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Adsorption of C.I. Basic Blue 9 on cyclodextrin-based material containing carboxylic groups

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Abstract

Cyclodextrin-based materials containing carboxylic groups (CD/CMC adsorbents) are used for the removal of C.I. Basic Blue 9 (BB 9) from aqueous solutions. Studies concerning the sorption kinetics (i.e. the effects of contact time, dye concentration and mass of sorbent) are presented and discussed. Results of adsorption experiments showed that these adsorbents exhibited high sorption capacities toward C.I. Basic Blue 9. The adsorption capacity of BB 9 on CD/CMC material increased as the dosage of the material increased and the adsorption kinetics followed a pseudo-second order model. However, the sorption was dependent on the presence of carboxylic groups. Four isotherm equations have been tested in the present study, namely Freundlich, Langmuir, Temkin and generalized. The characteristic parameters for each isotherm have been determined. The monolayer adsorption capacity was 56.5 mg g^{-1}. The Freundlich equation represented the best fit of experimental data than the other isotherm equations.

Keywords: Cyclodextrin; Adsorbent; C.I. Basic Blue 9; Adsorption; Isotherms

1. Introduction

The chemical contamination of water from a wide range of pollutants is a serious environmental problem owing to their potential human toxicity. Therefore, there is a need to develop technologies that can remove toxic pollutants found in wastewaters. Among all the treatments proposed, adsorption using sorbents is one of the more popular methods for the removal of pollutants from the wastewater [1–7]. The sorbents may be of mineral, organic or biological origin. Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing polysaccharides [6,7]. In particular, polysaccharides such as chitin and starch, and their derivatives deserve particular attention. These biopolymers represent an interesting and attractive alternative as adsorbents because of their particular structure, chemical properties, high reactivity and excellent selectivity towards aromatic compounds and metals, resulting from the presence of chemical reactive groups in polymer chains [6,8–10].

An important class of starch derivatives are the cyclodextrins or cycloamyloses [11]. The cyclodextrin (CDs) molecules are natural macrocyclic polymers, formed by the action of an enzyme on starch. The most characteristic feature of CDs is the ability to form inclusion compounds with various organic molecules through host–guest interactions: the interior cavity of the molecule provides a relatively hydrophobic environment into which an apolar pollutant can be trapped.

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Nomenclature

a_L	Langmuir isotherm constant (L mg^{-1})
A	Temkin isotherm constant
B	Temkin isotherm constant
C_o	initial dye concentration in liquid phase (mg L^{-1})
C_e	liquid phase dye concentration at equilibrium (mg L^{-1})
k	equilibrium rate constant of pseudo-second order sorption (g mg^{-1} min^{-1})
K	saturation constant (mg L^{-1})
K_F	Freundlich constant (L g^{-1})
K_L	Langmuir isotherm constant (L g^{-1})
q_e	amount of dye adsorbed at equilibrium (mg g^{-1})
q_t	amount of dye adsorbed at time t (mg g^{-1})
q_{max}	maximum adsorption capacity of the adsorbent (mg g^{-1})
m	mass of adsorbent used (g)
n	cooperative binding constant
n_F	Freundlich isotherm exponent
R^2	correlation coefficient
V	volume of dye solution (L)
x	amount of dye adsorbed (mg)

Several review articles were devoted to the detailed description of the industrial applications of CDs [11–15].

In our group, experiments are being conducted to evaluate the possibility of the use of beta-cyclodextrin-based material as sorbent in wastewater treatment [6]. Beta-cyclodextrin (β-CD) is a torus-shaped cyclic oligosaccharide, made up of seven α-1,4-linked D-glucopyranose units. In previous works [16–18], we proposed the use of these materials as new sorbents to sorb pollutants. Results of adsorption experiments showed that they exhibited high sorption capacities toward phenolic molecules and dyes. In particular, the β-CD-based polymers are very efficient in removing acid, direct, disperse and reactive dyes from solutions [18]. However, they had low affinity for basic (cationic) dyes. In order to extend their sorption properties, we proposed chemical grafting of carboxyl groups onto cyclodextrin as a means to confer the ability to adsorb basic dyes on polymer beads. Recently, we prepared and characterized by NMR techniques new organic sorbents based on β-CD containing carboxyl groups [6,19]. These organic sorbents have been prepared by reticulation of β-CD using epichlorohydrin in the presence of carboxymethylcellulose [19].

In this paper, we propose the use of cyclodextrin-based sorbents containing carboxylic groups for the sorption of C.I. Basic Blue 9 (BB 9). The adsorption properties, in terms of adsorption capacity, are described. The influence of several parameters (kinetics, contact time, sorbent amount and dye concentration) on the adsorption capacity is evaluated and discussed. The equilibrium data have been analyzed using Freundlich, Langmuir, Temkin and generalized isotherms. The characteristics parameters for each isotherm have been determined.

2. Materials and methods

2.1. Sorbent

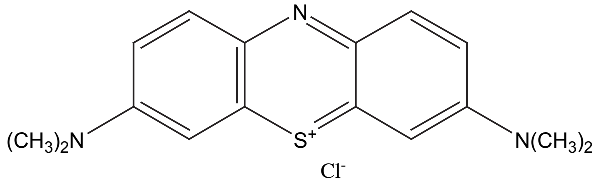
The sorbent has been prepared in one step by reticulation of β-CD using epichlorohydrin (EPI) as crosslinking agent in the presence of carboxymethylcellulose (CMC). The synthetic procedure has already been described in detail [19]. Among the crosslinking agents, the most popular is EPI. Although it is neither safe nor environmentally friendly, EPI is widely used in chemical industries as intermediates for synthesis of many products. The materials used as adsorbents are purified before use, and the presence of free unreacted EPI is improbable [6,13].

2.2. Adsorbate

The sorption capacity was investigated using C.I. Basic Blue 9 (BB 9) as model guest solute. BB 9 is a cationic blue dyestuff, C.I. Classification Number 52015. This dye was commercial product and used without purification (see Fig. 1 for the structural formulae).

2.3. Sorption studies

In order to calculate the concentration from each experiment, a calibration curve of BB 9 was first prepared. Different concentrations were prepared and absorbance values were recorded at $\lambda_{max} = 660$ nm. The adsorption experiments were carried out in a batch process at the room temperature by using aqueous solutions of BB 9. In each experiment, a fixed mass of material was weighed into flasks and brought into contact with 20 ml of dye solution at a known concentration. The pH was adjusted to 8. The solution



C.I. Basic Blue 9

Fig. 1. Chemical structure of C.I. 52015 Basic Blue 9 (BB 9).

was then stirred on a rotating shaker until equilibrium was reached. Two hours was found to be sufficient for reaching adsorption equilibrium. At $t = 0$ and equilibrium, the dye concentrations of the solutions were measured at 660 nm for each solution by UV–Vis spectrometer. These data were used to calculate the adsorption capacity of the adsorbent. Each experimental data were an average of two independent adsorption tests.

The dye concentration at equilibrium, q_e, was calculated from:

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

where C_o is the initial dye concentration in liquid phase (mg L^{-1}); C_e is the liquid phase dye concentration at equilibrium (mg L^{-1}); V is the volume of dye solution used (L); and m is the mass of sorbent used (g). Finally, q_e was plotted against C_e.

3. Results and discussion

Adsorption properties and equilibrium data, commonly known as adsorption isotherms, describe how pollutants interact with sorbent materials and so are critical in optimizing the use of adsorbents. 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 [20–24].

3.1. Adsorption of C.I. Basic Blue 9 on CD-based sorbents

Fig. 2 shows the adsorption capacity of C.I. Basic Blue 9 (BB 9) on two sorbents, CD and CD/CMC, respectively, with and without carboxymethylcellulose (CMC). The adsorption capacity was expressed in percentage uptake (R in %) which represents the ratio between the amount of adsorbed dye and the starting amount of dye. The experiments were performed in triplicate under identical conditions. As shown in Fig. 2, CD material without carboxylic groups exhibits lower sorption capacities. In a previous work, we showed that cyclodextrin polymers exhibited poor adsorption properties toward cationic dyes [18]. Results obtained with the CD/CMC adsorbent demonstrate that effective and efficient extraction of BB 9 is achieved. The presence of carboxyl groups in the material permits to increase significantly the sorption properties: this demonstrates that these groups contribute to the sorption mechanism through electrostatic interactions between COO^- groups of the material and the reactive group of BB 9 [19]. In each experiment, a change in the pH of the solution was systematically observed after contact with the modified material, suggesting an ion exchange mechanism. BB 9 possesses cationic properties originating from positively charged nitrogen or sulfur atoms: it has an affinity to materials with net negative charges. The carboxyl groups grafted onto CD material may serve as electron donors in an alkaline environment to confer on beta-cyclodextrin the ability to adsorb basic dyes. Fig. 2 also shows that the sorption properties are reproducible. Tests showed that the standard deviation of the measurement was ±2%.

Fig. 3 shows the amount of BB 9 adsorbed (q in mg g^{-1}) versus the contact time at three different dosages. The concentration of dye solution was kept constant. The amount of dye adsorbed increased with increase in contact time and reached equilibrium after 120 min for the three dosages. Also, q increases as the dosage of the CD/CMC sorbent increases and this confirmed strong chemical interactions between BB 9 and carboxylic groups.

To find the order of adsorption kinetics of BB 9, the first-order kinetics equation was tested but the straight lines could not be obtained. Then, t/q_t versus t graphs

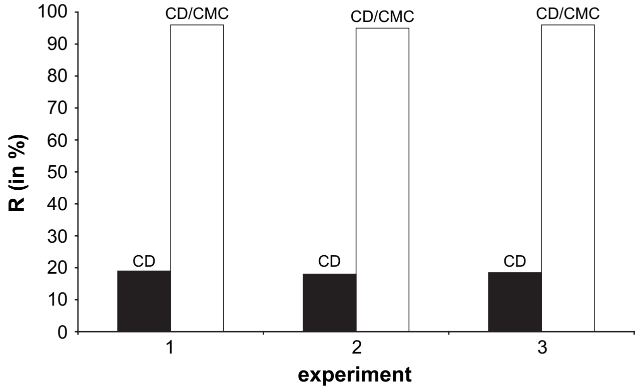


Fig. 2. Comparison between adsorption capacity (R in %) of C.I. Basic Blue 9 on two materials. CD/CMC adsorbent contains carboxylic groups while CD material does not (dye concentration = 20 mg L^{-1}; contact time = 2 h; temperature = 25 °C; pH = 8).

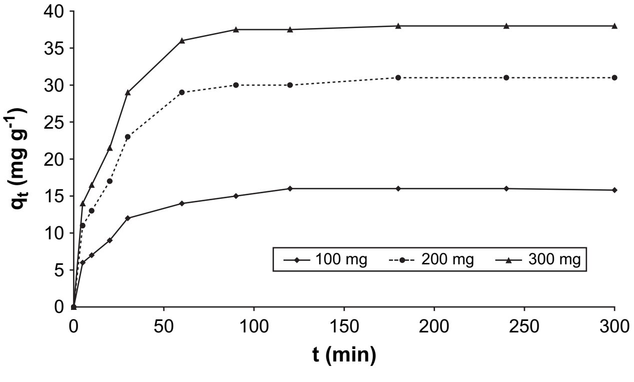


Fig. 3. Kinetics of adsorption capacity of C.I. Basic Blue 9 by CD/CMC material at three different dosages (dye concentration = 15 mg L^{-1}; temperature = 25 °C; pH = 8).

were plotted (Fig. 4). The sorption kinetics may be described by a pseudo-second order model. The differential equation is as follows [22]:

$$\frac{dq}{dt} = k(q_e - q_t)^2 \qquad (1)$$

where q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}); q_t is the amount of dye adsorbed at time t (mg g^{-1}); and k is the equilibrium rate constant of pseudo-second order sorption (g mg^{-1} min^{-1}).

Integrating Eq. (1) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \qquad (2)$$

which is the integrated rate law for a pseudo-second order reaction.

Eq. (2) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (3)$$

and

$$h = kq_e^2$$

where h is the initial sorption rate (mg g^{-1} min^{-1}).

The rate parameters k and q_e can be directly obtained from the intercept and slope of the plot of t/q_t against t. Fig. 4 shows the pseudo-second order kinetics of BB 9 adsorption onto CD/CMC adsorbent at three different dosages. Values of k and q computed from Fig. 4 are listed in Table 1. It is clear that the kinetics of BB 9 adsorption on CD/CMC material follows this model, with regression coefficients higher than 0.998 for the three dosages used in this study. Also, the adsorption capacity, q_e, increases as the dosage of the material increases, which is also shown in Fig. 3. The calculated values agree very well with the experimental data, indicating that the sorption system studied belongs to the second order kinetic model. Similar results are published in adsorption of C.I. Basic Blue 9, C.I. Reactive Red 189, C.I. Basic Blue 69 and C.I. Acid Blue 9 on silica material [5], chitosan beads [20], activated clay [21] and on mixed sorbents [22], respectively.

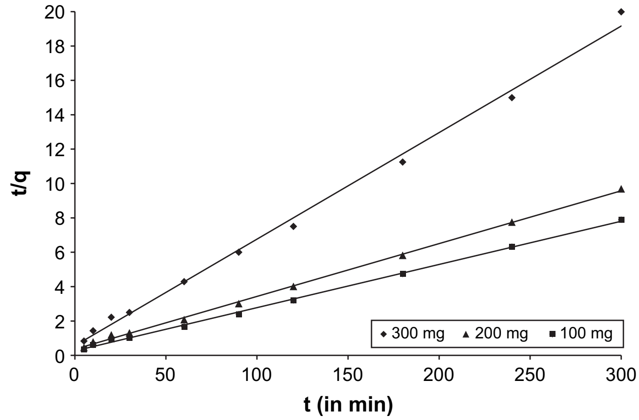


Fig. 4. Pseudo-second order kinetics of C.I. Basic Blue 9 adsorption onto CD/CMC adsorbent at three different dosages (dye concentration = 15 mg L^{-1}; temperature = 25 °C; pH = 8).

Table 1
Kinetic parameters for C.I. Basic Blue 9 adsorption onto CD/CMC adsorbent with different dosages (dye concentration = 15 mg L^{-1}; temperature = 25 °C; pH = 8)

Dosage (mg)	k (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
100	0.0053	16.66	0.9987
200	0.0026	32.57	0.9998
300	0.0024	39.94	0.9988

3.2. Equilibrium studies

An adsorption isotherm represents the relationship existing between the amount of pollutant adsorbed and the pollutant concentration remaining in solution. Adsorption equilibrium is established when the amount of pollutant being adsorbed onto the material is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phase concentration graphically it is possible to depict the equilibrium adsorption isotherm. There are many theories relating to sorption equilibrium [23–30].

3.2.1. The influence of the dye concentration on adsorption capacity

Fig. 5 shows the equilibrium adsorption of BB 9 (q_e versus C_e) using CD/CMC adsorbent. The isotherm rises sharply in the initial stages for low C_e and q_e values, indicating that there are plenty of readily accessible sites. The adsorbent is saturated when the plateau is reached. The decrease in the curvature of the isotherm, tending to

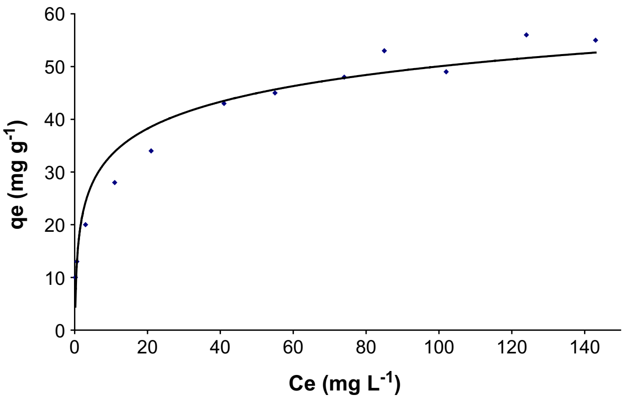


Fig. 5. Adsorption isotherm for C.I. Basic Blue 9 by CD/CMC adsorbent (contact time = 2 h; sorbent = 100 mg; temperature = 25 °C; pH = 8).

a monolayer, considerably increasing the C_e values for a small increase in q_e, is due to the less active sites being available at the end of the adsorption process.

There are several isotherm equations available for analyzing experimental sorption equilibrium data, including the Freundlich, the Langmuir, the Temkin, the Redlich–Peterson, the Toth, the Dubinin–Radushkevich, and the Sips isotherms [23–30]. However, the two most common types of isotherms are the Langmuir and the Freundlich models, and the Langmuir sorption isotherm is the best known of all isotherms describing sorption [31]. Recently, Song and Shin proposed a new three-parameter empirical isotherm model [32]. Four isotherm equations have been tested in the present study, namely Freundlich, Langmuir, Temkin and generalized.

3.2.2. The Freundlich isotherm

The Freundlich isotherm is the earliest known relationship describing the sorption equation [33]. The application of the Freundlich equation suggests that sorption energy exponentially decreases on completion of the sorptional centres of an adsorbent. This isotherm is an empirical equation employed to describe heterogeneous systems and is expressed by the following equation [23,33]:

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

where q_e is the equilibrium dye concentration on adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), K_F is Freundlich constant (L g^{-1}), and $1/n_F$ is the heterogeneity factor. The capacity constant K_F and the affinity constant n_F are empirical constants dependent on several environmental factors. A linear form of the Freundlich expression can be obtained by taking logarithms of Eq. (4):

$$\ln q_e = \ln K_F + \frac{1}{n_F}\ln C_e \tag{5}$$

Therefore, the plot of $\ln q_e$ versus $\ln C_e$ was employed to generate the intercept value of K_f and the slope of $1/n_F$. The results are given in Fig. 6(a) and Table 2. The fit is well for the adsorption system under the concentration range studied (correlation coefficient, $R^2 > 0.997$). The value of R^2 is higher than the other three isotherm values and the value of n was >1, reflecting the favorable adsorption. Apparently, the plots in Fig. 6 demonstrate

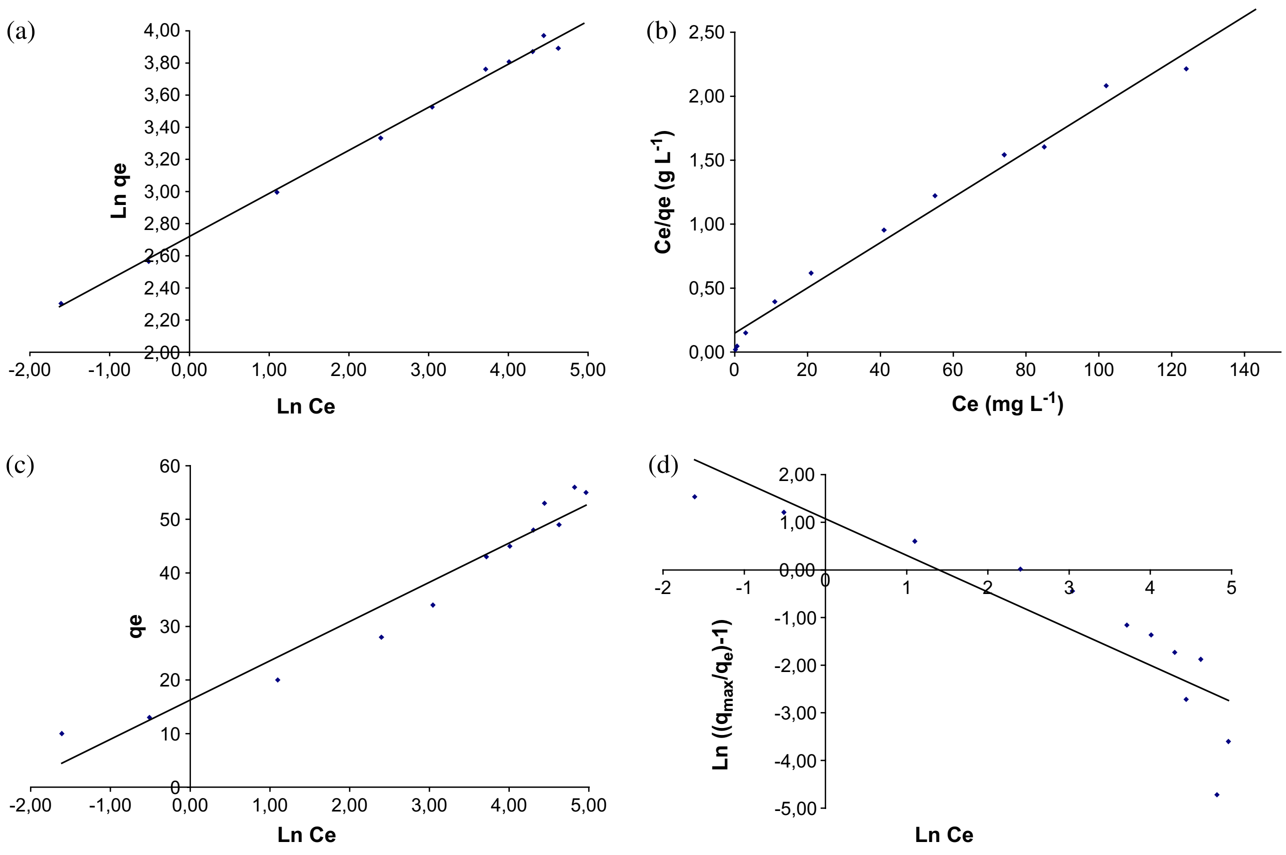


Fig. 6. Adsorption isotherms for C.I. Basic Blue 9 by CD/CMC adsorbent (a) Freundlich isotherm; (b) Langmuir isotherm; (c) Temkin isotherm and (d) generalized isotherm.

Table 2
Summary of the isotherm constants and the correlation coefficients for different isotherms

Freundlich isotherm			Langmuir isotherm				Temkin isotherm			Generalized isotherm		
K_F ($L g^{-1}$)	n	R^2	K_L ($L g^{-1}$)	a_L ($L mg^{-1}$)	q_o ($mg g^{-1}$)	R^2	A ($L g^{-1}$)	B	R^2	K ($mg L^{-1}$)	n	R^2
15.12	3.72	0.9973	6.76	0.119	56.5	0.9876	9.16	7.34	0.9500	2.93	0.768	0.7791

that the Freundlich equation provides a reasonable description of the experimental data.

3.2.3. The Langmuir isotherm

The Langmuir sorption isotherm is most widely used for the sorption of a pollutant from a liquid solution assuming that the sorption takes place at specific homogeneous sites within the adsorbent [23,34,35]. The application of the Langmuir model suggests that the sorptional energy is constant and does not depends on the degree of occupation of the active centres of an adsorbent. It also assumes that once a dye occupies a site, no further sorption can take place at that site. All sites are energetically equivalent and there is no interaction between molecules adsorbed on neighbouring sites. The linearized equation of Langmuir is represented as follows:

$$q_e = \frac{x}{m} = \frac{K_L C_e}{1 + a_L C_e} \tag{6}$$

where x is the amount of dye adsorbed (mg); m is the amount of adsorbent used (g); C_e ($mg L^{-1}$) and q_e ($mg g^{-1}$) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively; K_L ($L g^{-1}$) and a_L ($L mg^{-1}$) are the Langmuir isotherm constants.

The Langmuir isotherm constants, K_L and a_L are evaluated through linearisation of Eq. (6):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{7}$$

Hence 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. The theoretical monolayer capacity is q_o (or q_{max} the maximum adsorption capacity of the adsorbent) and is numerically equal to K_L/a_L.

The Langmuir equation is applicable to homogeneous sorption, where the sorption of each molecule onto the surface has equal sorption activation energy. The equation is thermodynamically consistent and follows Henry's Law at low concentrations. As C_e becomes lower, $a_L C_e$ is much less than unity and $q_e = K_L C_e$, that is analogous to Henry's law. Alternatively, at high adsorbate concentrations, the model predicts a constant monolayer adsorption capacity [23].

The plot of equilibrium concentrations of BB 9 in the solid and liquid phases, that is C_e/q versus C_e is presented in Fig. 6(b). From this plot, the Langmuir constants were found to be: $q_o = 56.5\ mg\ g^{-1}$; $K_L = 6.76\ L\ g^{-1}$; $a_L = 0.119\ L\ mg^{-1}$ with $R^2 = 0.9876$.

The value of the monolayer saturation capacity demonstrates that the CD/CMC adsorbent exhibits interesting sorption properties toward cationic dyes. Compared with some recent data in the literature [36–43] (Table 3), the results also reveal the potential of CD/CMC material to be an effective sorbent for removing basic dyes. However, equilibrium adsorption data of BB 9 did not fit to the Langmuir isotherm well. The value of R^2 is much lower than the Freundlich isotherm value. The Freundlich model yields a much better fit than the Langmuir model, suggesting that the boundary layer thickness is increased.

3.2.4. The Temkin isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centres of an adsorbent is increased. This model takes into account the presence of indirect adsorbate/adsorbate interactions and suggests that because of these interactions the heat of adsorption of all molecules in the layer would decrease linearly with coverage.

Table 3
Recent reported maximum adsorption capacities (q_o in $mg g^{-1}$) in the literature for C.I. Basic Blue 9 obtained on non-conventional low-cost sorbents

Adsorbents	q_o ($mg g^{-1}$)	Reference
Pinewood	556	[3]
Clay	300	[33]
Diatomite	156.6	[2]
Coir pith	120.43	[34]
Sewage sludge	114.94	[1]
Fly ash	75.52	[4]
CD/CMC	56.5	this study
Silica	56.2	[5]
Banana peel	20.8	[35]
Rice husk	19.83	[36]
Orange peel	18.6	[35]
Dead biomass	18.54	[37]
Date pits	17.3	[38]
Silica	11.21	[39]
Hazelnut shell	8.82	[40]

The Tempkin isotherm has been used in the following form [23,44]:

$$q_e = \frac{RT}{b} \ln AC_e \tag{8}$$

A linear form of Eq. (8) can be expressed as:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \tag{9}$$

where $RT/b = B$ and A are the Temkin isotherm constants. The constant B is related to the heat of adsorption.

Ignoring very low and very large values of concentration, the adsorption data can be analyzed according to the Temkin equation (Eq. (10)):

$$q_e = B \ln A + B \ln C_e \tag{10}$$

A plot of q_e versus ln C_e enables one to determine the constants A and B.

The values of the Temkin constants and the correlation coefficient are listed in Table 2. The correlation coefficient is lower than Freundlich and Langmuir values. From the Fig. 6(c), it is also clear that the Freundlich model yields a much better fit than the Temkin model.

3.2.5. Generalized isotherm

The generalized adsorption isotherm has been used in the following form [45]:

$$q_e = q_{\max} \frac{C_e^n}{K + C_e^n} \tag{11}$$

A linear form of this equation is:

$$\ln\left[\frac{q_{\max}}{q_e} - 1\right] = \ln K - n \ln C_e \tag{12}$$

where K is the saturation constant (mg L^{-1}); n is the cooperative binding constant; $q_{\max}$ is the maximum adsorption capacity of the adsorbent (mg g^{-1}); q_e (mg g^{-1}) and C_e (mg L^{-1}) are the equilibrium dye concentrations in the solid and liquid phase, respectively. A plot of the equilibrium data in form of $\ln[(q_{\max}/q_e) - 1]$ versus ln C_e gives K and n constants. The $q_{\max}$ value was taken as 56.5 mg g^{-1} in calculating the other constants. From the slope and intercept of the best-fit line presented in Fig. 6(d), the following values were found for the constants of the generalized adsorption isotherm: $K = 2.93$ L mg^{-1}, $n = 0.768$ with $R^2 = 0.7791$. The value of correlation coefficient is much lower than the other three isotherm values. The generalized equation represents the poorest fit of experimental data than the other isotherm equations. Similar results are also published by Kargi and Ozmihci [45] in adsorption of direct yellow 12 on activated sludge.

4. Conclusions

Equilibrium and kinetic studies were made for the adsorption of C.I. Basic Blue 9 (BB 9) from aqueous solutions onto CD/CMC material. Results of adsorption showed that cyclodextrins, an important class of starch derivatives, can be effectively used as an adsorbent for the removal of cationic dye. These adsorbents exhibited high sorption capacities toward BB 9: the monolayer adsorption capacity was 56.5 mg g^{-1}. The adsorption capacity increased as the dosage of the material increased. However, the sorption was dependent on the presence of carboxylic groups. The straight lines in plot of t/q_t versus t showed good agreement of experimental data with the second order kinetic model for different initial sorbent concentration. The equilibrium data have been analyzed using Freundlich, Langmuir, Temkin and generalized isotherms and the characteristic parameters for each isotherm have been determined. The results showed that the experimental data were correlated reasonably well by the Freundlich adsorption isotherm.

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