CELLULOSE CHEMISTRY AND TECHNOLOGY

STUDY OF BIOSORPTION PARAMETERS: ISOTHERM, KINETICS AND THERMODYNAMICS OF BASIC BLUE 9 BIOSORPTION ONTO FOUMANAT TEA WASTE

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In this research, the biosorption of basic blue 9(BB9) was studied in batch mode using Foumanat tea waste (FTW) as low-cost adsorbent. In this attempt, there is a cost-saving potential given that there was no further modification of FTW (just washed with distilled water to remove dirt and color, then dried in an oven). Equilibrium data were fitted to the Langmuir, Freundlich, Temkin, Sips and Redlich-Peterson models. Maximum saturated monolayer sorption capacity of FTW for BB9 was 242 mg/g at 303 K. The removal of BB9 by FTW followed pseudo-second order reaction kinetics based on Lagergren equations. Various thermodynamic parameters, such as ΔG°, ΔH°, ΔS° and E_a, have been calculated. The findings of this investigation suggested that physical sorption plays a role in controlling the sorption rate. We investigated the adsorption mechanism by FTIR and SEM techniques. FTIR data indicate that BB9 binding occurredmostly at –OH and C=O groups of FTW.

Keywords: isotherm, kinetic, thermodynamic, basic blue 9,biosorption, tea waste

INTRODUCTION

Rapid industrialization and urbanization have resulted in the generation of large quantities of aqueous effluents, many of which contain high levels of toxic pollutants.[1-2] Various physicochemical and biological processes are usually employed to remove pollutants from industrial wastewaters before discharge into the environment.[3] In the case of treatment of adsorptive pollutants, such as heavy metals and ionic dyes, however, most of the conventional treatment processes, especially chemical precipitation or coagulation, become less effective and more expensive when the adsorbates are in a low concentration range.[4-6] Although ionexchange resins and activated carbons have long been recognized as effective commercial adsorbents for treating industrial wastewaters containing adsorptive pollutants, their high cost and low efficiency have limited their commercial use in actual industrial scenarios.[2]Since any type of solid material has the capacity to adsorb pollutants to some degree, a number of industrial inorganic wastes, such as ash, or natural inorganic materials like clay, synthetic materials like zeolite, as well as, living or nonliving biomass/biomaterials, have been investigated as cheap adsorbents capable of replacing the well-known, but more expressive ones.[7-11] Considering their cost and efficiency, biomass-based adsorbents, or biosorbents as they are commonly called, are the most attractive alternatives to ionexchange resins and activated carbons.[2] In recent years, the screening of sorbents of cellulosic origin has continued to be a relentless exercise, embarked upon by environmental scientists and engineers, due to the inherent merits they possess. They have been found to be accessible, cheap, reliable, and to have the ability to compete favorably with conventional sorbents. It is of note that concerns over the task of sorbent regeneration and the mode of handling of the product of the sorption process (i.e. the used sorbent) has also been allayed by the inherent fact that some of these

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sorbents are very cheap and need no regeneration hence they can end up as biofuels.[12]

Recently, a comparative study of cationic and anionic dye adsorption by agricultural solid wastes has been reported[13] and biosorption was strongly recommended as an economically viable sustainable technology for the treatment of wastewater streams. The importance and usefulness of biosorption in wastewater treatment is well established. Biosorption in environmental engineering is now the object of attention and consideration for all nations, owing to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions.[14-16]

In this work, basic blue 9(BB9) has been selected as a model compound in order to evaluate the capacity of Foumanat tea waste (FTW) for the removal of BB9 from solutions. The sorption capacity parameter obtained from a batch experiment is useful in providing information about the effectiveness of the dye–biosorbent system. Therefore, the objective of this investigation was to explore the potential of FTW as a low cost adsorbent for the removal of BB9 from aqueous solutions. The kinetic and equilibrium data of adsorption studies were processed to understand the mechanism of basic blue 9 adsorption onto the Foumanat tea waste.

EXPERIMENTAL

Biosorbent preparation

The tea waste was collected from the Cafeteria of the Faculty of Fouman. The collected materials were washed several times with boiled water and finally with distilled water to remove any adhering dirt. The washed materials were then dried in the oven at 60°C for 48 h. The dried tea waste was then ground and sieved to a size range of 100-500 µm. Finally, the resulting product was stored in an air-tight container for further use.

Adsorption procedure

Equilibrium isotherms were determined by shaking a fixed mass of tea waste (0.7 g) with 200 mL of BB9 solutions with different initial concentrations (50, 100, 200, 300, 400 and 500 mg/L) in 250 mL stopperred glass Erlenmeyer’s flasks at the temperature of 20°C and pH=7. The procedure was repeated at temperatures of 30, 40 and 50°C. Initial pH adjustments were carried out by adding either 0.01 M hydrochloric acid or 0.01 M sodium hydroxide solution. After shaking the flasks for 120 min, the reaction mixtures were filtered through filter paper, and then the filtrates were analyzed as to the remaining BB9 concentrations by spectrometry at the wavelength of maximum absorbance, 668 nm, using a double beam UV–Vis spectrophotometer (Shimadzu, Model UV 2100, Japan).

Kinetic studies

Adsorption kinetics experiments were performed by contacting 400 mL BB9 solution of different initial concentrations ranging from 50 to 200 mg/L with 1.40 g FTW in a 500 mL-stopperred conical flask at room temperature. At fixed time intervals, the samples were taken from the solution and analyzed.

Characterization

Fourier transform infrared (FTIR) analysis was applied to determine the surface functional groups, using an FTIR spectroscope (FTIR-2000, Bruker), where the spectra were recorded from 3500 to 500 cm^{-1}. Surface morphology was studied using Scanning Electron Microscopy (Vegall-TescanCompany). Specific surface area based on nitrogen physisorption was measured by a Sibata surface area apparatus 1100. The samples were degassed at 250 °C for 2 h prior to the sorption measurement.

Isotherm modeling

The non-linear forms of the Langmuir, Freundlich, Temkin, Sips and Redlich-Peterson isotherm models were used to analyze the equilibrium isotherm data.[17] The fitness of these models was evaluated by the non-linear coefficients of determination (R^2). The Matlab (version 7.13) software package was used for computing.

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application for many processes of monolayer adsorption. The Langmuir isotherm can be written in the form (1):

$$q_e = (Q_{max}K_LC_e)/(1+K_LC_e) \qquad (1)$$

where q_e is the adsorbed amount of the dye, C_e is the equilibrium concentration of the dye in solution, Q_{max} is the monolayer adsorption capacity and K_L is Langmuir adsorption constant.

The Freundlich isotherm is an empirical equation, which assumes that the adsorption occurs on heterogeneous surfaces. The Freundlich equation can be expressed as:

$$q_e= K_LC_e^{1/n} \qquad (2)$$

where K_F and 1/n are fitting constants, which can be regarded roughly, the capacity and strength of adsorption, respectively.

The Sips model is an additional empirical model, which has the features of both the Langmuir and Freundlich isotherm models.

As a combination of the Langmuir and Freundlich isotherm models, the Sips model contains three parameters, Q_{max}, K_s and 1/n, which can be evaluated by fitting the experimental data. The Sips adsorption isotherm model can be written as follows:

$q_e = (Q_{max}K_sC_e^{1/n})/(1+K_sC_e^{1/n})$ (3)

Similar to the Sips isotherm, Redlich and Peterson, also proposed an isotherm with the features of the Langmuir and Freundlich isotherms:

$q_e = K_{rp}C_e/(1+\alpha_{rp}C_e^{\beta})$ (4)

where K_{rp} and α_{rp} are the Redlich–Peterson constants, and β is basically in the range of zero to one. If β is equal to 1, the equation reduces to the Langmuir isotherm equation, while in the case where the value of the term $\alpha_{rp}C_e^{\beta}$ is much higher than one, the Redlich–Peterson isotherm equation can be approximated by a Freundlich-type equation.

The Temkin isotherm was first developed by Temkin and Pyzhevandand is based on the assumption that the heat of adsorption would decrease linearly with the increase in coverage of the adsorbent:

$q_e = RT \ln (a_tC_e)/b_t$ (5)

where R is the gas constant, T – the absolute temperature in Kelvin, b_t– the constant related to the heat of adsorption and a_t is the Temkin isotherm constant. The Temkin isotherm equation has been applied to describe adsorption on heterogeneous surface.

Kinetic models

The Lagergrenrate equation[18] is one of the most widely used adsorption rate equations for the adsorption of solute from a liquid solution. The pseudo-first-order kinetic model of Lagergren may be represented by: $dq/q_e\text{-}q = k_1dt$ (6)

Integrating this equation for the boundary conditions t=0 to t=t and q=0 to $q=q_t$, gives:

$\ln(q_e\text{-}q_t)= \ln qe\text{-}k_1t$ (7)

where q_e and q_t are the amounts of adsorbate (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). The validity of the model can be checked by the linearized plot of $\ln(q_e–q_t)$ versus t. Also, the rate constant of pseudo-first-order adsorption is determined from the slope of the plot.

The pseudo-second-order equation based on the adsorption equilibrium capacity can be expressed as:

$dq/ (q_e\text{-}q_t)^2= k_2dt$ (8)

Considering the boundary conditions t=0 to t=t and q=0 to $q=q_t$, the integrated linear form the above equation can be rearranged to the following equation:

$1/(q_e\text{-}q_t) – 1/q_e = k_2t$ (9)

Rearranging the variables gives the equation:

$t/q_t = 1/k_2q_e^2 + t/q_e$ (10)

where the theoretical equilibrium adsorption capacity (q_e) and the second-order constants k_2 (g mg^{-1} min^{-1}) can be determined experimentally from the slope and intercept of plot t/q versus t.

Studies on point zero charge (pH_{pzc})

In pH_{zpc} determination, 0.01M NaCl was prepared and its pH was adjusted in the range of 2-11 by adding 0.01M NaOH or HCl. Then, 50 mL of 0.01M NaCl was put in a conical flask and 0.1 g of the FTW was added to this solution.[19] The flask was kept for 72 h and the final pH of the solution was measured by using a pH meter. Graphs were then plotted for pH_{final} versus $pH_{initial}$.

RESULTS AND DISCUSSION

Isotherm modeling

The analysis of the isotherm data is important to develop equations that correctly represent the results and could be used for design purposes. Figure 1 and Table 1 show the fitting parameters for the measured isotherm data for BB9 adsorption onto FTW on the non-linear forms of Langmuir, Freundlich, Temkin, Redlich-Peterson and Sips models. The values of non-linear correlation coefficients (R^2) for the Langmuir, Sips and Rudlich-Peterson isotherm models indicate good fit with the three models. The application of the Langmuir, Sips and Rudlich-Peterson isotherms showed that there was effective monolayer sorption and a homogeneous distribution of active sites on the surface of the biosorbent.

For all the temperatures, the Temkin isotherm represented the poorest fit of the experimental data in comparison with the other isotherm equations. The Freunlich equation yielded a better fit to the experimental data than the Temkin isotherm in this study. The value of exponent 1/n for the Sips model is close to unity, indicating that adsorptions are quite homogeneous. Also, there is similarity between Q_{max}values obtained from the Langmuir and Sips models at all temperatures. The maximum BB9 adsorption capacity (mg g^{-1}) belongs to FTW as has been shown in Table 1.The monolayer capacity (Q_{max}) is 242 mg g^{-1} as calculated from Langmuir or Sips models at 303K. The magnitude of the Freundlich constant n gives a measure of favorability of biosorption. Values of n>1 represent a favorable biosorption process.[20] For the present study, the value of n also presents the same trend at all the temperatures, indicating the favorable nature of biosorption of BB9 by FTW.

Adsorption kinetic studies

The transient behavior of the dye adsorption process was analyzed by using the pseudo-first and pseudo-second-order kinetic models. Plotting $\ln(q_e–q_t)$ against t permits calculation of k_1 (Figure 2a). The rate constants, k_1, evaluated from these plots with the correlation coefficients obtained are listed in Table 2. Plotting t/q against t (Figure 2b) gives a straight line where k_2 can be calculated. The R^2values listed for the pseudo-first-order kinetic model were between 0.918 and 0.984. The R^2 values for pseudo-second-order model were ≥0.999, which is higher than the R^2 values obtained for the pseudo-first-order model and closer to unity. Therefore, the adsorption kinetics could be more favorably described by the pseudo-second-order kinetic model for BB9 adsorption onto FTW.

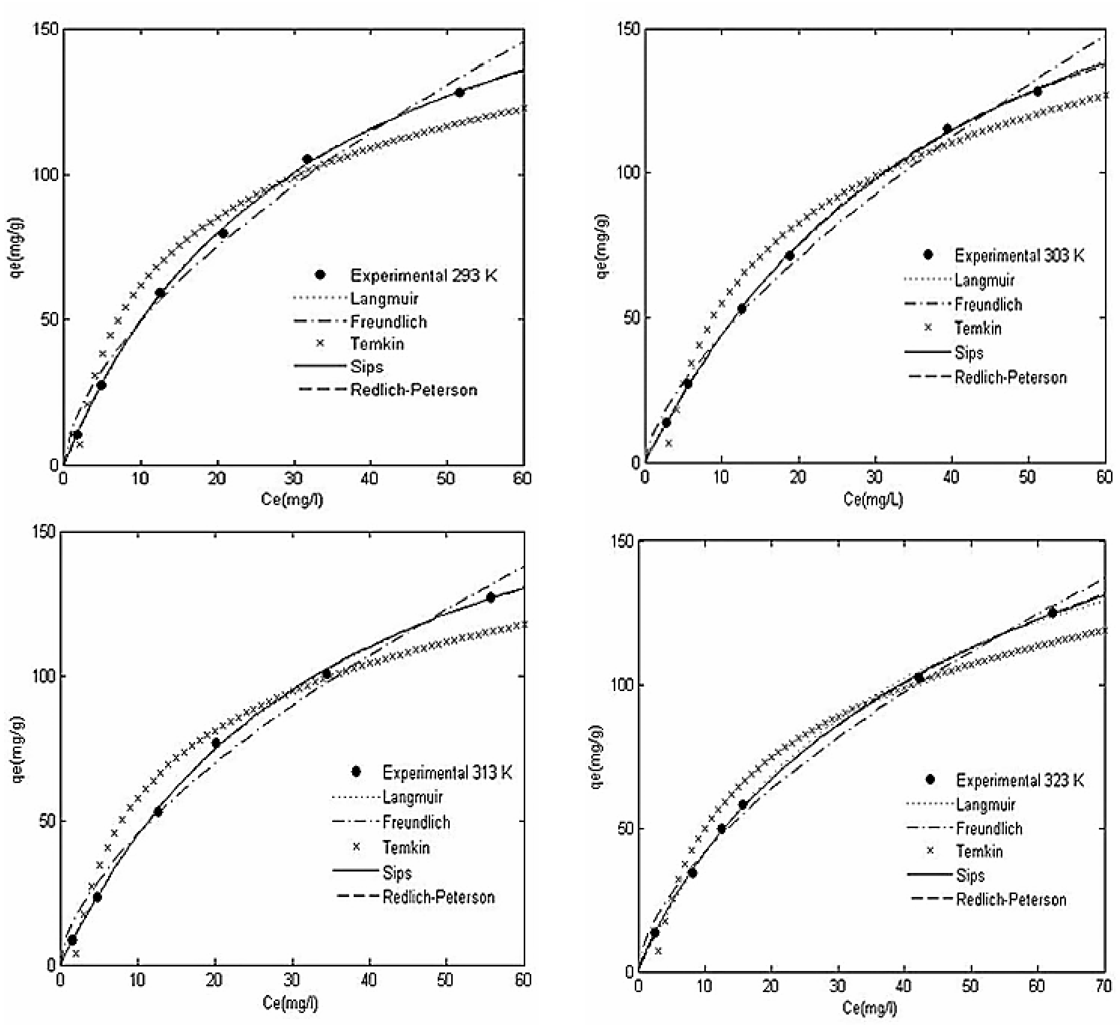


Figure1:Isotherm plots for BB9 adsorption onto FTW at different temperatures

Table 1
Isotherm parameters for BB9 adsorption by FTW

		Langmuir		
Temperature (K)	293	303	313	323
Q_{max}(mg/g)	207.40	242.34	210.48	201.29
k_L(L/mg)	0.0316	0.0224	0.0273	0.0256
R^2	0.9993	0.9996	0.9993	0.9988
		Freundlich		
Temperature (K)	293	303	313	323
n	1.66	1.49	1.61	1.64
k_F(mg/g)$(dm^3/mg)^{1/n}$	12.46	9.45	10.90	10.26
R^2	0.9875	0.9923	0.9865	0.9946
		Temkin		

Temperature (K)	293	303	313	323
B/RT	0.02937	0.02492	0.02984	0.02824
k_T(L/mg)	0.6152	0.3925	0.5597	0.4101
R^2	0.9514	0.9592	0.9446	0.9465
		Sips		
Temperature (K)	293	303	313	323
Q_{max} (mgg^{-1})	207.40	242.34	210.42	201.29
K_s ((mg^{-1})$^{-1/n}$)	0.03155	0.02239	0.02729	0.02565
1/n	0.9732	1.0320	1.0380	0.8959
R^2	0.9993	0.9996	0.9993	0.9988
		Redlich-Peterson		
Temperature (K)	293	303	313	323
K_{rp} (LKg^{-1})	6.705	5.072	5.559	6.160
α_{rp} (Kgmg^{-1})	0.03699	0.01082	0.0212	0.07594
β	0.969	1.154	1.850	0.800
R^2	0.9993	0.9998	0.9993	0.9995

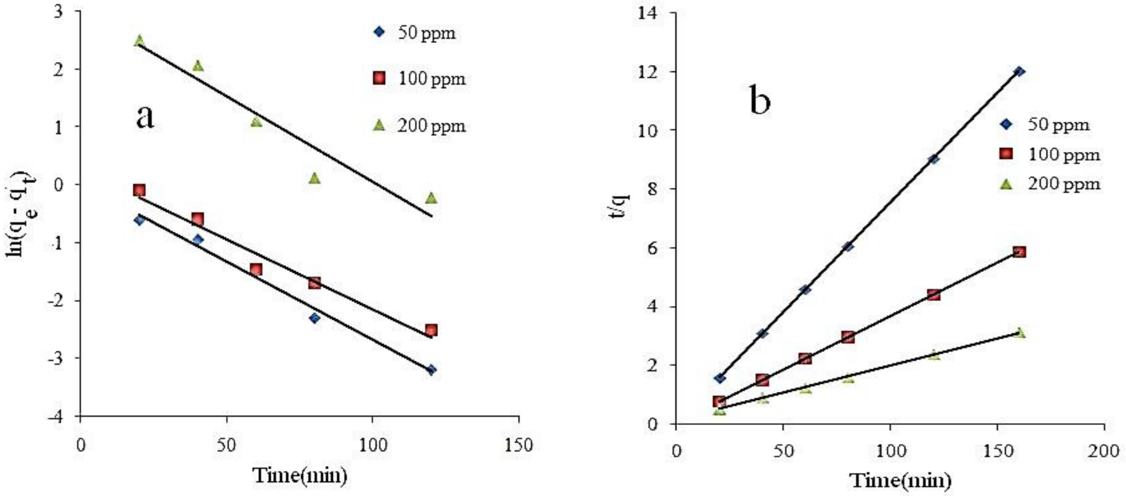


Figure 2: Kinetic models for adsorption of BB9 onto FTW; (a) pseudo-first-order and (b) pseudo-second-order rate equations

Table 2
Kinetic parameters for adsorption of BB9 onto FTW based on Lagergren rate equation

C_0	Pseudo-first order			Pseudo-second order		
(mg/L)	q_e(mg/g)	k_1 (1/min)	R^2	q_e(mg/g)	k_2(g/mg.min)	R^2
50	1.03	0.027	0.984	13.5	0.056	1.00
100	1.31	0.024	0.966	27.8	0.036	1.00
200	20.10	0.029	0.918	55.6	0.0022	0.999

FTIR study and adsorption mechanism

FTIR spectra of FTW before and after BB9 adsorption are shown in Figure 3. In the FTIR spectrum of tea waste before adsorption (Figure 3a), the broad and intense absorption peaks at around 3343cm^{-1} correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin, thus showing the presence of “free” hydroxyl groups on the adsorbent surface.[21] The peak at 2921 cm^{-1} is attributed to the symmetric and asymmetric C–H stretching vibration of aliphatic acids.[21] The precursor had C=O stretching of aldehyde group peaks located at 1738 cm^{-1}.[22] The peak at 1655 cm^{-1} is due to asymmetric stretching vibrations of

C= O and the peaks observed at 1512, 1540, 1610 cm^{-1} can be assigned to C=C vibration in aromatic rings. The other prominent peaks are due to NH_2, C=O and –C–C– (1440, 1066 and 875 cm^{-1}, respectively) groups. Some distinct changes are noted in the spectrum of tea waste after BB9 adsorption compared to that obtained before adsorption (Figure 3b). After BB9 adsorption, there is remarkable shift in the positions of –OH, C=O and –C–C– group peaks, which indicates BB9 binding mostly to –OH and C=O groups. The peak at 1372 cm^{-1} shows C–O–H bending and the band width of 1382 cm^{-1} had N–O stretch, respectively. The changes in FTIR spectra confirm the complexation of BB9 with the functional groups present in the adsorbents.[20,22-25]

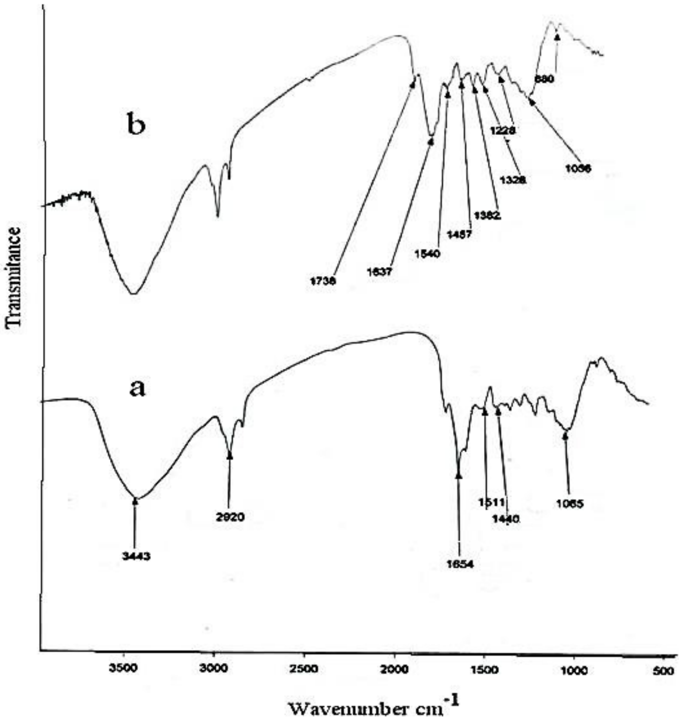


Figure 3: FTIR spectra of FTW a) before and b) after BB9 adsorption

SEM and BET surface area of tea waste

Figure 4 shows the SEM micrographs of tea waste samples before and after BB9 adsorption. Figure 4a shows that the tea waste possesses rough surface morphology with some pores. The surface of BB9-loaded adsorbent (Figure 4b), however, shows that the pores of tea waste are covered with BB9 molecules. The BET surface area and pore volume were measured to be 21 m^2/g and 0.008 cm^3/g, respectively, for tea waste before BB9 adsorption.

Determination of point zero charge (pHpzc)

The point zero charge (pH_{pzc}) is an important factor that determines the linear range of pH sensitivity and then indicates the type of surface active centers and the adsorption ability of the surface.[26]Many researchers studied the point zero charge of adsorbents prepared from agricultural solid wastes in order to better understand the adsorption mechanism. Cationic dye adsorption is favored at $pH>pH_{pzc}$, due to presence of functional groups, such as OH^-, COO^- groups. Anionic dye adsorption is favored at $pH<pH_{pzc}$, where the surface becomes positively charged.[27-28]The graph of pH_{intial} *vs* pH_{final} was plotted as shown in Figure 5. The intersection of the curve with the straight line is known as the end point of the pH_{pzc}, and this value is 6.4 for FTW.

Adsorption thermodynamics

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously.[29] Gibb's free energy change, $\Delta G°$, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if $\Delta G°$ is a negative value. The thermodynamic parameters of $\Delta G°$, enthalpy change, $\Delta H°$, and entropy change, $\Delta S°$, for the adsorption processes are calculated using the following equations[20].

$\Delta G^\circ = - RT1nK_D$ (11)

K_D is given by the following equation:

$K_D=q_e/C_e$ (12)

where K_D is the distribution coefficient and:

$\ln K_D= -\Delta H^0/R\ (1/T) + \Delta S^0/R$ (13)

where R is a universal gas constant (8.314 J/mol K) and Tis the absolute temperature in K. The plot of $\ln K_D$ versus 1/T was found to be linear.

The values of ΔH° and Δ*S*° were respectively determined from the slope and intercept of the plot. The thermodynamic parameter, ΔG°, is shown in Table 3. ΔH° and ΔS° for the sorption process were calculated to be -11.51 kJ/mol and -30.88 J/mol K, respectively. The negative value of Δ*G*° confirms the feasibility of the process and the spontaneous nature of sorption with a high preference for BB9 to sorb onto tea waste. The value of ΔH° was negative, indicating that the sorption reaction was exothermic. The negative value of Δ*S*° reflects the affinity of the tea waste for BB9 and suggests some structural changes in BB9 and tea waste interaction. In addition, the negative value of change in entropy Δ*S*° reflects the decreased randomness at the solid/solution interface during the adsorption of BB9 on tea waste. This is a direct consequence of: (i) opening up of tea waste structure, (ii) enhancing the mobility and extent of penetration within the tea waste, and (iii) overcoming the activation energy barrier and enhancing the rate of intraparticle diffusion.[30-31]

The activation energy (E_a) was obtained from the slope of plot ln(1-θ)against 1/T, where the surface coverage (θ) was calculated from the relation (14).[32]

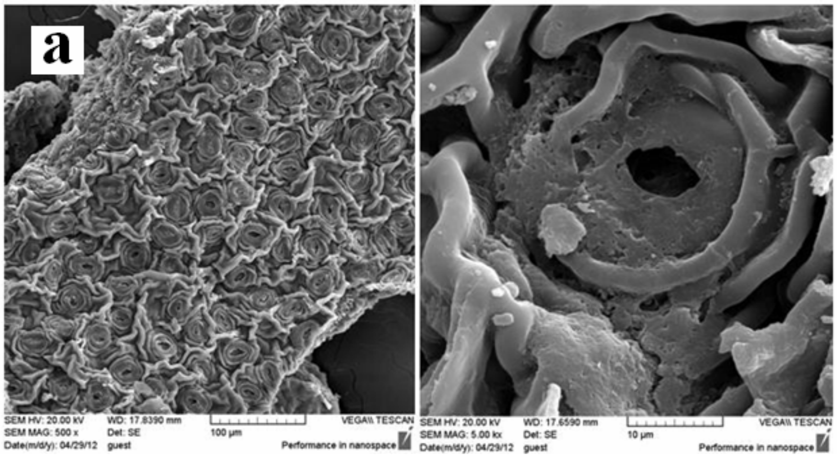
$\theta= 1-C/C_0$ (14)

whereC$_0$ and C are the initial and residual concentration of BB9 in solution, respectively (mg/L).

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of sticking probability (*S**) was estimated from the experimental data. It was calculated using a modified Arrhenius type equation related to surface coverage as expressed in Eq. (15).[33]

$S^*= (1-\theta)\ e^{-(E_a/RT)}$ (15)

The parameter *S** indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely. It can be expressed as in Table 3. The effect of temperature on the sticking probability was evaluated throughout the temperature range from 293 to 323K by calculating the surface coverage at various temperatures. The apparent activation energy (E_a) and the sticking probability (*S**) are estimated from the plot with a reasonably good fit for the BB9 on the tea waste. The E_a values calculated from the slope of the plot were found to be -5.5 kJ/mol. The negative values of E_a indicate that lower solution temperature favors BB9 removal by adsorption onto tea waste and the adsorption process is exothermic in nature. Relatively low values of E_a suggest that BB9 adsorption is a diffusion controlled process. The results as shown in Table 3 indicate that the probability of BB9 to stick to the tea waste surface is very high as $0< S^*<1$ for BB9 (Table 3). These values confirm that the sorption process is physisorption.[33]



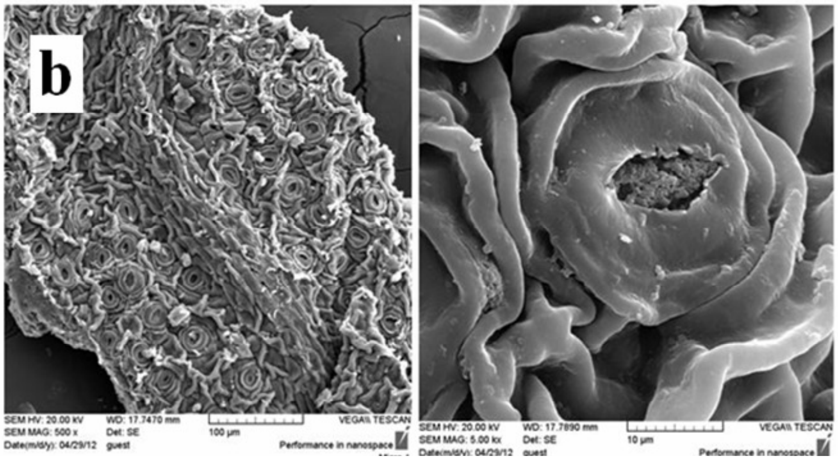


Figure 4: SEM micrographs of FTW a) before and b) after BB9 adsorption

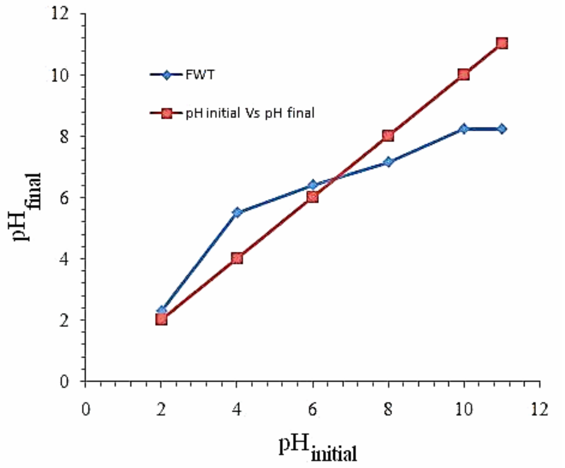


Figure 5: Plot for determination of point zero charge of FTW

Table 3
Thermodynamic parameters for the adsorption of BB9 onto FTW

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	E_a (kJ/mol)	S*
293	-2.482	-11.51	-30.88	-5.50	0.933
303	-2.234				
313	-1.863				
323	-1.579				

*S**: sticking probability

CONCLUSION

Foumanat tea waste had a good adsorption capacity for BB9 in aqueous solutions. The values of non-linear correlation coefficients (R^2) for the Langmuir, Sips and Rudlich-Peterson isotherm models indicate a good fit with the three models. Kinetic model analyses revealed that the experimental data fitted well the pseudo-second order model. Thermodynamic data indicated that the adsorption process was exothermic and spontaneous.

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