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# The removal of Basic Blue 3 from aqueous solutions by chitosan-based adsorbent: Batch studies

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**Abstract**

Chitosan-based adsorbent (CHITOD material) is used for the removal of Basic Blue 3 (BB 3) from aqueous solutions. The adsorption of BB 3 on CHITOD material was studied as a function of time, sorbent mass and concentration. The influence of these parameters on the adsorption capacity was evaluated using the batch method. Results of adsorption experiments and kinetic data showed that (i) the CHITOD adsorbent exhibited high sorption capacities toward BB 3; (ii) the Langmuir equation represented the best fit of experimental data; (iii) the dye sorption on material was exothermic and spontaneous in nature; (iv) the kinetic measurements showed that the process was rapid; (v) the adsorption kinetics followed a pseudo-second order model; and (vi) the sorption was dependent on the presence of sulfonate groups. Non-linear method was also found to be more appropriate method for estimating the isotherm and kinetic parameters.


*Keywords:* Chitosan; Adsorbent; Adsorption; Basic Blue 3; Cationic dye; Batch method; Kinetic and isotherm models; Correlation coefficient; Chi-square

## 1. Introduction

Chitosan, a linear copolymer composed of (1–4)-linked D-glucosamine and *N*-acetyl-D-glucosamine, is a polysaccharide prepared by *N*-deacetylation of chitin (second abundant polymer in nature after cellulose) [1]. Chitin is obtained from the exoskeleton of crustaceous, the cuticles of insects and the cell walls of fungi. However, chitin and chitosan are only commercially extracted from crustaceans (crab, krill, crayfish) primarily because a large amount of the crustacean's exoskeleton is available as a by-product of food processing.

As a functional biological polymer, chitosan offers an interesting set of characteristics, including non-toxicity, biodegradability, biocompatibility, bioadhesivity, and bioactivity. This material also presents economical advantages (in many countries fishery wastes are low-cost sources and suitable for producing chitosan) and exhibits remarkable physicochemical properties such as an hydrophilic character, a sufficient flexibility of the linear chain, an easy chemical derivatization, a capability to interact and to adsorb various substrates, and cationic properties which are unique among abundant polysaccharides.

Chitosan and its derivatives exhibit innumerable applications in a wide range of fields such as food [2,3], pharmacy [4–6], biomedicine [7–9], cosmetics [10], biotechnology [10,11] and agriculture [10,12]. These versatile materials are also widely applied in the textile, pulp and paper industries [10], and in clarification and water purification [13–24] as coagulating [13,14], flocculating [15,16], chelating [10,17,18] and complexing agents [10,17,18]. Different reviews have recently been reported for wastewater treatment purposes, including metal complexation [19,20], dye removal [21], complexing adsorbent matrices [22,23], and membranes [24].

As already mentioned, chitosan has widely been studied for pollutant adsorption from aqueous solutions: the cationic character, along with the presence of reactive functional groups in polymer chains, has given it particular possibilities as efficient adsorbent agents. It is evident from the abundant literature data

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**Nomenclature**

| | |
|---|---|
| $a_L$ | Langmuir isotherm constant (l/mg) |
| $A$ | Temkin isotherm constant (l/g) |
| $B$ | Temkin isotherm constant |
| $C_e$ | liquid phase dye concentration at equilibrium (mg/l) |
| $C_o$ | initial dye concentration in liquid phase (mg/l) |
| $k_1$ | equilibrium rate constant of pseudo-first order sorption ($min^{-1}$) |
| $k_2$ | equilibrium rate constant of pseudo-second order sorption (g/mg min) |
| $k_i$ | intraparticle diffusion rate constant ($mg/g\ min^{-1/2}$) |
| $K$ | saturation constant (mg/l) |
| $K_F$ | Freundlich constant (l/g) |
| $K_L$ | Langmuir isotherm constant (l/g) |
| $m$ | mass of adsorbent used (g) |
| $n$ | cooperative binding constant |
| $n_F$ | Freundlich isotherm exponent |
| $q_e$ | amount of dye adsorbed at equilibrium (mg/g) |
| $q_{max}$ | maximum adsorption capacity of the adsorbent (mg/g) |
| $q_t$ | amount of dye adsorbed at time $t$ (mg/g) |
| $r^2$ | non-linear correlation coefficient |
| $R^2$ | linear correlation coefficient |
| $t$ | time (min) |
| $t_e$ | equilibrium time (min) |
| $V$ | volume of dye solution (l) |
| $x$ | amount of dye adsorbed (mg) |

*Greek symbols*

| | |
|---|---|
| $\alpha$ | initial adsorption rate (mg/g min) |
| $\beta$ | Elovich desorption constant (g/mg) |
| $\chi^2$ | Chi-square test statistic |

that this biomaterial offers a great potential in the adsorption field and might be a promising adsorbent for environmental purpose [19–22]. In particular, one of the major applications is based on its ability to bind strongly heavy and toxic metals. It represents an attractive alternative to other conventional commercial adsorbents because of its low cost and local availability, high reactivity, excellent chelation behavior and high selectivity towards heavy metals [17,19,20].

Chitosan is also known as an effective adsorbent for proteins [25], saccharides [26], drugs [27], oils [28], bacterial suspensions [29], phenolic derivatives [17,30,31], and also for dye wastewater removal [10,21]. In recent years, numerous studies on chitosan-based biomaterials for dye removal demonstrated that these versatile biosorbents are efficient and have a high affinity for many classes of dyes [32–47], including acid, direct, mordant, reactive and disperse dyes (Table 1). However, only a limited number of published studies can be found on the use of chitosan as an adsorbent for cationic (basic) dye removal.

In this paper, we propose chemical grafting of sulfonate groups onto chitosan as a means to confer the ability to adsorb basic dyes, in particular Basic Blue 3 (BB 3). Several adsorption and kinetic studies are presented and discussed here. The equilibrium data were analyzed using Freundlich, Langmuir, Temkin and Generalized isotherms. In order to investigate the mechanism of sorption, adsorption data were modeled using the pseudo-second order kinetic equation, Elovich equation and intraparticle diffusion model. The characteristics parameters for each model were determined. A comparison was made between the linear and non-linear methods of estimating isotherm and kinetic parameters.

## 2. Experimental

### 2.1. Adsorbents

Two chitosan-based sorbents, namely CHITO and CHITOD, were used in this study. Their characteristics are reported in Table 2. CHITO (prepared from crab shells, degree of acetylation = 20%) was supplied by Protan (USA). CHITOD was prepared in one step by reacting chitosan with 4-formyl-1,3-benzene sodium disulfonate in the presence of sodium cyanoborohydride (Fig. 1). The synthesis of CHITOD has already been described in detail in previous works [48,49].

### 2.2. Dye

The sorption capacity was investigated using C.I. Basic Blue 3 (BB 3, Classification Number 51004; chemical class monox-

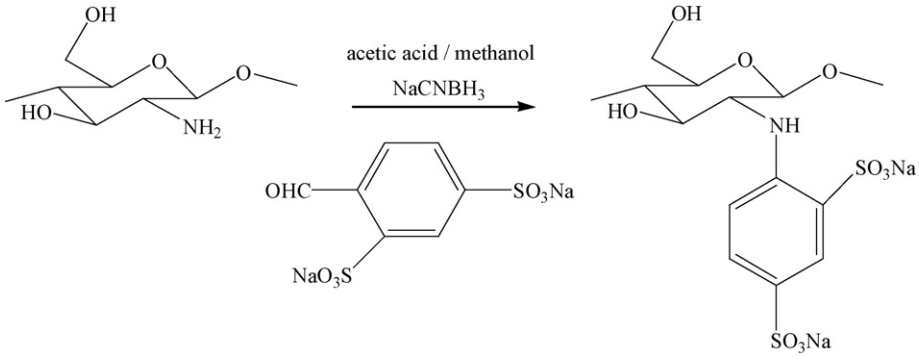


Fig. 1. Synthesis of CHITOD.

Table 1
Recent research on dye capture by chitosan-based adsorbents (selected papers)

| Dye investigated | Classification | Chemical type | $q_{max}$[a] | Reference |
|---|---|---|---|---|
| Acid black 1 | Anionic | Diazo | 800[b] | [38] |
| Acid blue 113 | Anionic | Diazo | 250[b] | [38] |
| Acid orange 7 | Anionic | Monoazo | 1940 | [35] |
| Acid orange 10 | Anionic | Monoazo | 922.9 | [36] |
| Acid orange 12 | Anionic | Monoazo | 1883 | [33] |
| Acid orange 12 | Anionic | Monoazo | 1954 | [35] |
| Acid orange 12 | Anionic | Monoazo | 973.3 | [36] |
| Acid green 25 | Anionic | Anthraquinone | 1471 | [33] |
| Acid green 25 | Anionic | Anthraquinone | 645.1 | [36] |
| Acid green 25 | Anionic | Anthraquinone | 525 | [37] |
| Acid green 25 | Anionic | Anthraquinone | 850[b] | [38] |
| Acid red 14 | Anionic | Monoazo | 1940 | [35] |
| Acid red 18 | Anionic | Monoazo | 693.2 | [36] |
| Acid red 73 | Anionic | Diazo | 728.2 | [36] |
| Acid violet 5 | Anionic | Monoazo | 160[b] | [38] |
| Acid yellow 25 | Anionic | Monoazo | 220[b] | [38] |
| Metanil yellow | Anionic | Monoazo | 1334 | [32] |
| Direct blue 14 | Anionic | Diazo | 90[b] | [38] |
| Direct red 81 | Anionic | Diazo | 2383 | [35] |
| Direct yellow 4 | Anionic | Diazo | 620 | [38] |
| Mordant blue 29 | Anionic | Triphenylmethane | 420[b] | [38] |
| Mordant brown 33 | Anionic | Monoazo | 2000[b] | [38] |
| Mordant orange 10 | Anionic | Diazo | 1600[b] | [38] |
| Reactive black 5 | Anionic | Diazo | 440[b] | [38] |
| Reactive black 5 | Anionic | Diazo | 750–1000[b] | [44] |
| Reactive blue 2 | Anionic | Anthraquinone | 2498 | [35] |
| Reactive red 2 | Anionic | Monoazo | 2422 | [35] |
| Reactive red 141 | Anionic | Diazo | 67.9 | [46] |
| Reactive yellow 2 | Anionic | Monoazo | 2436 | [35] |
| Reactive yellow 86 | Anionic | Monoazo | 1911 | [35] |
| Basic Blue 9 | Cationic | Thiazine | 330[b] | [43] |
| Basic violet 3 | Cationic | Triphenyl methane | 1546[b] | [40] |

[a] $q_{max}$: monolayer adsorption capacity in mg/g.
[b] In μmol/g.

Table 2
Characteristics of chitosan-based adsorbents

| Adsorbents | Source | Type | BET[a] | $SO_3^-$ content[b] | DS[c] |
|---|---|---|---|---|---|
| CHITO | Crab | Bead | 18 | 0 | |
| CHITOD | Crab | Powder | 25 | 3.1 | 83 |

[a] Specific surface areas, in $m^2/g$.
[b] In meq/g, from potentiometric method.
[c] Degree of substitution in %, from NMR data.

azine; MW 359.9 g/mol) as model guest solute. This cationic dye was commercial product and used without purification (see Fig. 2 for the structural formulae). An accurately weighted quantity of the dye was dissolved in double-distilled water to prepare stock solution (200 mg/l). Experimental solutions of the desired concentrations were obtained by successive dilutions. The calculated concentrations take into account the dye purity. Dye concentration in solutions was determined spectrophotometrically using a UV/vis Uvikon spectrophotmeter (UVK-Lab-Serlabo, France). The dye solution was initially calibrated for concentration in terms of absorbance unit.

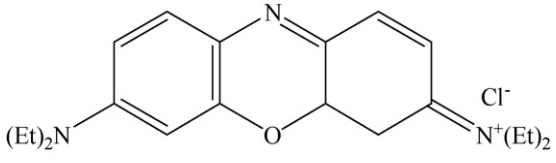


Fig. 2. Chemical structure of C.I. 51004 Basic Blue 3 (BB 3, chemical class: monoxazine).

### 2.3. Sorption of BB 3 by batch technique

Adsorption isotherms and kinetics were determined by the batch method. In each experiment, a fixed mass of chitosan was mixed with 20 ml of a NaCl 0.1 mol/l aqueous solution of BB 3 at a known concentration in a tightly closed flask. The initial pH of the solution was adjusted to $3.0 \pm 0.1$. The solution was then stirred on a rotating shaker at $25\,^{\circ}C \pm 1\,^{\circ}C$. Initial pollutant concentration in the solution was varied to investigate its effect on the adsorption capacity. Studies were also conducted for various time intervals to determine when adsorption equilibrium was reached. The dye concentration of the supernatant was determined by spectrophotometry at 654 nm. Before measurement of the dye concentration, the mixture was filtered through a membrane filter. Blanks were run without any adsorbent to determine the extent of dye removal by filter.

### 2.4. Error analysis

In the single-component isotherm studies, the optimization procedure requires an error function to be defined in order to quantitatively compare the applicability of different models in fitting to data. To determine isotherm constants for two-parameter isotherms, two methods are available: fitting the isotherm equation to the data in its non-linear form or converting the equation in a linear form by transforming the isotherm variables. In this study, both linear and non-linear coefficients of determination were determined. Moreover, as it is also necessary to analyze the data set to confirm the best-fit isotherm for the sorption system, the Chi-square test was used. The Chi-square test statistic ($\chi^2$) is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The values were calculated for the non-linear models but also for their linearized forms, using back-transformation of the calculated data to allow both forms to be compared. If modeled data are similar to the experimental data, $\chi^2$ will be a small number; if they are different, $\chi^2$ will be a large number.

## 3. Results and discussion

### 3.1. Adsorption of BB 3 on chitosan-based adsorbents

Fig. 3 shows the sorption capacity (expressed in percentage uptake, $R$ in %) of Basic Blue 3 (BB 3) on two chitosan-based adsorbents, raw chitosan (CHITO) and modified chitosan (CHITOD), respectively without and with sulfonate groups. Preliminary kinetic experiments had shown that 40 min contact time was sufficient for reaching sorption equilibrium. The experiments were performed in triplicate under identical conditions and were found reproducible (experimental error within 3%). $R$ was calculated from:

$$R = \frac{100(C_o - C_e)}{C_o}$$

where $C_o$ and $C_e$ are the initial and equilibrium concentrations of BB 3 in solution (mg/l), respectively.

As expected, BB 3 did not interact with raw chitosan ($R = 7\%$) at pH 6.5. The sorption capacity was very low due to weak electrostatic interactions between the dye and polymer. As a matter of fact, BB 3 is a basic dye containing cationic functions (see Fig. 2) and chitosan presents a certain neutrality in the experimental pH conditions. For CHITOD, which contained sulfonate groups, an increase of the sorption capacity was observed ($R = 45\%$). As described in Table 2, no drastic changes in the specific surface area values of the samples were observed, suggesting that the differences in the capacities of the CHITOD sample were mainly due to its sulfonate groups content. This result clearly demonstrated that these groups contributed to the sorption mechanism through electrostatic interactions between $SO_3^-$ groups of the sorbent (which are known as strong cation exchangers) and the cationic sites of BB 3. Fig. 3 also shows the influence of the presence of NaCl on the adsorption capacity. Addition of NaCl produced an important increase of the performance of the adsorbent ($R = 84\%$). This showed that the sorption capacities depended on the ionic strength of the solution. Elsewhere, NaCl is currently used in textile dyeing processes as it promotes the sorption of the dyes by the fibers.

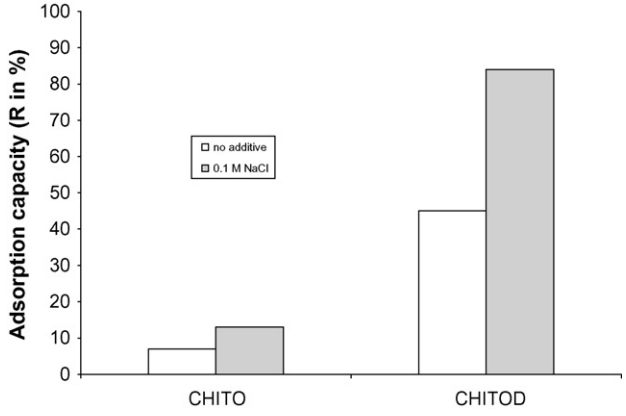


Fig. 3. Comparison between adsorption capacity ($R$ in %) of BB 3 on raw chitosan (CHITO) and modified chitosan (CHITOD) (*conditions*: dye concentration = 40 mg/l; contact time = 40 min; NaCl concentration = 0.1 mol/l; pH 6.5).

### 3.2. Equilibrium studies

#### 3.2.1. Influence of the initial dye concentration on adsorption capacity

The dye concentration at equilibrium ($q_e$ in mg/g) was plotted against equilibrium concentration ($C_e$ in mg/l) (Fig. 4). This figure shows the relationship between the amount of BB 3 adsorbed per mass unit of chitosan and its final concentration in the solution. The quantity of sorbent was kept constant. $q_e$ (in mg/g) was

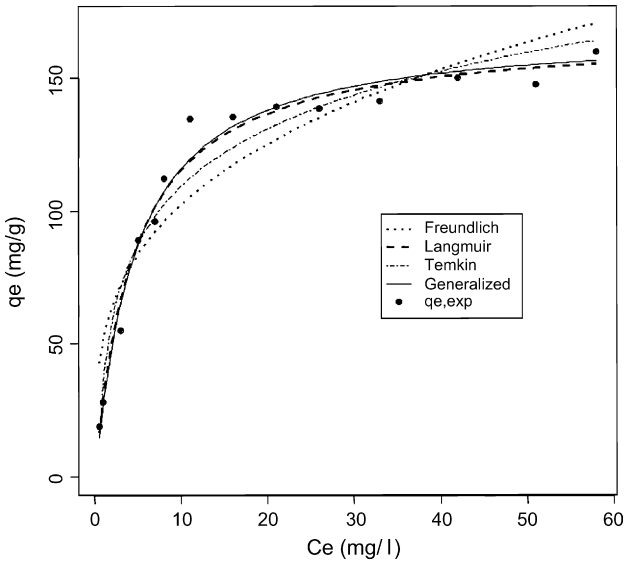


Fig. 4. Adsorption isotherm for BB 3 by CHITOD adsorbent: experimental data and comparison of four isotherm models (*conditions*: sorbent = 40 mg; contact time = 40 min; NaCl concentration = 0.1 mol/l; pH 3; temperature = 25 °C).

calculated using the following relationships:

$$q_e = \frac{V(C_o - C_e)}{m}$$

where $C_o$ and $C_e$ are the initial and equilibrium concentrations of dye in solution (mg/l), respectively; $V$ is the volume of dye solution used (l); and $m$ is the mass of sorbent used (g).

Fig. 4 clearly indicates that the sorption capacity initially strongly increases with the initial concentration in BB 3 and then tends to a plateau. This is due to the saturation of the sorption sites on the adsorbents.

### 3.2.2. Adsorption equilibrium models

In order to optimize the design of an adsorption system to remove dye from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Adsorption equilibrium is established when the amount of dye being adsorbed onto the adsorbent is equal to the amount being desorbed. It is possible to depict the equilibrium adsorption isotherms by plotting the concentration of the dye in the solid phase versus that in the liquid phase. Several isotherms models can be used to describe the equilibrium of adsorption. Four common isotherm equations were tested in the present study: Langmuir [50,51], Freundlich [52], Temkin [53] and Generalized models [54]. These equations are given below:

$$\text{Langmuir}: \quad \frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{1}$$

$$\text{Freundlich}: \quad \ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \tag{2}$$

$$\text{Temkin}: \quad q_e = B \ln A + B \ln C_e \tag{3}$$

$$\text{Generalized}: \quad \ln\left[\frac{q_{max}}{q_e} - 1\right] = \ln K - n \ln C_e \tag{4}$$

In Eq. (1), $C_e$ (mg/l) and $q_e$ (mg/g) are the liquid phase concentration and solid phase concentration of an adsorbate at equilibrium, respectively; $K_L$ (l/g) and $a_L$ (l/mg) are the Langmuir isotherm constants. By plotting $C_e/q_e$ against $C_e$, it is possible to obtain the value of $K_L$ from the intercept which is $1/K_L$ and the value of $a_L$ from the slope, which is $a_L/K_L$. $q_{max}$ (mg/g) is the maximum adsorption capacity of the adsorbent and is numerically equal to $K_L/a_L$. $q_{max}$ is a constant related to the area occupied by a monolayer of adsorbate, reflecting the limiting adsorption capacity. In Eq. (2), $K_F$ is a constant (l/g) for the system, related to the bonding energy. The Freundlich constant can be defined as an adsorption or distribution coefficient and represents the quantity of dye adsorbed onto an adsorbent for an equilibrium concentration unit. $1/n_F$ (heterogeneity factor, ranging between 0 and 1) is a measure for the adsorption intensity or surface heterogeneity. A plot of $\ln q_e$ versus $\ln C_e$ enables the empirical constants $K_F$ and $1/n_F$ to be determined from the intercept and slope of the linear regression, respectively. In Eq. (3), $A$ and $B$ are the Temkin isotherm constants. The constant $B$ is related to the heat of adsorption. A plot of $q_e$ versus $\ln C_e$ enables one to determine the constants $A$ and $B$. In Eq. (4), $q_e$ and $C_e$ are as defined in Eq. (2); $K$ is the saturation constant (mg/l) and $n$ is the cooperative binding constant. $q_{max}$ is the theoretical monolayer capacity (as defined in Eq. (1)). A plot of the equilibrium data in form of $\ln[(q_{max}/q_e) - 1]$ versus $\ln C_e$ gives $K$ and $n$ constants. Applicability of the isotherm equations was compared by judging the correlation coefficients.

Fig. 5 shows a comparison of adsorption isotherms for curve fitting of the experimental results with above four adsorption

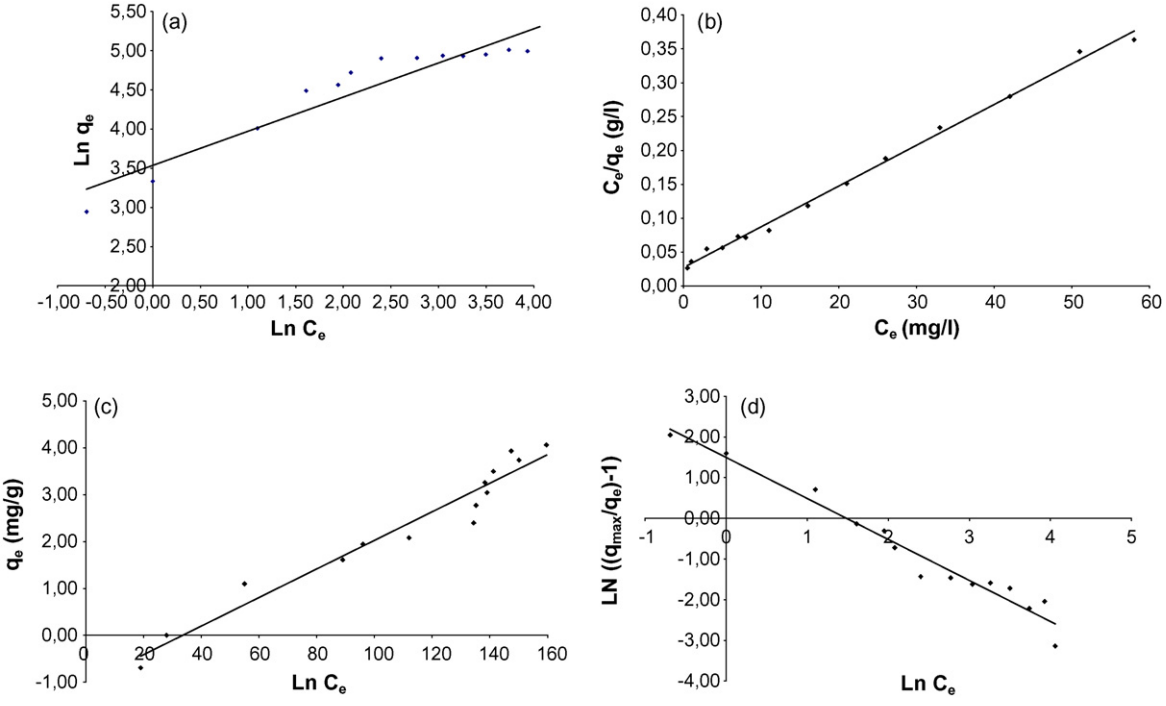


Fig. 5. Adsorption isotherms for Basic Blue 3 by CHITOD adsorbent (a) Freundlich isotherm; (b) Langmuir isotherm; (c) Temkin isotherm; and (d) Generalized isotherm.

Table 3
Summary of the isotherm constants, and comparison of linear ($R^2$) and non-linear ($r^2$) correlation coefficients and the Chi-square test statistics ($\chi^2$) for different isotherm models

| Isotherm | Linear form | | | Non-linear form | | |
|---|---|---|---|---|---|---|
| | Parameters | $R^2$ | $\chi^2$ | Parameters | $r^2$ | $\chi^2$ |
| Freundlich | $K_F = 34.28$ (l/g)<br>$n_F = 2.29$ | 0.8982 | 62.3484 | $K_F = 52.41$ (l/g)<br>$n_F = 3.44$ | 0.8738 | 46.6598 |
| Langmuir | $K_L = 37.03$ (l/g)<br>$a_L = 0.222$ (l/mg)<br>$q_{max} = 166.5$ (mg/g) | 0.9965 | 6.2125 | $K_L = 36.99$ (l/g)<br>$a_L = 0.221$ (l/mg) | 0.9787<br>$q_{max} = 167.4$ (mg/g) | 6.1897 |
| Temkin | $A = 3.30$ (l/g)<br>$B = 31.23$ | 0.9512 | 15.0866 | $A = 3.29$ (l/g)<br>$B = 31.23$ | 0.9512 | 15.0812 |
| Generalized | $K = 4.47$ (mg/l)<br>$n = 1.01$ | 0.9624 | 7.2147 | $K = 4.99$ (mg/l)<br>$n = 1.05$ | 0.9793 | 6.3741 |

isotherms. The model parameters from all isotherms obtained are presented in Table 3. Obviously, it can be seen in Fig. 5 that the Langmuir model was found to represent the equilibrium data with a much better fit as compared to the others models tested. On the basis of $R^2$ values, the experimental data were also correlated reasonably well by the Langmuir adsorption isotherm (the fit is well for the adsorption system under the concentration range studied). The Freundlich equation represented the poorest fit of experimental data than the other equations although the value of $n_F > 1$ reflects the favorable adsorption (Table 3). The Freundlich model is an empirical equation employed to describe heterogeneous systems and multilayer sites. The Temkin model also takes into account the presence of indirect dye/adsorbent interactions.

The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites on the material, since the Langmuir model assumes that the surface is homogeneous. This model is also based on monolayer, uniform and finite adsorption site assumptions, and there is no interaction between molecules adsorbed on neighbouring sites. It is also noted in Table 3 that the monolayer adsorption capacity (i.e., $q_{max} = 166.5$ mg/g) is significantly important: this adsorbent exhibited high sorption capacities toward cationic dye. A direct comparison of literature data using different chitosan-based materials is not possible since both adsorbents, dyes and experimental conditions are not the same. However, it was observed that the $q_{max}$ of the modified chitosan was comparable to those of the other available materials for cationic dye removal [21].

The free energy change ($\Delta G$) for adsorption at 25 °C was calculated using the following equation:

$$\Delta G = -RT \ln K_L \quad (5)$$

where $R$ is the gas constant (8.314 kJ/mol K); $T$ is the temperature and $K_L$ is the Langmuir constant. The calculated $\Delta G$ value was found to be −6.4 kJ/mol. The negative value of free energy change indicated the spontaneous nature of adsorption and confirmed the affinity of CHITOD material for BB 3.

### 3.2.3. Selection by error analysis

The equilibrium isotherm is an invaluable tool for the analysis and design of adsorption systems and also for the theoretical evaluation and interpretation of thermodynamic parameters. An isotherm may fit experimental data accurately under one set of conditions but fail entirely under another. No single model has been found to be generally applicable [55]. This is readily understandable in the light of the assumptions associated with their respective deviations. For example, the use of $R^2$ is limited to solving linear forms of isotherm equation which measure the difference between experimental data and theoretical data in linear plots only, but not the errors in isotherm curves. However, linear regression is the most commonly used technique to estimate the sorption. Recently, several studies showed that the linearization of a non-linear isotherm expression produces different outcomes. Wong et al. [36] showed that the values of the individual isotherm constants changed with the error methodology selected. They obtained contradicting results from linearization using different error functions. Similar observations also reported by Allen et al. [55]. Ho et al. [56] showed that linear regression and the non-linear Chi-square analysis gave different models as the best-fitting isotherm for the given data set, thus indicating a significant difference between the analytical methods. They reported that the non-linear Chi-square test provided a better determination for the experimental data.

In this study, both coefficients of correlation and Chi-square test statistics were used for both linear and non-linear forms of the isotherms. Fig. 4 shows the isotherms curves for BB 3 onto CHITOD adsorbent at 25 °C along with the experimental data. The curves were generated using the non-linearized equation of different equilibrium models. The Chi-square test statistic ($\chi^2$) and non-linear coefficient of correlation ($r^2$) were obtained and are shown in Table 3. Based on $\chi^2$ comparisons between models, it was observed that, in simulation, the equilibrium data were very well represented by the Langmuir isotherm model when compared to the others. There was a good agreement between the experimental values and the calculated values. According to the fitting method (linear or non-linear forms of the model), isotherm parameter estimates might change (Table 3). Accurate calculations of the $\chi^2$ for the linear and the non-linear forms of the models provide qualitative information to compare and

choose the best fitting method. Therefore, in our experimental conditions, the non-linear method appeared as a better way to obtain accurate model parameters for the four isotherms tested (Table 3). These results match up with those of Vasanth Kumar and Sivanesan [57] who recently showed the better efficiency of the non-linear method to estimate Langmuir, Freundlich and Redlich–Peterson parameters for basic dyes onto activated carbon.

### 3.3. Adsorption kinetics

#### 3.3.1. Effect of contact time

The adsorption data of BB 3 versus contact time is presented in Fig. 6. The adsorbate concentration in the solution ($q_t$ in mg/g) was determined at different times from 20 mg/l initial dye solutions and in the presence of 10, 20 and 40 mg of sorbent. All the experiments were realized at pH 3 and at 25 °C ± 1 °C. The plots representing the dye adsorption by chitosan can be split in three distinct regions: the first one indicates the instantaneous sorption of the dye within 4 min of contact time, suggesting rapid external diffusion and surface adsorption; the second one shows a gradual equilibrium and the third one indicates the equilibrium state. The amount of dye adsorbed increased with contact time and this confirmed strong interactions between the dye and the material driven by electrostatic interactions between the cationic dye and the $SO_3^-$ groups of CHITOD. The kinetics of sorption were fast (the equilibrium time, $t_e$, was found to be 40 min in the three experiments) and was independent from the mass of sorbent present in the batch. Fig. 6 also displays that $q_t$ increased proportionally with regard to the amount of sorbent. $q_t$ increased from 33.5 to 134.5 mg/g as the adsorbent dose was increased from 10 to 40 mg. The plots are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of dye on the surface of the adsorbent, and this confirms the applicability of the Langmuir model.

#### 3.3.2. Kinetic models

The kinetics of dye adsorption on the sorbent were analyzed using pseudo-second order and Elovich kinetic models. The

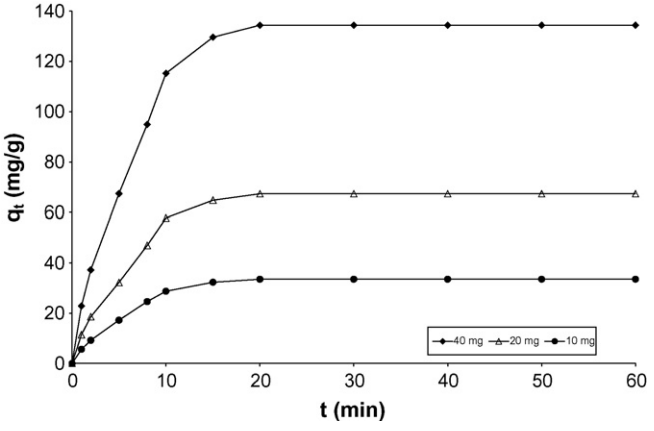


Fig. 6. Kinetics of adsorption capacity of BB 3 by CHITOD adsorbent at three concentrations in the batch (10, 20 and 40 mg) (*conditions*: dye concentration = 20 mg/l; NaCl concentration = 0.1 mol/l; pH 3; temperature = 25 °C).

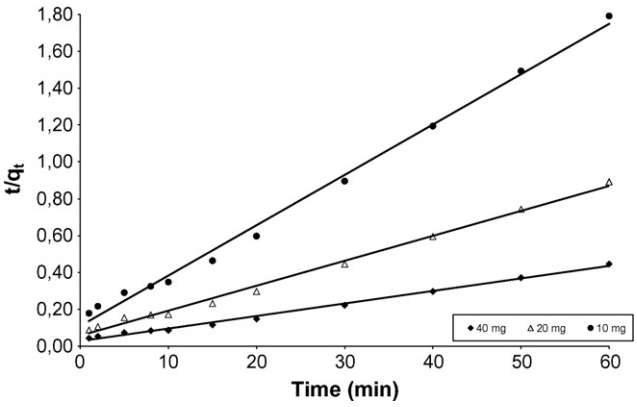


Fig. 7. Pseudo-second order kinetics of BB 3 adsorption onto CHITOD adsorbent at three concentrations in the batch (10, 20 and 40 mg), according to the pseudo-second order kinetic model proposed by Ho and McKay [56,57].

pseudo-second order model proposed by Ho and McKay [58,59] can be represented in the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where $q_t$ (mg/g) and $q_e$ (mg/g) are the amount of dye adsorbed at time $t$ and equilibrium, respectively; and $k_2$ is the equilibrium rate constant of pseudo-second order sorption (g/mg min). The parameters $k_2$ and $q_e$ can be directly obtained from the intercept and slope of the plot of $t/q_t$ against $t$.

To find the order of the kinetics of adsorption of BB 3, the first-order kinetic equation was tested but no linear correlation was observed. Then, $t/q_t$ versus time graphs were plotted, as shown in Fig. 7. The $k_2$ and $q_{e,calc}$ values, computed from Eq. (6) along with calculated correlation coefficients are listed in Table 4. It is clear that the kinetics of dye adsorption on material followed this model, suggesting that chemisorption might be the rate-limiting step that controlled the adsorption process. The plots gave a linear relationship with correlation coefficients were above 0.993. The calculated $q_{e,calc}$ values agreed with experimental $q_{e,exp}$ values. These results also showed that the sorption system studied fitted with the pseudo-second order model for the entire sorption period. It was also noted that increasing the sorbent mass four times, the sorption pseudo-second order equilibrium constant rate decreased from 0.00674 to 0.00164. Recently, Azizian [60] reported similar observation.

Table 4
Pseudo-second order kinetic parameters for the adsorption of Basic Blue 3 at various adsorbent dose

| Adsorbent dose (mg) | Pseudo-second order model | | | |
|---|---|---|---|---|
| | $q_{e,exp}$ (mg/g) | $k_2$ (mg/mg min) | $q_{e,cal}$ (mg/g) | $R^2$ |
| 40 | 134.4 | 0.00164 | 137.1 | 0.9942 |
| 20 | 67.3 | 0.00314 | 70.1 | 0.9937 |
| 10 | 33.5 | 0.00674 | 34.6 | 0.9949 |

*Conditions*: dye concentration = 20 mg/l; NaCl concentration = 0.1 mol/l; temperature = 25 °C; pH 3.

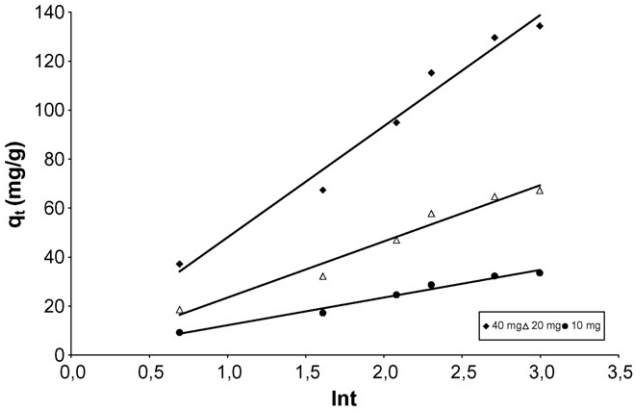


Fig. 8. Plots of Elovich equation for sorption of BB 3 onto CHITOD adsorbent at three concentrations in the batch (10, 20 and 40 mg).

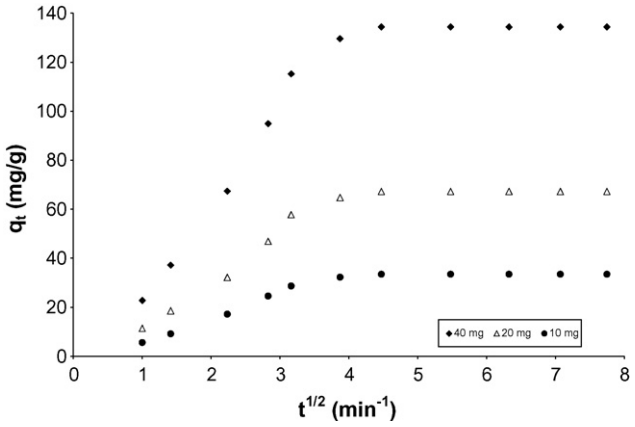


Fig. 9. Amount of dye adsorbed versus $t^{1/2}$ for intraparticle transport of BB 3 by CHITOD adsorbent at three concentrations in the batch (10, 20 and 40 mg), according to the intraparticle diffusion model proposed by Weber and Morris [58].

The Elovich model equation [61–63] is generally expressed as:

$$q_t = \frac{\ln\alpha\beta}{\beta} + \frac{1}{\beta}\ln t \quad (7)$$

where $\alpha$ (mg/g min) and $\beta$ (g/mg) are the initial adsorption rate and the desorption constant, respectively, during any one experiment. If BB 3 adsorption fits the Elovich model, a plot of $q_t$ versus $\ln t$ should yield a linear relationship with a slope of $1/\beta$ and an intercept of $\ln\alpha\beta/\beta$.

Fig. 8 shows that the dye adsorption also fits the Elovich equation. Table 5 lists the kinetic constants obtained from the plots of $q_t$ against $\ln t$. The results showed that the values of initial adsorption rate ($\alpha$) and desorption constant ($\beta$) varied in function of the sorbent amount. Thus on increasing the sorbent quantity from 10 to 40 mg, the value of $\beta$ increases from 0.022 to 0.088 g/mg.

### 3.3.3. Intraparticle diffusion model

In a batch system under rapid stirring, there is a possibility that the transport of the adsorbate from the solution into the bulk of the adsorbent is the rate-controlling step. This possibility was tested in terms of a graphical relationship between the amount of dye adsorbed and the square root of time. According to the intraparticle diffusion model proposed by Weber and Morris [64], the initial rate of intraparticle diffusion is given by the equation:

$$q_t = k_i t^{1/2} + C \quad (8)$$

where $q_t$ is the amount of dye on the surface of the sorbent at time $t$ (mg/g), $k_i$ is the intraparticle diffusion rate constant (mg/g min$^{1/2}$), $t$ is the time (min) and $C$ is the intercept (mg/g). According to Eq. (8), a plot of $q_t$ versus $t^{1/2}$ should be a straight line when adsorption mechanism follows the intraparticle diffusion process.

The variation of $q_t$ versus $t^{1/2}$ was given in Fig. 9. Values of $k_i$ and correlation coefficient are listed in Table 6, from which it will be seen that the kinetics of the dye sorption on the sorbent follows this model with the correlation coefficients higher than 0.998 for all the three experiments carried out with 10, 20 and 40 mg of sorbent. The results also showed that the sorption process tends to be followed by two phases: the initial curved portion of the plot was due to surface adsorption and rapid external diffusion, indicating a boundary layer effect while the second linear portion was due to intraparticle diffusion. The linear portion of the curves do not pass through the origin suggesting that the mechanism of BB 3 removal on modified chitosan is complex and both the surface adsorption as well as intraparticle diffusion contribute to the adsorption process. Some authors have reported that it is essential for the plots to cross the origin if the intraparticle diffusion is the sole rate-limiting step [32,39,41,45,58,59]. Since this was not the case in this study, it may be concluded that the adsorption of the dye on the modified chitosan was a multi-step process, involving adsorption on the external surface, diffusion into the bulk and chemical reaction (adsorption of dye at an active site via ion-exchange and/or complexation). It was also observed that the intraparticle rate constants ($k_i$ values in Table 6) decreased with increasing sor-

Table 5
Elovich parameters for the adsorption of Basic Blue 3 at various adsorbent dose

| Adsorbent dose (mg) | $\alpha$ | $\beta$ | $R^2$ |
|---|---|---|---|
| 40 | 48.22 | 0.022 | 0.9749 |
| 20 | 23.55 | 0.043 | 0.9666 |
| 10 | 12.26 | 0.088 | 0.9794 |

*Conditions*: dye concentration = 20 mg/l; NaCl concentration = 0.1 mol/l; temperature = 25 °C; pH 3.

Table 6
Intraparticle diffusion parameters for the adsorption of Basic Blue 3 at various adsorbent dose

| Adsorbent dose (mg) | Intraparticle diffusion model | |
|---|---|---|
| | $k_i$ (mg/g min$^{-1/2}$) | $R^2$ |
| 40 | 1.411 | 0.9996 |
| 20 | 1.723 | 0.9989 |
| 10 | 1.935 | 0.9991 |

*Conditions*: dye concentration = 20 mg/l; NaCl concentration = 0.1 mol/l; temperature = 25 °C; pH 3.

Table 7
Comparison of linear ($R^2$) and non-linear ($r^2$) correlation coefficients and the Chi-square test statistic ($\chi^2$) for three kinetic models

| Adsorbent dose (mg) | Pseudo-second order | | | Intraparticle diffusion | | | Elovich model | | |
|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $r^2$ | $\chi^2$ | $R^2$ | $r^2$ | $\chi^2$ | $R^2$ | $r^2$ | $\chi^2$ |
| 40 | 0.9942 | 0.9741 | 7.7056 | 0.9996 | 0.7812 | 58.0456 | 0.9749 | 0.9050 | 17.0124 |
| 20 | 0.9937 | 0.9715 | 4.2196 | 0.9989 | 0.7838 | 28.7063 | 0.9666 | 0.9032 | 8.7611 |
| 10 | 0.9949 | 0.9751 | 1.9459 | 0.9991 | 0.7752 | 14.6612 | 0.9794 | 0.9033 | 4.3844 |

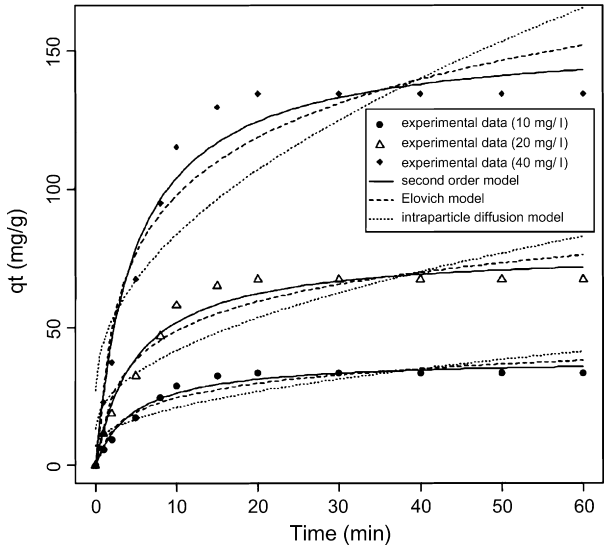


Fig. 10. Comparison between the measured and modeled time profiles for adsorption of BB 3 by CHITOD adsorbent using three different kinetic models.

bent concentration. These values are comparable with some of those reported in the literature [39,45].

Table 7 presents the results of fitting experimental data with pseudo-second order model, intraparticle diffusion model and Elovich kinetic model using linear ($R^2$) and non-linear ($r^2$) coefficients of determination, and also the non-linear Chi-square test ($\chi^2$). From this table, the comparison of error analysis showed that the order of deviation was intraparticle diffusion model > Elovich model > pseudo-second order, which indicated that the pseudo-second order model was the best one in describing the adsorption kinetics of dye on material. This was also confirmed in Fig. 10. This figure typically illustrates the comparison between the calculated and measured kinetic results.

## 4. Conclusions

In this paper, results of adsorption using chitosan-based adsorbent for the removal of Basic Blue 3 from aqueous solutions were presented. This adsorbent exhibited interesting sorption properties toward cationic dye (the maximum adsorption capacity was 166.5 mg/g), depending on the presence of sulfonate groups. The experimental data were examined using four adsorption models and it was found that the Langmuir model represented the best fit of experimental data. Error analysis investigations highlighted the non-linear method as a better way to obtain the isotherm parameters. The negative value of free energy change indicated the spontaneous nature of adsorption. The kinetic measurements showed that both the process was rapid and followed a pseudo-second order model. The sorption mechanism was a multi-step process, involving adsorption on the external surface, diffusion into the bulk and electrostatic interactions. Works concerning the influence of pH, temperature and dye structure on adsorption are in progress in order to clarify the sorption mechanism and also to show the interest to use these modified chitosans.

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