterial sources (*Bacillus* species) was evaluated for its efficiency in removing basic dyes from aqueous solution. Sorption studies under batch mode were conducted using C.I. Basic blue 9 (BB9) and C.I. Basic green 4 (BG4) as test dyes. Equilibrium process conformed well with the Redlich-Peterson isotherm equation and the monolayer sorption capacity obtained from the Langmuir model was 352.76 and 293.32 mg/g for BB9 and BG4 dyes, respectively. The kinetic studies of dye sorption on γ-PGA gave high coefficients of determination (>0.98) for a pseudo second-order equation. An ion-exchange model, which assumes adsorption as a chemical phenomenon, was also found to fit the kinetic data precisely. The dye sorption largely depended on the initial pH of the solution with maximum uptake occurring at pH above 5. About 98% of the dye adsorbed on γ-PGA could be recovered at pH 1, which facilitates the reuse of spent γ-PGA.
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## 1. Introduction

Colored wastewater discharged from dyeing processes, besides being aesthetically displeasing, can pose destructive impact on the environment. About two percent of the total dyes produced (7 lakh ton) annually are discharged directly into effluent, with the proportion of dye released varying according to type of dye, fiber and relative degree of dye fixation [1–3]. As these effluents possess high biochemical oxygen demand, they interfere with the bacterial growth causing eutrophication (a condition of overpopulating with algae) that affects the photosynthetic processes in water. This, combined with the absorption of sunlight by dye itself, can reduce the oxygen levels in water and prove to be fatal to aquatic flora and fauna [2,3]. It is therefore inevitable to remove the dissolved dyes before such colored effluents could be discharged into any watercourses. However, the wastewater containing dyes are difficult to treat as the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to heat, light and oxidizing agents [3].

The environment-friendly, economic feasibility and efficiency criteria limit the practical application of various conventional methods [2]. Amongst the numerous techniques of dye removal, adsorption is a procedure of choice for the removal of dissolved organic compounds from wastewater. Adsorption has a specific advantage of removing the complete dye molecule, unlike certain removal techniques, which destroy only the dye chromophore leaving the harmful residual moieties (like metals) in the effluent. Activated carbon adsorption has been recognized by United States Environmental Protection Agency (USEPA) as one of the best available control technologies [2,3]. However, its widespread use is restricted, particularly in developing countries, due to its high cost. Other current techniques employ adsorbents such as alum, polyaluminum chloride and silica gel that are not eco-friendly themselves [2]. Thus, several attempts have been made to develop cheaper and effective adsorbents. Crini [3] has recently made a critical review on non-conventional adsorbents for dye removal.

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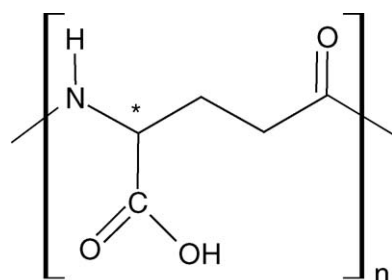
Fig. 1. Structure of γ-PGA.

Biopolymer-based materials are of particular interest for use as adsorbents due to their biodegradable and non-toxic nature. Several polysaccharide materials like chitin, chitosan, galactomannans, starch and their derivatives, pectin, carrageenan and alginic acid, derived from plant and marine sources have been used as adsorbents for the removal of dyes [2–4]. Nevertheless, natural polymers obtained from bacterial sources were also used as adsorbents [5]. Poly-γ-glutamic acid (γ-PGA), an anionic biopolymer produced from *Bacillus* sp. (chiefly from *B. licheniformis* and *B. subtilis*), is composed of many glutamic acid units connected by amide linkages between α-amino and γ-carboxylic acid groups (Fig. 1). The enzyme PGA synthetase plays a crucial role in γ-PGA biosynthesis and a commercial production of 50 g/l was achieved using *B. subtilis* [6]. It can be produced in different ionic forms (Ca, Na, H-forms) and in varying molecular weights ranged from 10,000 to 2 million Daltons for application in various industrial fields like food, cosmetics, medicine and in wastewater treatment [6,7]. However, except for very few reports on using γ-PGA for metal removal [5,8], its application as an adsorbent, particularly for the removal of dyes, remains unknown and requires further exploration. Therefore, the objectives of this study were to evaluate the potential of using γ-PGA (H-form) as adsorbent for the removal of basic dyes C.I. Basic blue 9 (BB9) and C.I. Basic green 4 (BG4) from aqueous solution. Batch experiments were performed as a function of initial dye concentration, agitation time and pH.

## 2. Materials and methods

### 2.1. Sorbent/sorbate

γ-PGA (H-form; M. wt.: 990 kDa), available commercially from Vedan Enterprise Corp. (Taichung, Taiwan) was obtained and its characteristics as given in the product specification are summarized in Table 1. In addition, parameters like bulk density and decolorizing power of γ-PGA were determined following the standard procedures [9]. Decolorising power, one of the important parameter for evaluation of an adsorbent for decolorisation purposes, was defined as milligrams of methylene blue dye (BB9) completely adsorbed by 1 g of adsorbent within 5 min of each addition of known concentration of the dye. Prior to each batch experiment, γ-PGA was activated at $105 \pm 5\,^{\circ}\mathrm{C}$ in a hot-air oven for 1 h to remove any adhering moisture or volatile compounds.

Table 1
Characteristics of γ-PGA

| Physical appearance | White, granulate, free-flow powders |
|---|---|
| Purity | 95% (HPLC) |
| Molecular weight | 990 kDa (HPLC) |
| pH | 2–2.5 |
| Clarity, $OD_{400}$ | 0.18 |
| Moisture content | 5% (automatic infrared analyzer) |
| Bulk density | 0.32 g/ml |
| Decolorising power (methylene blue dye) | 135 mg/g |
| Heavy metals | Total (as Pb): 15 mg/l |
| | Pb: 5 mg/l |
| | Cd: 2 mg/l |
| | $As_2O_3$: 2 mg/l |
| *E. coli* | ND[a]/1 g |
| *Salmonella* | ND/1 g |
| Particle size | 100% through 100 mesh |

[a] Not detectable.

The test basic dyes BB9 (98% purity) and BG4 (80–89% purity) as chloride and oxalate salts, respectively, were procured from Sigma (St. Louis, MO, USA) and used without further purification. The structure of dyes along with their commercial names, color index number and formula weight are given in Fig. 2. A stock dye solution of 1000 mg/l was prepared by dissolving 1 g of each dye in 1 l distilled water and different dye concentrations were prepared by making suitable dilutions.

### 2.2. Batch experiments

The dye solution (50 ml) of desired concentration at natural pH (5.45 for BB9 and 5.65 for BG4) was taken in Erlenmeyer
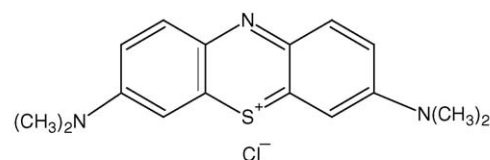


C.I. Basic blue 9
(Methylene blue, FW=373.9 g, C.I.No.52015)
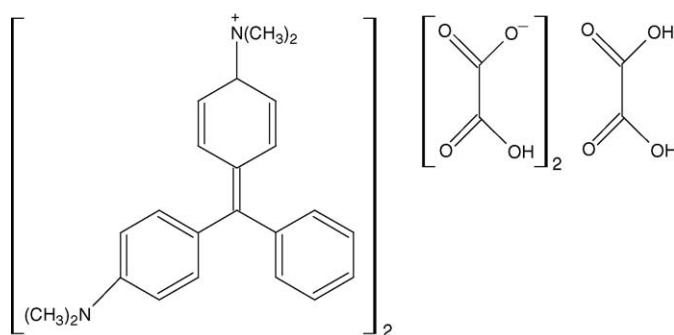


C.I. Basic green 4
(Malachite green, FW=929.0 g, C.I.No.42000)

Fig. 2. Structure of basic dyes.

flasks and agitated with a known weight of γ-PGA at room temperature ($28 \pm 0.5\,^\circ$C) in a Firstek B601D reciprocating water bath shaker (Firstek Scientific Co., Tau-yen, Taiwan) at 120 rpm. After equilibrium or defined time intervals, samples were withdrawn from the shaker, filtered through a $0.2\,\mu$m membrane filter and the filtrate was analyzed for residual dye concentration using a Beckman DU 640 spectrophotometer (Beckman Instruments Inc., CA, USA). Earlier the wavelength at which maximum absorbance $\lambda_{max}$ (nm) occurred for each dye in aqueous solution was determined (663 for BB9 and 617 for BG4) by performing full range (200–800 nm) wavelength scans. Concentrations of dyes in solution were estimated quantitatively using the linear regression equations obtained by plotting a calibration curve for each dye over a range of concentrations. A very little dye adsorption occurred on Erlenmeyer flask and during filtration was determined by performing control experiments and was accounted while computing the amount of dye adsorbed by γ-PGA. Similarly, in all adsorption experiments, the unadsorbed dye washed after filtration was analyzed and taken into account during calculation.

Equilibrium data were obtained by agitating various dye concentrations (10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160 and 200 mg/l) of BB9 and BG4 separately with a fixed γ-PGA dose of 0.4 g/l (0.02 g/50 ml) until equilibrium (2 h) was established. The fixed γ-PGA dose of 0.4 g/l was chosen after performing several trial studies to accomplish maximum equilibrium sorption capacity for the dye concentration range (10–200 mg/l) investigated. For kinetic study, 100 mg/l dye solutions were agitated with 0.4 g/l γ-PGA for predetermined intervals of time. The influence of pH on dye removal was studied by adjusting dye solutions (100 mg/l) to different pH values (1, 2, 3, 4, 5, 6 and 7) and agitated with 0.4 g/l of γ-PGA for 1 h. After equilibrium, the final pH value in each case was measured, followed by analyzing the dye remaining in solution. For desorption study, initially the sorption experiment was carried out with a mixture of 100 mg/l of dye solutions and 0.4 g/l of γ-PGA. After equilibrium, the γ-PGA loaded with dye was separated and gently washed with distilled water to remove any unadsorbed dye. The dye-laden γ-PGA was then agitated separately with 50 ml distilled water adjusted to various pH values (1, 2, 3, 4, 5 and 6) for 30 min and the dye desorbed in each solution was determined. As the desorption of dyes from spent γ-PGA surface was instantaneous with the addition of pH-adjusted distilled water, 30 min was sufficient enough to cause maximum desorption of dyes. It was also ensured that no additional desorption of dyes occurred beyond 30 min. The pH of dye solution and distilled water was adjusted to the desired value using dilute HCl or NaOH. It is worth pointing out that γ-PGA was not soluble in water in the pH range (1–7) experimentally studied, however, a perceptible solubility occurred above pH 8.5.

### 2.3. Data analyses

Each set of experiment was performed in duplicate and the mean values were taken for calculation. Standard deviation and analytical errors were calculated and the maximum error was $\pm 3\%$. The amount of dye adsorbed at time $t$, $q_t$ and at equilibrium, $q_e$ was calculated from the mass balance equation:

$$q_t = (C_0 - C_t)\frac{V}{m} \tag{1}$$

where $C_0$ and $C_t$ (mg/l) are the initial and final dye concentrations, respectively, $V$ (l) the volume of dye solution and $m$ (g) is the mass of γ-PGA. When $t$ is equal to the equilibrium agitation time (i.e., $C_t = C_e$, $q_t = q_e$), then the amount of dye adsorbed at equilibrium, $q_e$, is calculated using Eq. (1). In pH study, the dye adsorbed at various solution pH was expressed as percentage removal, which was calculated using the following equation:

$$R = \frac{100(C_0 - C_e)}{C_0} \tag{2}$$

where $R$ is the percentage dye removal. Adsorption isotherm and kinetic modeling were done by a non-linear regression method, which involves Marquardt-Levenberg algorithm, using GNU-PLOT software program (Version 3.7 for Windows). The degree of fitting the theoretical models with the experimental data was measured by applying two error functions, namely, coefficient of determination ($r^2$) and chi-square statistic ($\chi^2$). The $r^2$ values were directly obtained from a Microsoft Excel function, while $\chi^2$ was calculated using the following equation:

$$\chi^2 = \sum \frac{(q_{exp} - q_{mod})^2}{q_{mod}} \tag{3}$$

where $q_{exp}$ and $q_{mod}$ (mg/g) are experimental and modeled amounts of dye adsorbed, respectively, at time $t$ or at equilibrium.

## 3. Results and discussion

### 3.1. Sorption equilibrium

The equilibrium data are critical in optimizing the design parameters for any sorption system and provide sufficient information on the physiochemical data in evaluating the sorption process as a unit operation. Equilibrium experiments conducted with a range of initial dye concentration showed an increase in sorption amount from 24.81 to 381.66 mg/g and 24.61 to 291.60 mg/g, respectively, for BB9 and BG4, when the dye concentration was raised from 10 to 200 mg/l. The distribution of solutes between the liquid phase and the solid adsorbent is a measure of the position of equilibrium and can be generally expressed by two equations, namely, the Freundlich [10] and the Langmuir [11] isotherm equations, which can be expressed in non-linear forms as

$$q_e = K_F C_e^{1/n_F} \tag{4}$$

$$q_e = \frac{K_L C_e}{1 + b_L C_e} \tag{5}$$

where $K_F$ (mg/g) and $n_F$ are Freundlich constants indicating adsorption capacity and intensity of adsorption, respectively, $K_L$ (l/g) is the product of $q_m$ (mg/g) and $b_L$ (l/mg), which represent the maximum adsorption capacity and energy of adsorption, respectively. However, both models suffer from a drawback
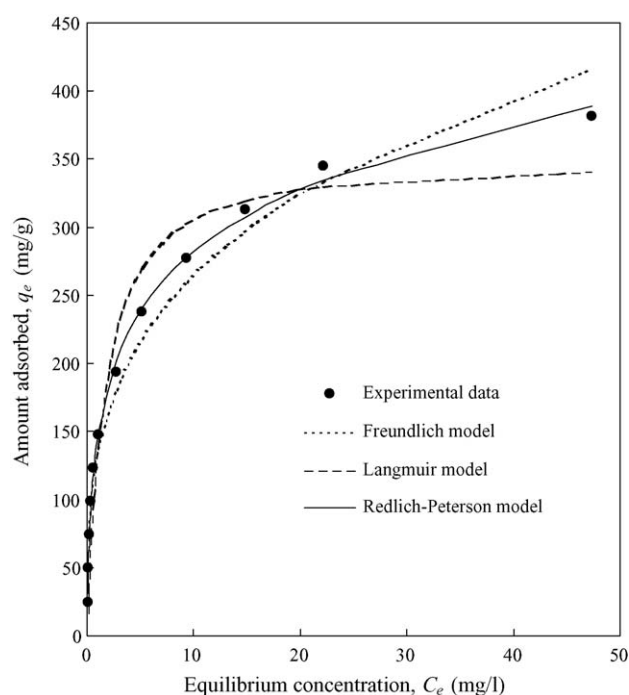
Fig. 3. Isotherm curves with fitted models for BB9/γ-PGA system. Dye concentration range: 10–200 mg/l; γ-PGA dose: 0.4 g/l; pH: 5.45; temperature: 28 ± 0.5 °C; equilibrium time: 2 h.
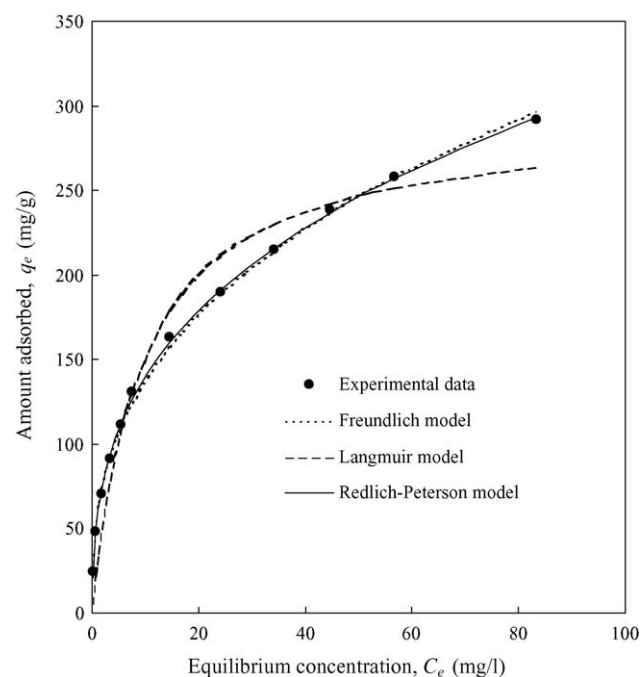


Fig. 4. Isotherm curves with fitted models for BG4/γ-PGA system. Dye concentration range: 10–200 mg/l; γ-PGA dose: 0.4 g/l; pH: 5.65; temperature: 28 ± 0.5 °C; equilibrium time: 2 h.

that equilibrium data over a wide concentration range cannot be fitted with a single set of constants. Therefore, a three-parameter Redlich-Peterson isotherm equation [12], which combines the features of both Freundlich and Langmuir models, was also tested for the present sorption systems. This intermediate isotherm should provide a more realistic representation of the sorption system over a wide concentration range. The non-linear form of the Redlich-Peterson model is expressed as

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\alpha} \tag{6}$$

where $K_R$ (l/g), $a_R$ (l/mg)$^\alpha$ and $\alpha$ are the Redlich-Peterson constants. The exponent $\alpha$ lies between 0 and 1. For $\alpha = 1$, Eq. (6) converts to the Langmuir form.

The equilibrium data for sorption of BB9 and BG4 dyes onto γ-PGA were fitted with Eqs. (4)–(6) and the fitted models along with the experimental data for comparison are illustrated in Figs. 3 and 4, respectively. The fitted sorption parameters of each isotherm model and their corresponding error functions are reported in Table 2. It is evident from $r^2$ and $\chi^2$ values that the equilibrium data of both sorption systems were well explained by Redlich-Peterson model when compared to Fre-

undlich and Langmuir models. However, in the BG4/γ-PGA system, the Redlich-Peterson model approached more closely with the Freundlich model, which was exemplified by a higher degree of fitness between the two models (Table 2). This may be due to the relatively higher $a_R$ value in Redlich-Peterson model obtained for the BG4/γ-PGA system than that for the BB9/γ-PGA system. This finding is consistent with the fact that the more the $K_R$ and $a_R$ values in Redlich-Peterson model are higher than 1, the more the isotherm approaches the Freundlich model. Ho [13] also observed a similar phenomenon on the sorption of cadmium onto tree fern and pointed out that the Freundlich model is a special case of Redlich-Peterson isotherm when the constants $K_R$ and $a_R$ are much greater than 1. The Freundlich constant ($n_F$) values (3.43 for BB9 and 2.75 for BG4) obtained between 1 and 10 demonstrated that the sorption of BB9 and BG4 on γ-PGA was favorable [14].

Though the Langmuir model did not show a precise fit, its sorption parameters can still provide valuable information. The maximum sorption capacity parameter $q_m$ has been universally recognized to compare the efficiency of an adsorbent. The $q_m$ values for sorption of BB9 and BG4 onto γ-PGA were found to be 352.76 and 293.32 mg/g, respectively. The $q_m$ values obtained for the present system in comparison with those reported [15–35]

Table 2
Fitted parameters of the isotherm models with error functions $r^2$ and $\chi^2$ for sorption of basic dyes on γ-PGA

| Dye | Freundlich model | | | | Langmuir model | | | | Redlich-Peterson model | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $K_F$ (mg/g) | $n_F$ | $r^2$ | $\chi^2$ | $K_L$ (l/g) | $b_L$ (l/mg) | $r^2$ | $\chi^2$ | $K_R$ (l/g) | $a_R$ (l/mg)$^\alpha$ | $\alpha$ | $r^2$ | $\chi^2$ |
| BB9 | 135.21 | 3.43 | 0.970 | 45.64 | 225.28 | 0.64 | 0.965 | 59.85 | 545.61 | 2.79 | 0.82 | 0.996 | 2.82 |
| BG4 | 59.31 | 2.75 | 0.998 | 2.65 | 31.30 | 0.11 | 0.971 | 130.05 | 299.03 | 4.37 | 0.67 | 0.999 | 1.21 |

Table 3
Some reported sorption capacities $q_m$ (mg/g) for removal of BB9 and BG4 dyes by various non-conventional adsorbents

| Adsorbent | Adsorbate | $q_m$ (mg/g) | References |
|---|---|---|---|
| Bark | Basic blue 9 | 914.58 | [15] |
| Pinewood | Basic blue 9 | 556.00 | [16] |
| Rice husk carbon | Basic green 4 | 511.00 | [17] |
| Waste newspaper | Basic blue 9 | 390.00 | [18] |
| Poly-γ-glutamic acid | Basic blue 9 | 352.76 | This study |
| Treated peat | Basic green 4 | 350.00 | [19] |
| Coal | Basic blue 9 | 323.68 | [15] |
| Rice husk | Basic blue 9 | 312.00 | [15] |
| Clay | Basic blue 9 | 300.00 | [20] |
| Poly-γ-glutamic acid | Basic green 4 | 293.32 | This study |
| Cotton waste | Basic blue 9 | 277.78 | [15] |
| Activated sludge biomass | Basic blue 9 | 256.41 | [21] |
| TriSyl silicas | Basic green 4 | 208.00 | [22] |
| Activated furniture | Basic blue 9 | 200.00 | [23] |
| Jackfruit peel carbon | Basic green 4 | 166.37 | [24] |
| Hair | Basic blue 9 | 158.23 | [15] |
| Mango seed kernel powder | Basic blue 9 | 153.85 | [25] |
| *Spirodela polyrrhiza* biomass | Basic blue 9 | 144.93 | [26] |
| Activated tyres | Basic blue 9 | 130.00 | [23] |
| Activated sewage char | Basic blue 9 | 120.00 | [23] |
| *Pithophora* species | Basic green 4 | 117.65 | [27] |
| Pearl millet husk carbon | Basic blue 9 | 82.37 | [28] |
| Raw date pits | Basic blue 9 | 80.30 | [29] |
| Pyrolysed furniture | Basic blue 9 | 80.00 | [23] |
| Treated sawdust | Basic green 4 | 74.50 | [30] |
| Modified cyclodextrin | Basic blue 9 | 56.50 | [31] |
| Banana peel | Basic blue 9 | 20.80 | [32] |
| Iron humate | Basic green 4 | 19.20 | [33] |
| Orange peel | Basic blue 9 | 18.60 | [32] |
| Activated date pits (900 °C) | Basic blue 9 | 17.30 | [29] |
| Sugarcane dust | Basic green 4 | 4.88 | [34] |
| Neem sawdust | Basic green 4 | 3.42 | [35] |

Table 4
Separation factor $R_L$ for dye sorption onto γ-PGA

| Initial dye concentration, $C_0$ (mg/l) | Separation factor ($R_L$) | |
| | BB9/γ-PGA | BG4/γ-PGA |
|---|---|---|
| 10 | 0.1354 | 0.4838 |
| 20 | 0.0726 | 0.3191 |
| 30 | 0.0496 | 0.2380 |
| 40 | 0.0377 | 0.1898 |
| 50 | 0.0304 | 0.1579 |
| 60 | 0.0254 | 0.1351 |
| 80 | 0.0192 | 0.1049 |
| 100 | 0.0154 | 0.0857 |
| 120 | 0.0129 | 0.0724 |
| 140 | 0.0111 | 0.0627 |
| 160 | 0.0097 | 0.0553 |
| 200 | 0.0078 | 0.0448 |

of 100 mg/l. This result suggests rapid surface adsorption of dyes on γ-PGA. The rate and order of the reaction are the important factors required when designing a batch sorption system. The kinetic data were initially fitted with a simple pseudo first-order equation [37]:

$$q_t = q_e[1 - \exp(-k_1 t)] \tag{7}$$

where $k_1$ (l/min) is the first-order rate constant. The fitted curves (Fig. 5) and the error functions (Table 5) revealed that the kinetic data were not predicted well by the pseudo first-order kinetic equation. Therefore, the kinetic data was also fitted with the Ho and McKay pseudo second-order model [38], which is based on the assumption that the sorption process involves chemisorption mechanism. The differential equation of such reactions can be
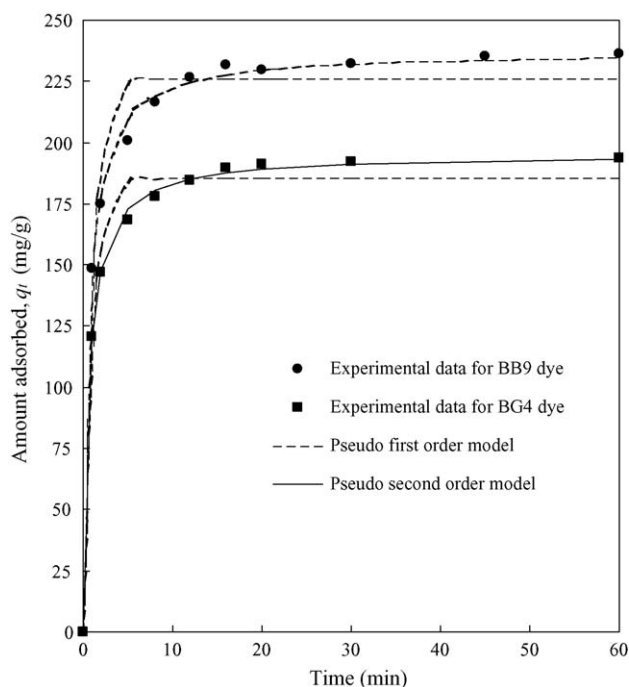
for sorption of BB9 and BG4 by various non-conventional adsorbents (Table 3) revealed γ-PGA was an effective adsorbent in removing basic dyes. Similarly, the essential features of the Langmuir isotherm can be expressed by a dimensionless constant separation factor or equilibrium parameter $R_L$ [36], which is defined as $R_L = 1/(1 + b_L C_0)$, where $b_L$ is the Langmuir constant. The value of $R_L$ indicates the shape of isotherm to be either unfavorable ($R_L > 1$) or linear ($R_L = 1$) or favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Accordingly, the $R_L$ values present in Table 4 indicate the favorable uptake of BB9 and BG4 dyes by γ-PGA.

### 3.2. Sorption kinetics

Process performance and ultimate cost of a sorption system has been shown to depend upon the effectiveness of process design and efficiency of process operation, which often requires an understanding of the kinetics of uptake or the time dependence of the concentration distribution of the solute in both bulk solution and solid adsorbent. The time–profile curves for sorption of BB9 and BG4 dyes by γ-PGA are illustrated in Fig. 5. The kinetic plots depicted that the sorption was very rapid with maximum uptake (95%) taking place within 12 min and attains equilibrium at 45 min for an initial dye concentration



Fig. 5. Kinetic curves with fitted models for sorption of basic dyes on γ-PGA Dye concentration: 100 mg/l; γ-PGA dose: 0.4 g/l; pH: 5.45 for BB9 and 5.65 for BG4; temperature: 28 ± 0.5 °C.

Table 5
Fitted parameters of the kinetic models with error functions $r^2$ and $\chi^2$ for sorption of basic dyes on γ-PGA

| Dye | Pseudo first-order model | | | | Pseudo second-order model | | | | | Ion-exchange model | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $q_e$ (mg/g) | $k_1$ (l/min) | $r^2$ | $\chi^2$ | $q_e$ (mg/g) | $k_2$ (g/mg min) | $h$ (mg/g min) | $r^2$ | $\chi^2$ | $S$ (l/min) | $r^2$ |
| BB9 | 226.17 | 0.8995 | 0.848 | 6.45 | 237.22 | $6.37 \times 10^{-3}$ | 358.44 | 0.981 | 0.80 | 0.1918 | 0.997 |
| BG4 | 185.45 | 0.9227 | 0.882 | 3.68 | 195.25 | $7.91 \times 10^{-3}$ | 301.66 | 0.992 | 0.25 | 0.1799 | 0.988 |

expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

where $k_2$ (g/mg min) is the pseudo second-order rate constant. Rearranging the variables in Eq. (8) gives

$$\frac{dq_t}{(q_e - q_t)^2} = k_2\,dt \tag{9}$$

integrating Eq. (9) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$ gives

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{10}$$

if the initial sorption rate is $h = k_2 q_e^2$, then Eq. (10) becomes

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \tag{11}$$

when the experimental data was fitted with Eq. (11), a much closer fit was observed as shown in Fig. 5 for both systems studied. The fitted sorption parameters $q_e$, $k_2$ and $h$ along with the error functions were determined and are summarized in Table 5. A relatively higher $r^2$ and lower $\chi^2$ values obtained for this model implied the sorption of BB9 and BG4 dyes by γ-PGA to follow a pseudo second-order reaction. This phenomenon suggests that the process controlling the rate may be a chemical sorption, which involves valence forces through sharing or exchange of electrons between γ-PGA and dyes [27,38].

As γ-PGA is an anionic polymer containing numerous carboxylic groups, the chemical sorption of cationic dyes may involve an electrostatic interaction between the carboxylate anions (COO$^-$) of γ-PGA and the cation part of the dye molecules. This is evidenced by a sharp decrease in pH of the solution during the initial 5-min reaction period, which accounts for about 85% of dye sorption. Consequently, the kinetic data were analyzed using an ion-exchange model proposed by Boyd et al. [39], who postulated the adsorption kinetics for exchange sorption of ions by organic zeolites to be a chemical phenomenon. The exchange reaction between two monovalent ions can then be expressed according to the mass law as

$$A^+ + BR \rightleftharpoons B^+ + AR \tag{12}$$

If $m_{A^+}$ and $m_{B^+}$ denote the concentration of the ions $A^+$ and $B^+$ in solutions and $n_{AR}$ and $n_{BR}$ the moles of $A^+$ and $B^+$ in the

sorbent, then the net reaction rate can be written as follows:

$$\begin{aligned}\frac{dn_{AR}}{dt} &= k_1 m_A + n_{BR} - k_2 m_B + n_{AR} \\ &= -n_{AR}(k_1 m_{A^+} + k_2 m_{B^+}) + k_1 m_{A^+} E \end{aligned} \tag{13}$$

where $k_1$ and $k_2$ are the forward and reverse specific rate constants, respectively, and $E$ is a constant defined by $E = n_{AB} + n_{BR}$. When both concentrations of $A^+$ and $B^+$ in solution are kept constant, then, on integration, Eq. (13) becomes

$$n_{AR} = \frac{k_1 m_{A^+} E}{k_1 m_{A^+} + k_2 m_{B^+}}(1 - e^{-St}) = q_t \tag{14}$$

where $S = k_1 m_{A^+} + k_2 m_{B^+}$, and Eq. (14) can be rewritten as

$$\log(1 - F) = -\left(\frac{S}{2.303}\right)t \tag{15}$$

where $F$ is the fractional attainment of equilibrium at time $t$, obtained by the ratio between the amounts adsorbed at time $t$ and at infinite time ($F = q_t / q_\infty$), and $S$ (l/min) is a constant.

Plotting of $\log(1 - F)$ against time $t$ gave straight-line curves (Fig. 6) for both the systems and the rate parameter $S$ values calculated from the slope of the respective linear plots are presented in Table 5. A large $r^2$ value indicated high correlation
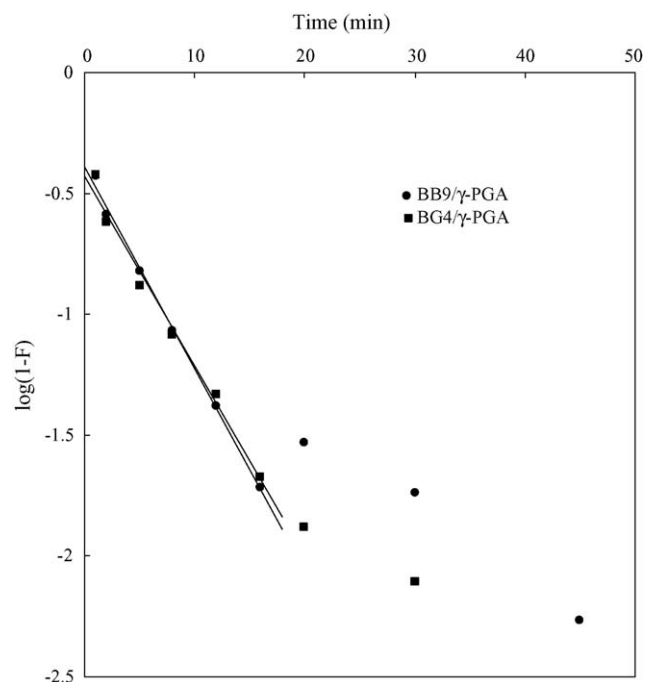


Fig. 6. Typical McKay's plots of $\log(1 - F)$ vs. time.

between the experimental data and the theoretical curves, which further proves the validity of this model for the present sorption systems. The deviation of experimental points beyond 16 min can be regarded as insignificant since the main sorption (98% of total dye) was already accomplished. An analogous trend was also reported for sorption of lead on tree fern [40]. Thus, the rate of uptake of BB9 and BG4 dyes by γ-PGA is mainly determined by the ion-exchange phenomenon.

From the practical viewpoint, it is necessary to establish the rate-determining step of a sorption process. Generally, any sorption process involves three main successive transport steps which are (i) film diffusion, (ii) intraparticle or pore diffusion and (iii) sorption onto interior sites. Among the three steps, the last step is considered negligible as it is assumed to be rapid and hence the rate of sorption should be controlled by either film diffusion or pore diffusion depending on which step is slower. Therefore, the kinetic data were further analyzed with a Boyd kinetic expression proposed for particle-controlled diffusion [39] given by

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2 Bt] \qquad (16)$$

$$B = \frac{\pi^2 D_i}{r_0^2} \qquad (17)$$

where $r_0$ (cm) represents the radius of the adsorbent particle determined by sieve analysis, $D_i$ (cm$^2$/s) the effective diffusion coefficient and $B$ is the time constant. As shown by Reichenberg [41], the $Bt$ values can be calculated for each value of $F$ and are plotted against time $t$ (plots not given). The plots obtained were linear, however, did not pass through the origin, which confirms that film-diffusion or external mass transport mainly governs the sorption process [25,27] for the dye concentration studied. This also suggests that during initial stages of adsorption, the intraparticle resistance is negligible. Assuming γ-PGA particles were spherical in nature, the effective diffusion coefficient $D_i$ values were determined using Eq. (17) and are $1.54 \times 10^{-4}$ and $1.55 \times 10^{-4}$ cm$^2$/s, respectively, for BB9 and BG4 dyes sorption by γ-PGA. Similar $D_i$ values in the order of $10^{-4}$ cm$^2$/s were also reported for film-diffusion controlled sorption of BB9 dye on mango seed kernel powder [25].

Furthermore, it was reported elsewhere [25] that film diffusion controls the sorption for a system with poor mixing, diluted concentration of solutes, small particle sizes of adsorbent and higher sorbate/sorbent interaction, while the pore diffusion is the rate-controlling step when the opposite is true. Apparently, the small-sized γ-PGA particles (1–150 μm) used with poor mixing (120 rpm) and less equilibrium time required due to high dye/γ-PGA interaction in the present systems ascertain that the exchange reaction through film diffusion is the process that dictates the overall sorption rate for the dye concentration studied.

### 3.3. Effect of pH on adsorption/desorption

The pH value of the solution is an important factor that determines the adsorption or desorption of solutes when the sorption principally occurs through chemisorption mechanism.
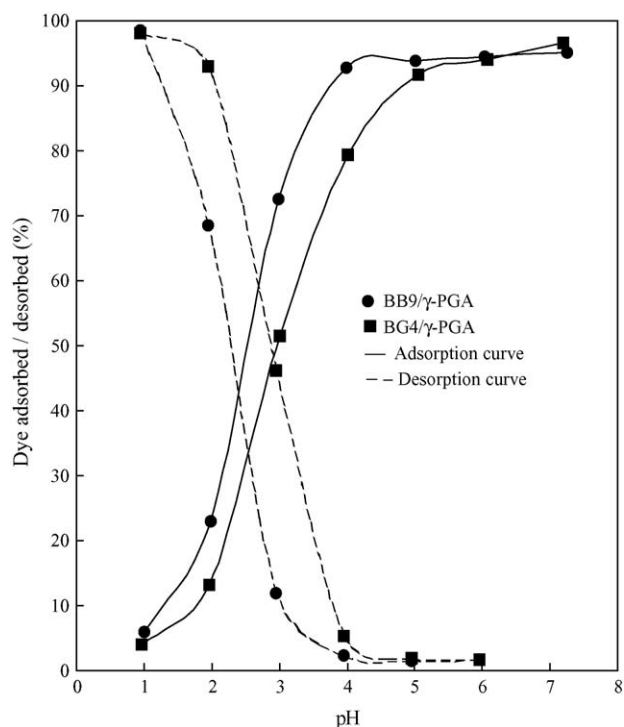


Fig. 7. Effect of pH on adsorption/desorption of basic dyes. Adsorption experiments—dye concentration: 100 mg/l; γ-PGA dose: 0.4 g/l; pH range: 1–7; temperature: 28 ± 0.5 °C; equilibrium time: 1 h. Desorption experiments—dye concentration: 100 mg/l; γ-PGA dose: 0.4 g/l; pH range: 1–6; temperature: 28 ± 0.5 °C; equilibrium time: 30 min.

The effect of initial pH on the dye sorption by γ-PGA showed a clear trend as indicated by solid lines in Fig. 7. With the initial dye concentration at 100 mg/l, the dye adsorption increased from 5.9 to 93.9% and 4.0 to 91.8% for BB9 and BG4, respectively, when the pH value of the dye solution was raised from 1 to 5. This outcome may be explained as follows: at low pH values, the excessive hydrogen ions in the solution may compete with the dye cations for the active sites (COO$^-$) of γ-PGA and hence a reduction in dye uptake was observed. Moreover, the reported p$K_a$ value (4.29) of glutamic acid in the protein p$K_a$ database (PPD) [42], which is mainly due to the ionizable group –COOH, suggests that the dye solution at pH above this p$K_a$ value would cause the –COOH group in γ-PGA to get completely deprotonated facilitating maximum exchange of dye cations. The sorption through exchange of ions is favored at high pH values especially when the sorption rate is largely controlled by ion exchange rather than by complexation [14,40]. This is further confirmed by a significant change in the initial pH value, due to the exchange of dye cations with concomitant release of hydrogen ions, when the dye solutions were equilibrated with γ-PGA by adjusting pH to 7, 6, 5 and 4 (Fig. 8). The dependence of BB9 dye sorption on the availability of carboxylic acid groups in the cyclodextrin-based adsorbents has been demonstrated by Crini and Peindy [31].

Desorption study performed with distilled water at different pH values (1–6) showed exactly a reversed trend (denoted by dotted lines in Fig. 7) when compared to that observed during dye uptake at varying pH, proving that the ion-exchange mechanism
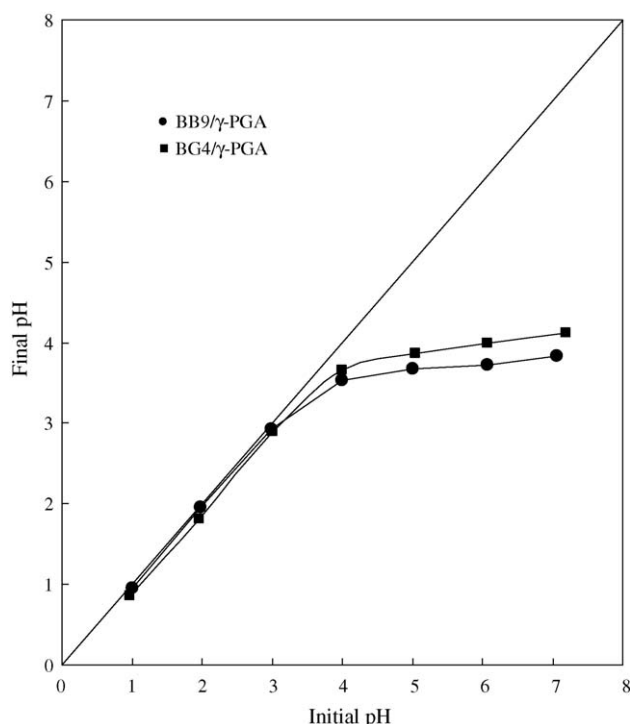
Fig. 8. Effect of initial pH on final pH for sorption of basic dyes on γ-PGA.

[14] is involved in dye sorption. A higher desorption of about 98% of both BB9 and BG4 dyes from the spent γ-PGA was achieved at pH 1. This result further extends the potential reuse of γ-PGA by subjecting the spent γ-PGA to proper regeneration procedures without losing its physico-chemical characteristics.

## 4. Conclusions

The study has demonstrated the biopolymer, γ-PGA to be a suitable adsorbent for the removal of basic dyes BB9 and BG4 from aqueous solution. Isotherm models showed that the equilibrium data were well described by a three-parameter Redlich-Peterson isotherm equation. The monolayer sorption capacity determined was reasonably high: 352.76 and 293.32 mg/g for BB9 and BG4 dyes, respectively. The sorption process was rapid and the kinetics of BB9 and BG4 dyes sorption followed a pseudo second-order reaction, suggesting a chemisorption mechanism. In addition, the Boyd's ion-exchange model also precisely fitted the kinetic data thus revealing that the uptake rate of dyes by γ-PGA was controlled by chemical sorption involving exchange of ions. Film diffusion was identified as the rate-determining step in the sorption process. Maximum dye uptake at high pH values, decrease in initial pH after equilibration with γ-PGA, and maximum desorption of dyes from the spent γ-PGA at pH 1 further substantiated the previous statements.

As γ-PGA by itself is non-toxic and biodegradable, the adsorption system developed could offer green solutions to the global dye application industry. The treatment cost can be substantially reduced by efficiently recycling the γ-PGA as almost complete recovery of dyes from spent γ-PGA could be accomplished. Further study is warranted to develop suitable regeneration methods to reuse γ-PGA for multi-operational cycles and perform sorption studies under non-equilibrium condition in fixed beds.

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