1 Introduction

On entering water bodies colored effluent, is highly visible and can result in unwanted consequences [1–3] including regulatory interest and/or action. Popular treatment practices are often incapable of entirely removing certain colorants and this obviously due to their high stability and solubility in aqueous solutions [2]. The inability of existing physiochemical methods for eliminating weakly interacting dyes can potentially be solved by adsorption based technology. Indeed, adsorption has been recommended as an efficient and safe method for removing dyes from solution [1–3]. Many food colorants contain the azo bond \((N=N)\) which is often associated with the chromophores of the compound [2]. Accordingly, chemical degradation of colorants might generate toxic by-products and contribute to nitrogen eutrophication [3]. This suggests adsorption as a convenient remediation practice toward removing dyes from solution. Utilizing pyrolyzed biomass for removing toxic pollutants, including dyes, is a well-documented research area [4–7]. Within the literature, numerous papers have described adsorption of dyes by many different adsorbents [8]. Using pine wood, particularly after activation, has been shown to be an efficient adsorbent for removing food dyes [9] and other undesirable organics from water [10].

Compared to single-solute adsorption systems, a particular problem contributed by multi-solute adsorption systems is the necessity for using advanced analytical methods to quantify unreacted solutes left in solution [1, 3, 11–13]. Accordingly, multi-solute adsorption studies have received less attention in environmental studies. For mixture adsorption, accurate quantification of each solute is necessary to obtain reliable interpretation on the competitive adsorption behavior and movement of solutes in the environment [11–13].

For multi-dye adsorption systems, few papers are reported and the adopted analytical methods extend beyond simple spectrophotometric methods [1, 11] to more sophisticated ones [12, 13]. The proper selection of the analytical method is highly dependent on the magnitude of spectral overlap between dyes or the presence of unknown interferences.

In this work, chemically activated pine wood was used to prepare biochar, which was used to study the competitive adsorption behavior of four colorants (allura red (AR), brilliant black (BB), tartrazine (TT), and sunset yellow (SY)). Dye concentrations in mixed solutions were simultaneously estimated by using partial least squares Kernel calibration. The analytical recovery of food dyes was 96.7–103.4% and prediction error was 1.4–9.4%. Adsorption isotherms of dyes (at pH 2 and 25°C) from multi-solute solutions were measured and the maximum adsorption capacities (according to the Jovanovich’s model) were 68.4, 40.0, 29.6, and 23.4 mg/g for SY, AR, TT, and BB, respectively. The biochar had a combined retention capacity of 186.9 mg/g for dyes. The effects of dosage of adsorbent, pH and number of competing solutes on %Removal-retention capacity were studied. The extent of competition between dyes toward the surface was assessed from the magnitudes of competition factors. The competition factors were 0.69, 0.70, 0.75, and 0.76 for AR, TT, BB, and SY, respectively. During adsorption of mixtures from solution, SY manifested stable performance while allura red negatively competed with the rest of the dyes. Partial least squares Kernel calibration was usefully applied for studying competitive adsorption behavior of four food-dyes with minimum experimental setup.

Keywords: Modeling; Multi-dye adsorption systems; Multi-solute interactions; Multivariate calibration

Received: June 11, 2016; revised: November 1, 2016; accepted: January 23, 2017

DOI: 10.1002/clen.201600333

Research Article

Application of Partial Least Squares-Kernel Calibration in Competitive Adsorption Studies Using an Effective Chemically Activated Biochar

In this work, chemically activated pine wood was used to prepare biochar, which was used to study the competitive adsorption behavior of four colorants (allura red (AR), brilliant black (BB), tartrazine (TT), and sunset yellow (SY)). Dye concentrations in mixed solutions were simultaneously estimated by using partial least squares Kernel calibration. The analytical recovery of food dyes was 96.7–103.4% and prediction error was 1.4–9.4%. Adsorption isotherms of dyes (at pH 2 and 25°C) from multi-solute solutions were measured and the maximum adsorption capacities (according to the Jovanovich’s model) were 68.4, 40.0, 29.6, and 23.4 mg/g for SY, AR, TT, and BB, respectively. The biochar had a combined retention capacity of 186.9 mg/g for dyes. The effects of dosage of adsorbent, pH and number of competing solutes on %Removal-retention capacity were studied. The extent of competition between dyes toward the surface was assessed from the magnitudes of competition factors. The competition factors were 0.69, 0.70, 0.75, and 0.76 for AR, TT, BB, and SY, respectively. During adsorption of mixtures from solution, SY manifested stable performance while allura red negatively competed with the rest of the dyes. Partial least squares Kernel calibration was usefully applied for studying competitive adsorption behavior of four food-dyes with minimum experimental setup.

Keywords: Modeling; Multi-dye adsorption systems; Multi-solute interactions; Multivariate calibration

Received: June 11, 2016; revised: November 1, 2016; accepted: January 23, 2017

DOI: 10.1002/clen.201600333

1 Department of Chemistry, The Hashemite University, Zarqa, Jordan
2 Preparatory Deanship, Prince Sattam Bin Abdulaziz University, Al-Kharj, Saudi Arabia
3 Department of Chemistry, Faculty of Science, The University of Jordan, Amman, Jordan
4 School of Energy, Construction and Environment, Faculty of Engineering and Computing, Coventry University, Coventry, UK

Correspondence: Dr. Alan P. Newman, School of Energy, Construction and Environment, Faculty of Engineering and Computing, Coventry University, Priory Street Coventry CV1 5FB, UK
E-mail: apx097@coventry.ac.uk

Abbreviations: AR, allura red; BB, brilliant black; PCR, principal component regression; PLS-Kernel, partial least squares Kernel calibration; PRESS, prediction error sum of squares; SY, sunset yellow; TT, tartrazine.
multisolute systems. Achieving this aim is significant for accurate design-building for adsorption systems as the influence of multisolute interactions would affect the final adsorption performance of the solid adsorbent [12, 13]. Practically, the new adsorbents should manifest high removal capacity for multiple solutes to be commercially feasible compared to traditional activated carbon. While single-solute tests are often adopted for quick assessment of an adsorbent, adsorption of mixtures is more informative on the real adsorption performance [13].

The most adopted analytical methods for dye quantification are high performance liquid chromatography-UV-vis, capillary electrophoresis, liquid chromatography-mass spectrometry, GC and electrochemical methods [14]. Running chromatographic-based methods for dye quantification in adsorption studies is laborious, time-consuming and has a high demand for good quality organic solvents [14, 15].

Multivariate calibration including partial least squares (PLS) and principal component regression (PCR) have been applied for analysing mixture of dyes in complex matrices without the need for solute-separation [14–17]. Various approaches within the broad range of PLS techniques are efficient tools to develop a quantitative relationship between dependent variables $X$ (spectral measurements) and properties of interest $y$ (independent variables). In the current work, $X$ matrix contains dependent variables or spectral data while $y$ vector contains dye concentration or independent variables. Mathematically, the relationship between $X$ and $y$ is presented as [18]:

$$y = Xb$$

where $y$, $X$, and $b$ dye or analyte standard concentrations in the calibration samples arranged in a vector, the data matrix containing the absorbances of standard solutions that measured at different wavelengths, and the calibration sensitivity which is necessary for predicting calibrated dye content in the unknown sample. PLS, in fact, is an efficient numerical method to find the proper calibration vector $b$. The main advantages of PLS regression is to eliminate or minimize sample preparation and to avoid application of laborious chromatographic or electrochemical analytical methods [14–16, 18]. The most adopted variants are PLS-NIPALS, PLS-SIMPLS, PLS-Kernel, and PLS-Bidirectionalization and the first two variants have many applications in industrial and environmental systems [18].

Each PLS variant has its own mechanism for running chemical analysis. For example, NIPALS is the best choice for handling many-variables-X-matrices and consumed long computational time and more memory-storage [19–21]. However, SIMPLS is faster than NIPALS but it is not applicable for many-variables-X-matrices. Kernel-PLS is an adjustable algorithm and workable for systems of many variables and many samples by creating condensed matrices form the original data [19–21].

Application of simple, reliable, and accurate analytical methods for quick quantifying mixture of solutes will be helpful for understanding competing behavior of the mixture and would give better insight on adsorption in complex matrices.

In fact, few studies have applied PLS for studying competitive adsorption of food dyes and the authors are unaware of any application of PLS-Kernel to the study of competitive adsorption of allura red (AR), brilliant black (BB), tartrazine (TT), and sunset yellow (SY) by chemically activated pine wood biochar. In a previous study, NIPALS-PLS and PCR were applied for quantifying a mixture of food dyes for studying their competitive adsorption behavior by untreated pine wood [22] and acid-activated kaolinite [23]. Moreover, single-solute adsorption of the investigated dyes by microwave-heated pine wood was reported [9].

In the current work, adsorption behavior of single and multisolute mixtures of food dyes was investigated with the help of PLS-Kernel calibration. The main aim of using PLS-Kernel is to avoid using chromatographic methods in adsorption tests. Chemically activated pine wood or biochar was prepared and tested as a solid adsorber for common food dyes removal from solution. Effects of solution pH, dosage of adsorbent, and number of competing solutes on dyes removal were investigated as being the most significant factors that affecting dye removal from solution. Adsorption isotherms are presented using several models including Langmuir, competitive-Langmuir, Freundlich, Halsey, and Jovanovic to provide a better insight on competitive dye adsorption and on the nature of solute–solute and solute–adsorbent interactions.

2 Materials and methods

2.1 Adsorbent preparation and characterization

Pine wood was collected from a local carpentry and stored in a closed polyethylene bag. The collected sample, which consisted of small wood flakes 1.0 × 1.5 cm, was washed with distilled water and dried at 105°C for 24 h. Conversion of raw pine wood into an efficient and porous adsorbent was carried out as outlined in the literature with some modifications [10]. Thirty grams of pine wood was mixed with 10 g K2CO3 and the whole mixture was soaked in 50 mL water for 8 h. The final mixture was agitated and the excess solvent was evaporated under gentle flow of air. The soaked pine wood was then dried at 70°C for 5 h before carbonization at 250°C under flow of nitrogen gas and heating rate 10°C/min. The black residue (yielding 55%) was washed with distilled water until a neutral extract was obtained and finally dried at 105°C for 24 h. The sample was sieved to a particle size of 125–250 μm and stored. More details on the activation procedure are outlined in the literature [10]. The following characterization tests were carried out for the prepared biochar. Infrared spectra of biochar before and after dye removal were recorded by Fourier transform IR spectroscopy (PerkinElmer Dynascan Interferometer AVI, USA) to determine the surface functional groups and the dye–surface interactions. The specific surface area and pore volume were also determined with a Brunauer, Emmett, and Teller (BET) surface area analyzer (Micromeritics ASAP 2020, surface area analyzer), by means of adsorption of ultrapure nitrogen at 77 K. The elemental analysis was performed using an elemental analyzer (CHN Autoanalyzer, PerkinElmer, USA). The pH of zero point charge (pHZPC) was measured using the pHDrift method as outlined in the literature and was found to be 7.9 [24].

2.2 Adsorbates

Four dyes, commonly used in the food industry were selected: AR ($C_{14}H_{18}N_{2}Na_{2}O_{8}S_{2}$, CAS NO. 25956-17-0), SY ($C_{14}H_{18}N_{2}Na_{2}O_{3}S$, CAS NO. 2783-94-0), (2) TT ($C_{16}H_{10}N_{4}Na_{3}O_{9}S_{2}$, CAS NO. 1934-21-0), and BB ($C_{24}H_{17}N_{5}Na_{4}O_{14}S_{4}$, CAS NO. 2519-30-4). The dyes were purchased from Sigma with variable purities (60–100%). A standard 1,000 mg/L solution of each single dye was prepared by dissolving an appropriate mass of the dye in a 1,000 mL volumetric flask using distilled water. A number of phosphate buffer solutions of
different pH values (2, 6, and 12) was prepared using H₃PO₄ (0.05 mol/L), NaH₂PO₄ (0.05 mol/L), and Na₂HPO₄ (0.05 mol/L). The buffers were used to fix pH in the tests. All necessary dilutions were carried out using distilled water. The chemical structures of dyes are shown in Tab. 1.

### 2.3 Adsorption of dyes from single and multi-solute solutions

The initial studies indicated that the dyes showed better adsorption under acidic conditions (pH < 4). Moreover, PLS-Kernel also shows a stable calibration performance for dye concentration predictions at pH 2. The concentration-variation adsorption method was conducted at pH 2 over the concentration range 10⁻¹⁻¹⁻⁰⁻⁻⁰ mg/L to study the adsorption isotherms of dyes. A mass of sorbent which varied over a range of 0.6–1.5 g was added to a set of 100 mL dye solutions. The mixtures were sealed and agitated for 24 h at 25°C using a thermostated shaker. The equilibrium time was estimated from separate kinetic tests and 24 h was found sufficient to achieve equilibrium. After 24 h, the solutions were centrifuged to remove solid particles in preparation for spectral measurement by double-beam spectrophotometer (Cary 3E UV-vis spectrophotometer, Varian). PLS-Kernel calibration was applied to evaluate dye concentrations remaining after adsorption. The surface concentration of dye at equilibrium was estimated from the mass balance equation:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

(2)

Percent removal of dye from solution was estimated as:

\[ \% \text{Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \]  

(3)

### Table 1. Structural formula of dyes\(^a\)

<table>
<thead>
<tr>
<th>Dye(^a)</th>
<th>Structural formula (Na-form)</th>
<th>(pK_a) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allura red (azo dye)</td>
<td><img src="image" alt="Structural formula" /></td>
<td>11.2</td>
</tr>
<tr>
<td>Brilliant black (azo dye)</td>
<td><img src="image" alt="Structural formula" /></td>
<td>6.3</td>
</tr>
<tr>
<td>Sunset yellow (azo dye)</td>
<td><img src="image" alt="Structural formula" /></td>
<td>10.4</td>
</tr>
<tr>
<td>Tartrazine (azo dye)</td>
<td><img src="image" alt="Structural formula" /></td>
<td>9.4</td>
</tr>
</tbody>
</table>

\(^a\) Dyes were purchased from Aldrich\(^a\) with the following purities 100, 90, 80, and 60% for TT, SY, AR, and BB, respectively.

\(^b\) Acidity constants were obtained from the work of Perez-Urquiza and Beltrán [2].

where \(C_0\), \(q_e\), \(V\), and \(m\) are dye concentration at equilibrium (mg/L), dye concentration at the surface (mg/g), volume of solution (L), and mass of adsorbent (g), respectively. In some cases, dilution of solutions was essential prior to obtaining the spectra. For multisolute adsorption, the earlier procedure was repeated using mixtures of dyes over the range 10⁻¹⁻¹⁻⁰⁻⁻⁰ mg/L. For single dye systems, pre-constructed calibration graphs (at \(\lambda_{\text{max}}\)) were used to estimate remaining dye concentrations. PLS-Kernel calibration was used to find individual content of each dye in the mixtures as described in the coming sections. Adsorption isotherms were plotted and the data were presented by application of a selection of different adsorption models.

### 2.4 Multivariate calibration

It was not possible to quantify a mixture of the selected dyes using conventional calibration methods due to the intense spectral overlap, hence multivariate calibration was necessary at this stage. Spectral measurements were recorded at different pH values and over the range of 330–700 nm at intervals of 5 nm. According to Brereton’s method, a calibration set (eight samples) based on three-level full-factorial design (1, 3, 5 mg/L) was created. Subsequently, a validation set (five samples) was randomly selected over the range of 1–5 mg/L. The composition of calibration and validation sets (which used for building and training PLS-Kernel) is presented in Tab. 2.

For each solution, a spectrum of 75 points was obtained. Accordingly, data matrices of 8 × 75 and 5 × 75 were created for calibration and validation sets, respectively. Another set was created by collecting the spectra of dyes from different adsorption tests.

#### 2.4.1 PLS-Kernel calibration

As mentioned earlier, PLS is an efficient tool for developing a quantitative relationship between \(X\) (spectral measurements) and \(Y\) (standard concentrations of dyes):

\[ Y = XB \]  

(4)

Using PLS-Kernel, \(B\) can thus be created and used for dye prediction in a new solution [18–21]. In general, the dimensions of the earlier quantities are \(X\) (\(I\) samples x \(J\) variables) and, \(Y\) (\(I\) samples x \(J\) [four dyes]), and \(B\) (\(J\) variables x 4). There are currently two common variants of the Kernel algorithm [20, 21], the first one can handle matrices of many samples where \(I\) is larger than \(J\) and the other one (which is suitable for the current study) was proposed for many variables \(X\)-matrices \((I > J)\). In all Kernel algorithms, condensed matrices are created from \(X\) and \(Y\) which is an essential step. In the adopted algorithm, two condensed matrices are created \(XX^T\) and \(YY^T\). Kernel matrix is then estimated as: \(XX^TYY^T\). The main steps of the algorithm [20–21] are:

1. The eigenvector of the kernel matrix is taken as the first \(X\) score vector \(t_1\). The \(Y\) score vector is then estimated as:

\[ u_1 = YY^Tt_1 \]  

(5)

2. The next step is to update the association matrices by eliminating the explained variable as follows:

\[ G_1 = I - t_1t_1^T(I \text{ identify matrix}) \]  

(6)
X_iX_i' = G_iXX_i'G_i \quad \quad \quad (7)

Y_iY_i' = G_iYY_i'G_i \quad \quad \quad (8)

The above operations make it unnecessary to go back to the original large matrices and calculation of association matrices. As can be seen, the matrices involved in the Kernel algorithm are simpler than the original matrices.

3. The next t and u vectors are estimated as outlined above using the updated matrices. The calibration matrix (containing the calibration vectors for the target solutes) are estimated from weight and loading matrices \( W, P, \) and \( Q \) as following \([20, 21]\):

\[
W = X'U \quad \quad \quad (9)
\]

\[
P = (T'X)(T'T)^{-1} \quad \quad \quad (10)
\]

\[
Q = (T'Y)(T'T)^{-1} \quad \quad \quad (11)
\]

Step 3 is repeated until the optimum number of PLS-variables is estimated.

It should be mentioned that all vectors in \( W \) should be normalized before creating the B matrix \([20, 21]\)[12].

The dye concentrations were predicted from the unknown spectrum \( a_{un} \) as following:

\[
c_{un} = a_{un}B \quad \quad \quad (12)
\]

In-house constructed Matlab® codes were developed to run the PLS-Kernel calibration. The calibration matrix was saved and used to evaluate the individual dye concentrations in new solutions as shown in Eq. (12).

### 2.5 Modeling equilibrium adsorption data

The adsorption data were plotted and further modeled by generating the following two plots. Plot I: plotting %Removal retention capacity as a function of experimental variable (i.e., pH, mass of adsorbent, and number of competing solutes), often called % Removal retention capacity plot \([25]\), and Plot II: the common concentration variation isotherm which was generated by plotting \( C_e \) (mg/L) against \( q_e \) (mg/g). The mechanism of dye removal was studied by analyzing adsorption isotherms (obtained in Plot II), using the Langmuir, Freundlich, competitive-Langmuir, Halsey, Temkin, and Jovanovic models. The earlier models have been applied for modelling mono- and multilayer adsorption systems. The Langmuir model, which assumed monolayer adsorption, active sites of equal energy, and no solute–solute interactions, is given as \([26–28]\):

\[
q_e = \frac{Q_{max}K_1C_e}{1 + K_1C_e} \quad \quad \quad (13)
\]

where \( C_e \) (mg/L), \( q_e \) (mg/g), and \( Q_{max} \) (mg/g) are the equilibrium concentration of dye, dye surface concentration at equilibrium, the removed amount at complete monolayer coverage. \( K_1 \) (L/mg) is the Langmuir parameter of the model and taken as equilibrium constant \([26]\). For mixture adsorption, the competitive-Langmuir model for n solutes is given as \([26, 27]\):

\[
q_{e,i} = \frac{Q_{max,i}K_{1,i}C_{e,i}}{1 + \sum_{i=1}^{n} K_{1,i}C_{e,i}} \quad \quad \quad (14)
\]

where \( q_{e,i} \), \( C_{e,i} \), \( Q_{max,i} \), and \( K_{1,i} \) are the surface concentration of ith dye, equilibrium concentration of ith dye, maximum adsorption capacity for ith dye, and the equilibrium constant for the ith solute, respectively. The model parameters were estimated as outlined elsewhere \([26]\). The empirical Freundlich model, which is based on adsorption by a heterogeneous surface, takes the form \([19, 26, 27]\):

\[
q_e = K_F C_e^{\frac{n}{m}} \quad \quad \quad (15)
\]

where \( K_F \) (mg/L) is the equilibrium constant indicative of relative adsorption capacity and \( n \) is the model exponent which characterizes quasi-Gaussian energetic heterogeneity of the surface. A favorable uptake of dye is indicated by higher \( n \) values \([1–10]\).

Another useful isotherm which assumes an expression for condensation of a multilayer at a relatively large distance from a heterogeneous surface is the Halsey’s isotherm \([29]\):

\[
q_e = \left( \frac{K_H}{C_e} \right)^{1/n_H} \quad \quad \quad (16)
\]

where \( K_H \) and \( n_H \) are the parameters of the isotherm and all have an empirical nature. Another important model is the Jovanovic model which has comparable assumptions to the popular Langmuir model \([30]\):

\[
q_e = Q_{max}(1 - e^{K_e C_e}) \quad \quad \quad (17)
\]

The model keeps the same formulations adopted in the Langmuir model but with addition that some mechanical contact occurs between adsorbing and desorbing molecules. The Jovanovic model
can predict the maximum adsorption value $Q_{\text{max}}$ and the energy parameter $K_f$ which are necessary for understanding dye adsorption from single and multi-dye solutions.

Based on the energy of adsorption between adsorbent–adsorbate interactions, Temkin and Pyzhev have derived the following equation [31]:

$$q_e = \frac{RT}{b} \ln(K_fC_o)$$

(18)

$KT$ (L/mg) and $b$ (kJ/mol) are the equilibrium binding constant (L/mmol) and the relative heat of adsorption. $R$ and $T$ are the universal gas constant (8.314 J/mol K) and temperature (K), respectively.

The parameters of the tested models were estimated following a non-linear fitting procedure. Data-solver (Excel®) was adopted to run all necessary numerical calculations. The degree of fit of a certain model to the experimental data was evaluated by estimating prediction error sum of squares (PRESS) [16]:

$$\text{PRESS} = \sum_{i=1}^{n} (q_{\text{e,pred}} - q_{\text{e,exp}})^2$$

(19)

where $q_{\text{e,pred}}$ and $q_{\text{e,exp}}$ are the predicted and experimental adsorption values, respectively. The chi-square value, $\chi^2$, was estimated to assess the fitness between actual and predicted values [32]:

$$\chi^2 = \sum_{i=1}^{N} \frac{(q_{\text{e,exp}} - q_{\text{e,pred}})^2}{q_{\text{e,pred}}}$$

(20)

In Eq. (20), $N$ is the number of experimental points. Higher $X^2$ values reflect the poor fitness of the model.

The competition between dyes was assessed by estimating the competition factor as following [3, 33]:

$$\text{CF} = \frac{Q_{\text{max}}(\text{multi – solute})}{Q_{\text{max}}(\text{single – solute})}$$

(21)

where $Q_{\text{max}}$ (multi-solute) and $Q_{\text{max}}$ (single-solute) are the maximum retention capacities estimated from single and multi-solute systems, respectively. In case of positive competition, the competition factor (CF) is greater than unity and adsorption is enhanced by other solutes. For CF = 1, adsorption is proceeded with no competition. The general case is CF < 1 which reflected that solute’s affinity is reduced due to negative competition with other solutes [3, 33, 34].

### 3 Results and discussion

#### 3.1 Physical properties and chemical composition of biochar

The main textural parameters along with chemical composition are provided in Tab. 3.

The measured physical parameters (such as specific surface area, total pore volume, and pore diameter) indicated that the prepared material will provide high adsorption from solution. In fact, the prepared biochar exhibited a large specific surface area (95.6 m$^2$/g) along with large pore volume (0.18 cm$^3$/g) which is essential for accumulation of dye molecules from solution. On the other hand, the average pore diameter was reported to be 0.39 nm indicating the microporous nature of the prepared biochar. Based on Galán’s recommendation, all physical parameters of prepared biochar would facilitate dye removal from solution with minimum competition with solvent molecules [35]. The results of elemental analysis revealed that carbon is the major component of the biochar, making 52.4% of the material. Accordingly, the prepared adsorbent has a carbonaceous nature. The other heteroatoms (N and S) originated from the starting precursor (pine wood).

#### 3.2 Surface functional groups and interaction with food dyes

The FTIR spectra of the biochar and dye-loaded-biochar are presented in Fig. 1.

The IR bands were mainly attributed to the surface functional groups of biochar and to adsorbed dyes in some cases. As shown in Fig. 1, the IR scan of biochar indicated the following main bands: 3500, 1660, 1250, 1000, 1100, 860, and 600 cm$^{-1}$. The band located at 3500 cm$^{-1}$ was mainly due to OH vibrations while the strong bands observed at 1000, 1100, and 1250 cm$^{-1}$ were attributed to vibrations of C-O-C systems in the adsorbent. The band at 1100 cm$^{-1}$ is also a characteristic band for the carboxylic acid functional group in activated carbon. The sharp and short IR band observed at 1660 cm$^{-1}$ was attributed to N-H stretching in N-based groups in primary amine.

Similar spectral observations were reported for activated carbon prepared from cashew nut shell and *L. camara* [36, 37]. On the other hand, the bands located at 860 and 600–750 cm$^{-1}$ were notably attributed to bending and stretching ester vibrations of mono-substituted aromatic rings [36]. For dye-loaded-biochar spectra, no significant changes in the positions of original bands, however, the intensities of the peaks were reduced (Fig. 1). For example, the bands at 3500 and 1660 cm$^{-1}$ had almost disappeared in the spectra of the BB–biochar system (Fig. 1). The new peaks were notably attributed to vibrations of C=O, C=O, and O=O of the functional groups of dyes (Tab. 1). On the other hand, new peaks were attributed to the stretching and bending vibrations of $S$–$C$ bond on the dye (Tab. 1) and this would confirm the direct interaction of $S$ atom with the polar surface functional groups. The detection of $BB$ on the surface was attributed to the high concentration of sulphonate groups in this dye (four groups per molecule) compared to the other solutes (Tab. 1). Besides the IR measurements, analysis of the surface by simple acid-base titration indicated that total acidic and basic groups were 0.65 and
1.4 mmol/g, respectively. The basic nature of the surface was mainly originated from N-based functional groups. The acidic nature was mainly attributed to the presence of carboxylic and phenolic/alcoholic functional groups. The basic nature of the prepared biochar was also confirmed from the basic value of pHZPC (7.9). The mechanisms of interaction between dyes and biochar in solution are discussed in some detail in Sections 3.5 and 3.6.

3.3 Dyes quantification in the quaternary mixture by PLS-Kernel

Dye quantifications by PLS-Kernel were carried out at pH 2, 6, and 12 to find the best pH value for detection. Before discussing PLS-Kernel performance, it was necessary to estimate the extent of spectral behavior and overlapping of the dyes and the possibility of using direct spectroscopic methods for dye quantification. Figure 2 depicts the spectra of dyes at pH 2.

As shown in Fig. 2, the spectra show extensive spectral overlap. The greatest overlap was between SY and AR and this obviously makes their quantification by simple spectrometry not possible. Spectral overlap between the dyes TT and SY was also significant. To obtain accurate quantification, two options must be considered: (i) running separation-based methods for accurate detection, and (ii) applying multivariate calibration which is often applied in such cases [14–16]. In this work, the performance of PLS-Kernel for dye concentration quantification was evaluated at different pH values. Both correlation coefficients $r^2$ and relative error of predictions (REP%) were estimated to evaluate the performance of PLS-Kernel for dyes prediction in the mixture. The earlier parameters were estimated as follows [16]:

$$r^2 = 1 - \left( \frac{\sum_{i=1}^{n} (C_{i,\text{pred}} - C_{i,\text{act}})^2}{\sum_{i=1}^{n} (C_{i,\text{act}} - C_{i,\text{act}})^2} \right)^2$$  \hspace{1cm} (22)

Figure 1. FTIR spectra of biochar and dye-loaded biochar (the region 2,000–3,000 cm$^{-1}$ was excluded from all spectra due to lack of informative information).

Figure 2. Visible spectra of dyes at pH 2 and 8 mg/L.
In the earlier equations, $n$, $C_{i,\text{pred}}$, $C_{i,\text{act}}$, and $\Sigma$ are number of samples of validation set, predicted dye concentrations (mg/L), actual dye concentrations (mg/L), and the average of dye concentrations in the set (mg/L). As is already known, pH has a significant effect on the spectral behavior of dyes due to the acid–base equilibria (Tab. 1). Accordingly, calibration was carried out over a range of pH values. Prediction of dyes in validation set by PLS-Kernel is summarized in Tab. 4.

As can be inferred from Tab. 4, the best pH for quantification is two while higher prediction errors are observed in basic conditions. The extreme case was observed for AR with REP% of 18.3 which is not an acceptable value. In addition to this modest prediction performance at pH 12, more PLS factors $A$ are needed indicating the complexity of collected spectral data as more factors are needed to explain the variability in the data. More factors are needed at pH 12 to account for acid–base equilibria of solutes, intense spectral overlap, and the possible interaction between dyes. At pH 2, all dyes are in their H-form as they are relatively weak acids (pK$_a$ 6.3–11.2). The interesting point in Tab. 4 is the perfect performance of PLS-Kernel for prediction of BB and TT in the mixture at all pH values.

This can be attributed to the less spectral overlap with other components. On the other hand, the intense spectral overlap between AR and SY is negatively reflected in the performance of PLS-Kernel. For BB prediction, PLS-Kernel was effective even at high pH with REP% of 5.6 and with fewer PLS factors. Based on the provided results, pH 2 appears optimal to run PLS-Kernel as the dye concentrations are simultaneously predicted with REP% values of 1.4, 2.7, 8.7, 9.4 for BB, TA, SY, and AR, respectively. Accordingly, from an analytical point of view, the best pH to carry out adsorption tests is two and if the adsorption pH needs to be changed then the pH should be re-adjusted to two to run PLS-calibration. Running PLS-Kernel for dye quantification is certainly an attractive analytical process since expensive chromatographic procedures are no longer needed in the current system. Using PLS-Kernel, competitive adsorption of food dyes from solution is satisfactorily studied as is illustrated in Sections 3.4–3.6.

3.4 Dye adsorption at different experimental variables

Adsorption of dyes by activated pine wood biochar is controlled by many factors. Effect of pH, mass of biochar and the number of competing solutes are studied while maintaining the following variables at constant levels: Dye concentration 1000 mg/L, temperature 25°C, volume of solution 100 mL, and shaking time 24 h. For the earlier factors, %Removal-retention capacity plots were generated to assess the best experimental conditions for dye removal from solution.

3.4.1 Effect of solution pH on adsorption of dyes

As discussed earlier, the dyes studied have acid–base equilibria due to sulphonate groups. Variation of pH with dye adsorption should then be correlated to the nature of solute–surface interactions, either electrostatic or non-electrostatic interactions. It should be mentioned that dyes are quantified at pH 2, hence, for pH 6 and 12 experiments, the pH values of final solutions were re-adjusted to pH 2 before measurements. The results are shown in Fig. 3 and Tab. 5.

As shown in Tab. 5, both %Removal and retention capacity showed the same trend, both decreased by increasing pH values. At pH 2, the following order was observed for adsorption of dyes: SY>AR>TT>BB. The maximum uptake (provided as %Removal) was estimated at 1,000 mg/L and found to be 84, 60, 41, and 36% for SY, AR, TT, and BB, respectively. The solution pH has a significant influence on dye removal; hence the nature of interaction would be deduced. The measured pH$_{zpc}$ of activated pine wood is 7.9 while the pK$_a$ of dyes was within the range of 6.3–11.2 (Tab. 1). Hence, at solution pH 2 the adsorbent is positively charged but dyes are in the H-form and this clearly does not support an electrostatic mechanism. At pH 12, dye molecules and biochar are both negatively charged which retarded dye adsorption and this was observed in a similar study [22]. It seems that OH$^-$ ions were favorably adsorbed compared to dye molecules at pH 12. Non-electrostatic interaction mechanisms (dipole–dipole, hydrophobic–hydrophobic, and H-bonding) were possibly controlling the overall process. At pH 6, the possibility of an electrostatic mechanism is rather low as dyes are in H-form while pine wood is positively charged.

### Table 4. PLS-Kernel prediction of dyes in validation samples at different pH values

<table>
<thead>
<tr>
<th>Dye</th>
<th>%Recovery and statistical indicator</th>
<th>pH 2</th>
<th>pH 6</th>
<th>pH 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allura red</td>
<td>Mean recovery</td>
<td>91.6</td>
<td>93.7</td>
<td>84.1</td>
</tr>
<tr>
<td></td>
<td>REP%</td>
<td>9.4</td>
<td>11.4</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.9442</td>
<td>0.9325</td>
<td>0.8821</td>
</tr>
<tr>
<td></td>
<td>$A$ ($^a$)</td>
<td>6</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Brilliant black</td>
<td>Mean recovery</td>
<td>103.4</td>
<td>106.4</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>REP%</td>
<td>1.4</td>
<td>2.8</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.9998</td>
<td>0.9921</td>
<td>0.9821</td>
</tr>
<tr>
<td></td>
<td>$A$ ($^a$)</td>
<td>6</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Sunset yellow</td>
<td>Mean recovery</td>
<td>92.7</td>
<td>95.2</td>
<td>88.4</td>
</tr>
<tr>
<td></td>
<td>REP%</td>
<td>8.7</td>
<td>9.5</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.9512</td>
<td>0.9452</td>
<td>0.9215</td>
</tr>
<tr>
<td></td>
<td>$A$ ($^a$)</td>
<td>6</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>Tartrazine</td>
<td>Mean recovery</td>
<td>101.6</td>
<td>100.3</td>
<td>95.6</td>
</tr>
<tr>
<td></td>
<td>REP%</td>
<td>2.7</td>
<td>6.5</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.9978</td>
<td>0.9785</td>
<td>0.9741</td>
</tr>
<tr>
<td></td>
<td>$A$ ($^a$)</td>
<td>4</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

$^a$ $A$ is the optimum PLS-Kernel factor estimated by cross-validation technique [15, 16].

3.4.2 Effect of adsorbent’s dosage on dyes adsorption

The effect of absorbent mass is a significant parameter to be optimized due to its importance in practical applications and when measuring adsorption isotherms. Effect of mass of adsorbent on retention capacity and %Removal of SY at 1000 mg/L is presented in Fig. 3B and the final results are also provided in Tab. 5. For all dyes, a better %Removal is reported at higher masses, while retention capacity decreases or slightly increases for certain dyes. The better %Removal at higher masses was mainly attributed to the number of active sites available for adsorption. For SY, %Removal was increased from 62 to 96% upon increasing the mass from 0.6 up to 1.5 g, while this gives retention values of 103.3 and 64.0 mg/g. The maximum %Removal and retention capacity are reported for SY at 1.5 and 0.6 g, respectively. The point of intersection between lines (Fig. 3B) is often taken as a balance point between retention capacity and %Removal [25]. The optimum mass is often selected from the intersection point: 0.9, 1.0, 1.1, and 1.3 g/100 mL for SY, AR, TT, and BB, respectively. Except for BB, 1 g adsorbent is appropriate for conducting adsorption isotherms.

3.4.3 Effect of competing solutes on dye adsorption

Figure 3C and Tab. 5 summarize the negative influence of competing solutes on dye adsorption from solution. For demonstration purposes, Fig. 3C displays the effect of competing solutes on BB adsorption at 1000 mg/L. Both %Removal and retention capacity decreased upon adding TT and further decreased by adding the other two solutes. In all cases, the highest reduction in %Removal and retention capacity is observed when introducing three competing solutes. As shown in Tab. 5, BB is the most affected dye with a reduction of 39% in retention capacity in the presence of the three competing dyes. On the other hand, AR is the least affected with 20% reduction upon adding the other dyes. In all cases, the reduction in retention capacity becomes more significant by adding the second and the third competing solute. For example, retention capacity of AR is reduced by 7, 17, and 27% when competing with SY, SY/TT, and SY/TT/BB, respectively. In fact, the competition between dye molecules for active sites is the logical explanation for the observed reductions in %Removal and retention capacity. As will be shown in the following section, CF (which was estimated from the maximum adsorption values) is a reasonable index to assess the degree of competition between dyes toward the surface.

3.5 Adsorption isotherms of dyes from single and multi-dye solutions

Few studies have applied multivariate calibration or derivative spectrophotometry in competitive adsorption of dyes [3, 12, 13]. Recently, some researchers applied simple spectrophotometry to quantify dyes after adsorption from solution [1, 28]. In the current system, four dyes showing intense spectral overlap were studied and in this case advanced multivariate calibration is necessary for accurate quantification. Multivariate calibration is necessary to handle the negative influence of unexpected interferences that may occur during adsorption of dye mixtures. For the first time, PLS-Kernel is applied to study the competitive adsorption of food dyes (AR, BB, SY and TT) by biochar. The adsorption behavior of food dyes from single and multi-solute solutions were measured at the following conditions: pH 2, concentration range 10–1000 mg/L, mass 0.9 g, 25°C, and shaking time 24 h. The isotherms are depicted in Fig. 4.

For single-solute isotherms (Fig. 4A), L2-shape isotherms were obtained for the four dyes according to Giles and Smith classification [39]. The L2-isotherm is indicating that adsorption of dyes from retention capacity and %Removal of SY at 1000 mg/L is presented in Fig. 3B and the final results are also provided in Tab. 5. For all dyes, a better %Removal is reported at higher masses, while retention capacity decreases or slightly increases for certain dyes. The better %Removal at higher masses was mainly attributed to the number of active sites available for adsorption. For SY, %Removal was increased from 62 to 96% upon increasing the mass from 0.6 up to 1.5 g, while this gives retention values of 103.3 and 64.0 mg/g. The maximum %Removal and retention capacity are reported for SY at 1.5 and 0.6 g, respectively. The point of intersection between lines (Fig. 3B) is often taken as a balance point between retention capacity and %Removal [25]. The optimum mass is often selected from the intersection point: 0.9, 1.0, 1.1, and 1.3 g/100 mL for SY, AR, TT, and BB, respectively. Except for BB, 1 g adsorbent is appropriate for conducting adsorption isotherms.

3.4.3 Effect of competing solutes on dye adsorption

Figure 3C and Tab. 5 summarize the negative influence of competing solutes on dye adsorption from solution. For demonstration purposes, Fig. 3C displays the effect of competing solutes on BB adsorption at 1000 mg/L. Both %Removal and retention capacity decreased upon adding TT and further decreased by adding the other two solutes. In all cases, the highest reduction in %Removal and retention capacity is observed when introducing three competing solutes. As shown in Tab. 5, BB is the most affected dye with a reduction of 39% in retention capacity in the presence of the three competing dyes. On the other hand, AR is the least affected with 20% reduction upon adding the other dyes. In all cases, the reduction in retention capacity becomes more significant by adding the second and the third competing solute. For example, retention capacity of AR is reduced by 7, 17, and 27% when competing with SY, SY/TT, and SY/TT/BB, respectively. In fact, the competition between dye molecules for active sites is the logical explanation for the observed reductions in %Removal and retention capacity. As will be shown in the following section, CF (which was estimated from the maximum adsorption values) is a reasonable index to assess the degree of competition between dyes toward the surface.

3.5 Adsorption isotherms of dyes from single and multi-dye solutions

Few studies have applied multivariate calibration or derivative spectrophotometry in competitive adsorption of dyes [3, 12, 13]. Recently, some researchers applied simple spectrophotometry to quantify dyes after adsorption from solution [1, 28]. In the current system, four dyes showing intense spectral overlap were studied and in this case advanced multivariate calibration is necessary for accurate quantification. Multivariate calibration is necessary to handle the negative influence of unexpected interferences that may occur during adsorption of dye mixtures. For the first time, PLS-Kernel is applied to study the competitive adsorption of food dyes (AR, BB, SY and TT) by biochar. The adsorption behavior of food dyes from single and multi-solute solutions were measured at the following conditions: pH 2, concentration range 10–1000 mg/L, mass 0.9 g, 25°C, and shaking time 24 h. The isotherms are depicted in Fig. 4.

For single-solute isotherms (Fig. 4A), L2-shape isotherms were obtained for the four dyes according to Giles and Smith classification [39]. The L2-isotherm is indicating that adsorption of dyes from
Table 5. %Removal and retention capacity of dyes obtained at different experimental conditions

<table>
<thead>
<tr>
<th>Expt.</th>
<th>%Removal</th>
<th>Retention capacity (mg/g)</th>
<th>%Removal</th>
<th>Retention capacity (mg/g)</th>
<th>%Removal</th>
<th>Retention capacity (mg/g)</th>
<th>%Removal</th>
<th>Retention capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>84</td>
<td>93.3</td>
<td>41</td>
<td>45.6</td>
<td>60</td>
<td>66.7</td>
<td>36</td>
<td>40.0</td>
</tr>
<tr>
<td>6.0</td>
<td>60</td>
<td>66.7</td>
<td>20</td>
<td>22.2</td>
<td>38</td>
<td>42.2</td>
<td>18</td>
<td>20.0</td>
</tr>
<tr>
<td>12.0</td>
<td>39</td>
<td>43.3</td>
<td>10</td>
<td>11.1</td>
<td>22</td>
<td>24.4</td>
<td>5.0</td>
<td>5.6</td>
</tr>
<tr>
<td>Mass (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>62</td>
<td>103.3</td>
<td>25</td>
<td>41.7</td>
<td>42</td>
<td>70.0</td>
<td>22</td>
<td>36.7</td>
</tr>
<tr>
<td>0.9</td>
<td>84</td>
<td>93.3</td>
<td>41</td>
<td>45.6</td>
<td>60</td>
<td>66.7</td>
<td>36</td>
<td>40.0</td>
</tr>
<tr>
<td>1.2</td>
<td>93</td>
<td>77.5</td>
<td>57</td>
<td>47.5</td>
<td>72</td>
<td>60.0</td>
<td>56</td>
<td>46.7</td>
</tr>
<tr>
<td>1.5</td>
<td>96</td>
<td>64.0</td>
<td>70</td>
<td>46.7</td>
<td>80</td>
<td>53.3</td>
<td>65</td>
<td>43.3</td>
</tr>
</tbody>
</table>

| Competition |          |                           |          |                           |          |                           |          |                           |
| System      | % Removal | Retention capacity (mg/g) |          |                           |          |                           |          |                           |
| SY          | 84        | 93.3                      | TT        | 41                        | AR       | 60                        | BB       | 36                        |
| SY with TT  | 79        | 87.8                      | TT with AR| 39                        | AR with SY | 56                        | BB with TT| 34                        |
| SY with TT & AR | 72 | 80.0                      | TT with AR & SY | 36                        | AR with SY & TT | 50                        | BB with TT & SY | 29                        |
| SY with TT & AR & BB | 66 | 73.3                      | TT with AR & SY & BB | 30                        | AR with SY & TT & BB | 44                        | BB with TT & SY & AR | 22                        |

\(^{a)}\)Values of %Removal were rounded to two significant figures.
\(^{b)}\)Experimental conditions for pH test: Mass 0.9 g, volume of solution 100 mL, dye level 1000 mg/L, temp. 25°C, and shaking time 24 h.
\(^{c)}\)Experimental conditions for mass test: pH 2, volume of solution 100 mL, dye level 1000 mg/L, temp. 25°C, and shaking time 24 h.
\(^{d)}\)Experimental conditions for competition test: Mass 0.9 g, pH 2, volume of solution 100 mL, dye level 1000 mg/L, temp. 25°C, and shaking time 24 h.
solution by biochar was accomplished by forming one layer only [39]. In fact, the L2-isotherm reflected the high adsorption affinity between dye molecules and biochar at lower concentrations and at higher concentrations the surface becomes more saturated. Adsorption isotherms of heavy metals and charged dye molecules have been reported to have the L2-shape [34]. As shown in Fig. 4B, the L2-isotherm for competitive system was observed [1, 34]. This is not commonly reported in the literature. In the current case, the typical L2-isotherm was attributed to modest competition between dyes toward the surface. The competition between dyes should increase at higher concentrations and this should disturb the typical L2-isotherm. To measure the maximum adsorption capacity of dyes and to study the mechanism of adsorption, equilibrium adsorption data were presented by different equations. Parameters of the models PRESS and $X^2$-values are provided in Tab. 6.

### 3.5.1 Langmuir isotherm

Langmuir was found to be applicable for modelling adsorption behavior of all solutes from single and multi-solute systems. For single dye-solutions, acceptable PRESS (5.3–8.3) and $X^2$ (1.3–1.9) values were obtained. $Q_{\text{max}}$ values predicted by the Langmuir model were measurably larger than experimental values (Fig. 4A). The same trend is observed in multi-solute system where the model predicts higher $Q_{\text{max}}$ values than those obtained experimentally (Fig. 4B). In fact, $Q_{\text{max}}$ values confirm the reduction in dye adsorption in the multi-solute system, for all dyes $Q_{\text{max}}$ in multi-solute systems is significantly lower than in single-solute systems. Although the individual adsorption capacity of each solute was reduced, the final performance of biochar was excellent with a combined uptake value of 186.9 mg/g (sum of the maximum adsorption values). On the other
hand, $K_r$ values (expressed as L/mmol) reflected the high affinity of the dyes to the solid medium in both systems. While the existence of competing dyes did not affect the equilibrium constants, the competing dyes have reduced the maximum retention values as indicated in Tab. 6 and for all dyes. Due to negative competition with other dyes, the adsorption value of SY was decreased from 94.2 to 76.4 mg/g but with a small variation in the equilibrium constant.

3.5.2 Freundlich and Halsey isotherms

As shown in Tab. 6, the Freundlich model was not as effective as the Langmuir model for presenting adsorption data as confirmed for the higher chi-square values, 7.2–9.1 and 6.3–11.6 for single and multi-solute systems, respectively. Although it is not highly applicable to the current system, the values of $n$ (exponents in the Freundlich model) would indicate the favorable uptake of dyes from single and multi-solute solutions. Furthermore, this model predicted the same trend that was obtained from Langmuir’s model and for both systems: SY>AR>TT>BB. Due to its poor performance, the final fitting results of the Halsey’s model are not presented in Tab. 6. With extremely high PRESS (53–86) and $X^2$-values (28–36), Halsey’s model manifested a limited application for presenting dye adsorption from single and multi-solute solutions. This conclusion supports the fact that multilayer adsorption of dyes, assumed by this model, was not achieved and adsorption proceeded with one molecular layer on the surface even in multi-solute systems. It is highly possible that the competition between dyes in multi-solute solution would retard the formation of a multilayer on the surface.

3.5.3 Temkin isotherm

This isotherm was found to be excellent for presenting the behavior of dye adsorption from single and multi-solute systems as confirmed from the low PRESS and $X^2$-values. $K_T$, the equilibrium constant, indicates the following affinity of dyes SY>AR>TT>BB and this trend holds true for both adsorption systems. The disadvantage of this model (compared to the Langmuir and Jovanovic models) is that $Q_{max}$ cannot be predicted. The variation of adsorption energy in the model (parameter $b$) was positive and comparable for both systems which proved that the adsorption process of dyes in both systems has an exothermic nature [31, 40]. For multi-solute systems, the predicted adsorption energies were 32.5, 26.4, 19.6, 15.4 kJ/mol SY, an exothermic nature [31, 40]. For multi-solute systems, the predicted adsorption energies were 32.5, 26.4, 19.6, 15.4 kJ/mol SY, 19.6, and 15.4 kJ/mol BB. Due to the poor performance, the final fitting results of the Halsey’s model are not presented in Tab. 6. With extremely high PRESS (53–86) and $X^2$-values (28–36), Halsey’s model manifested a limited application for presenting dye adsorption from single and multi-solute solutions. This conclusion supports the fact that multilayer adsorption of dyes, assumed by this model, was not achieved and adsorption proceeded with one molecular layer on the surface.

The applicability of the Langmuir model was reduced due to the formation of a multilayer on the surface. This conclusion supports the fact that multilayer adsorption of dyes, assumed by this model, was not achieved and adsorption proceeded with one molecular layer on the surface. The disadvantage of this model (compared to the Langmuir and Jovanovic models) is that $Q_{max}$ cannot be predicted. The variation of adsorption energy in the model (parameter $b$) was positive and comparable for both systems which proved that the adsorption process of dyes in both systems has an exothermic nature [31, 40]. For multi-solute systems, the predicted adsorption energies were 32.5, 26.4, 19.6, 15.4 kJ/mol SY, AR, TT, and BB, respectively. The energy related to the removal process ($\Delta H_{adsorption}$) is correlated to the following three processes [23]:

$$\Delta H_{adsorption} = \Delta H_{dye-water} + \Delta H_{dye-dye} + \Delta H_{dye-surface}$$

where $\Delta H_{dye-water}$, $\Delta H_{dye-dye}$ and $\Delta H_{dye-surface}$ are energy related to intermolecular forces between dye molecules and solvent, energy related to intermolecular forces between dye molecules, and energy related to the forces between dye molecules and biochar, respectively. In fact, the first two terms ($\Delta H_{dye-water} + \Delta H_{dye-dye}$) have positive values as they represent endothermic processes (bond breaking) while the last term ($\Delta H_{dye-surface}$) is negative as it accounted for an exothermic process (bond formation). As the whole process was exothermic, then this indicated that $\Delta H_{dye-water}$ has a large negative value which exceeded the total energies of the other two systems.

### Table 6. Modeling of dyes adsorption from single and multi-solute systems

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>PRESS</th>
<th>$X^2$</th>
<th>Parameter</th>
<th>PRESS</th>
<th>$X^2$</th>
<th>Parameter</th>
<th>PRESS</th>
<th>$X^2$</th>
<th>Parameter</th>
<th>PRESS</th>
<th>$X^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-dye adsorption system</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td>$Q_{max}$: 94.2</td>
<td>5.3</td>
<td>1.3</td>
<td>$Q_{max}$: 68.4</td>
<td>1.9</td>
<td>48.3</td>
<td>$Q_{max}$: 52</td>
<td>7.6</td>
<td>1.6</td>
<td>$Q_{max}$: 37.1</td>
<td>6.4</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>$K_r$: 172</td>
<td></td>
<td></td>
<td>$K_r$: 153</td>
<td></td>
<td></td>
<td>$K_r$: 52</td>
<td></td>
<td></td>
<td>$K_r$: 38</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$K_f$: 9.5</td>
<td>13.5</td>
<td>9.1</td>
<td>$K_f$: 4.3</td>
<td>7.9</td>
<td>4.3</td>
<td>$K_f$: 2.9</td>
<td>11.4</td>
<td>8.3</td>
<td>$K_f$: 1.3</td>
<td>12.6</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>$n$: 1.8</td>
<td></td>
<td></td>
<td>$n$: 1.5</td>
<td></td>
<td></td>
<td>$n$: 1.4</td>
<td></td>
<td></td>
<td>$n$: 1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$K_r$: 612</td>
<td>2.1</td>
<td>1.1</td>
<td>$K_r$: 353</td>
<td>1.0</td>
<td>2.9</td>
<td>$K_r$: 416</td>
<td>3.1</td>
<td>1.3</td>
<td>$K_r$: 311</td>
<td>2.9</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>$b$: 35.4</td>
<td></td>
<td></td>
<td>$b$: 29.5</td>
<td></td>
<td></td>
<td>$b$: 22.6</td>
<td></td>
<td></td>
<td>$b$: 18.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$K_f$: 90.5</td>
<td>1.7</td>
<td>0.6</td>
<td>$K_f$: 58.4</td>
<td>0.9</td>
<td>42.2</td>
<td>$K_f$: 34.2</td>
<td>2.1</td>
<td>1.0</td>
<td>$K_f$: 31.4</td>
<td>2.5</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>$K_f$: 76.3</td>
<td></td>
<td></td>
<td>$K_f$: 44.4</td>
<td></td>
<td></td>
<td>$K_f$: 34.2</td>
<td></td>
<td></td>
<td>$K_f$: 25.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temkin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jovanovic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Four-dye adsorption system |             |       |       |             |       |       |             |       |       |             |       |       |
| Langmuir                | $Q_{max}$: 76.4 | 6.4   | 1.3   | $Q_{max}$: 46.5 | 1.4   | 43.2  | $Q_{max}$: 59 | 7.1   | 1.4   | $Q_{max}$: 29.8 | 7.1   | 1.4   |
|                        | $K_r$: 175 |       |       | $K_r$: 149 |       |       | $K_r$: 57 |       |       | $K_r$: 42 |       |       |
| Competitive Langmuir    | $Q_{max}$: 73.2 | 4.6   | 1.5   | $Q_{max}$: 43.5 | 1.0   | 32.0  | $Q_{max}$: 30.2 | 6.5   | 1.5   | $Q_{max}$: 25.1 | 7.0   | 1.3   |
|                        | $K_r$: 6.3 | 18.9  | 6.3   | $K_r$: 3.1 | 7.3   | 3.1   | $K_r$: 2.1 | 22.4  | 11.6  | $K_r$: 1.2 | 19.5  | 9.0   |
|                        | $n$: 1.7   |       |       | $n$: 1.4 |       |       | $n$: 1.6 |       |       | $n$: 1.6 |       |       |
|                        | $K_r$: 598 | 2.9   | 1.0   | $K_r$: 516 | 1.1   | 422   | $K_r$: 422 | 3.2   | 0.9   | $K_r$: 329 | 1.9   | 1.0   |
|                        | $b$: 32.5  |       |       | $b$: 26.4 |       |       | $b$: 19.6 |       |       | $b$: 15.4 |       |       |
| Temkin                 |             |       |       |             |       |       |             |       |       |             |       |       |
| Jovanovic              |             |       |       |             |       |       |             |       |       |             |       |       |


Water (11 of 13) 1600333
endothermic processes. The high adsorption energy reported for AR (32.5 kJ/mol) was expected due to its high affinity compared with all other dyes as confirmed from the Langmuir, and Temkin as well as the Jovanovic models.

3.5.4 Competitive-Langmuir isotherm
Among the tested models, the competitive-Langmuir model would be the best choice as it accounts for the influence of other competing solutes (Eq. (14)). As expected, the model has good performance for presenting dye adsorption from multi-solute system as confirmed from statistical indicators. As shown in Tab. 6, the \( Q_{\text{max}} \) values are 73.2, 43.5, 32.0, and 25.1 mg/g for AR, SY, TT, and BB, respectively. The earlier adsorption values confirmed that the dyes investigated have a negative influence on their adsorption when compared to values obtained from single-solute isotherms (Fig. 4A).

3.5.5 Jovanovic isotherm
Interestingly, the lowest \( X^2 \)-values (0.6–1.2) are reported for Jovanovic’s model. The good fit of this model revealed that adsorption of dyes from solution can be explained by approximation of monolayer localized adsorption without lateral interaction. In fact, Jovanovic’s model maintains the same assumptions contained in the Langmuir model in addition to the possibility of some mechanical contact between the absorbing and desorbing molecules [30–41]. In fact, the Jovanovic, competitive-Langmuir, and Temkin models are the best performing models in terms of PRESS and \( X^2 \) for presenting dye adsorption behavior from both single and multi-solute solutions. The excellent performance of the Jovanovic and Temkin models is ascribed to the homogeneity of the surface and the possibility of mechanical contact between the adsorbate and desorbate molecules due to the existence of intermolecular interactions between solutes. For both systems, the Jovanovic model gives the best prediction of \( Q_{\text{max}} \) values as the nearest values to the experimental data in comparison with the other models. As shown in Fig. 4, adsorption isotherms of dyes were satisfactorily presented by Jovanovic’s isotherm.

3.6 Competition factors
The competition between competing solutes was assessed by estimating CF. The \( Q_{\text{max}} \) values needed to find CF were taken from Jovanovic’s model due to closeness to the experimental ones. The estimated CF values were 0.69, 0.70, 0.75, and 0.76 for AR, TT, BB, and SY, respectively. In all cases, CF values were <1, indicating a negative competition between dyes. The least affected dye was SY with CF of 0.76, while the most affected was AR with a CF value of 0.69. The high CF value of SY would be attributed to the high affinity of this dye toward biochar (as confirmed from \( Q_{\text{max}} \) of single-solute adsorption data). Surface characterization of biochar indicated that it has a high specific surface area, porosity and furnishes different functional groups, therefore adsorption mechanisms including H-bonding and dipole–dipole forces are also possible as the estimated density of functional group is 2.1 groups/nm\(^2\). From the chemical point of view and as indicated from IR scans (Fig. 1), removal of the four dyes was attained by the same mechanisms (H-bonding and dipole–dipole forces) and it is not possible to explain the competition toward the surface. However, the large molecular size of brilliant black (five cyclic rings) would be expected to negatively affect its removal from solution, modest surface diffusion and modest diffusion in solution.

4 Concluding remarks
Four food dyes AR, BB, SY, and TT were simply quantified in the mixture using Kernel-PLS with excellent accuracy and without the need for using expensive chromatographic methods. Biochar prepared by chemical activation of natural pine wood manifested a high affinity toward food dyes with a combined adsorption capacity of 186.9 mg/g at 25 °C. The competitive-Langmuir, Temkin, and Jovanovic models were all effective at modelling adsorption data for single and multi-solute systems. The Jovanovic model gives the best prediction for \( Q_{\text{max}} \) as being the nearest to the experimental values. Moreover, the Temkin model showed that adsorption from single and multi-solute systems has an exothermic nature. Competition factors indicated that AR was the most affected dye while SY was the least affected one.

Acknowledgments
The financial support from the Hashemite University/deanship of academic research is gratefully acknowledged.

The authors have declared no conflict of interest.

References


S. Sahin, C. Demir, S. G¨oger, Simultaneous UV-Vis Spectrophotometric Determination of Disperse Dyes in Textile Wastewater by Partial Least Squares and Principal Component Regression, Dyes Pigm. 2007, 73, 368–376.


