



Multivariate analysis of competitive adsorption of food dyes by activated pine wood

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Received 27 October 2015; Accepted 28 March 2016

ABSTRACT

In this work, competitive adsorption of four food dyes (Sunset Yellow, Allura Red, tartrazine, and Brilliant Black) by heated pine wood is studied using multivariate calibration. Partial least squares PLS1 and principal component regression PCR are effectively applied for simultaneous determination of food dyes with high accuracy (96.2–103.6%) and low relative prediction error (2.3–6.9%). Using multivariate calibration, the dyes are detected down to 0.11, 0.15, 0.24, and 0.29 mg L⁻¹. The removal of dyes increased at acidic solution and H-bonding is the main controlling mechanism. The maximum removal capacities (according to Langmuir model) are 3.4, 2.5, 4.8, and 7.1 mg g⁻¹ for tartrazine, Brilliant Black, Allura Red, and Sunset Yellow, respectively, at pH 2.0 and 25°C. The competition factors (CFs) are estimated from the isotherms to assess the degree of competition between dyes toward the surface. The CFs are 0.64, 0.66, 0.77, and 0.77 for Brilliant Black, Allura Red, Sunset Yellow, and tartrazine, respectively. Accordingly, Brilliant Black is the most affected dye while Sunset Yellow and tartrazine are the least affected in multi-solute adsorption. This study demonstrates the useful application of multivariate calibration for studying competitive adsorption of colored pollutants with minimum experimental efforts expenses.

Keywords: Competitive adsorption; Food dyes; Pine wood; Multivariate calibration

1. Introduction

Wastewater containing dyes can be challenging due to the existence of visible color with unwanted consequences [1–12]. Conventional treatment facilities are often unable to eliminate specific dyes from water; particularly those with higher solubility and low

biodegradability [4]. The failure of conventional physicochemical methods for removing problematic dyes might be overcome by adsorption. Hence, adsorption is proposed as an efficient method for removing dyes from aqueous solution [1–5]. Food dyes are characterized by nitrogen-to-nitrogen double bond N=N or azo bond associated with the chromophores of dyes [5]. Accordingly, degradation of food dyes would generate

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toxic byproducts making adsorption a safe procedure to eliminate dyes from solution. Activated carbon adsorption is often used to remove wide spectrum of pollutants from water including dyes [1–6]. Recently, more attention was given to natural materials [6–12]. The work of Mittal and co-workers on excellent application of hen feather is worth to be cited [12]. Hen feather manifested a high affinity toward Bismark Brown R [7], Brilliant Blue FCF [8], and malachite green [9].

Adsorption of single dye [3,7–9] or mixture of dyes [1,2] from solution using number of adsorbents is well reported in chemical and environmental literatures. For mixture of dyes, a separation step of solutes is often necessary before quantification [13–15]. For single dye adsorption tests, quantification of unreacted dye is carried out using direct spectral measurement [3,7–9]. For multi-dye systems, more attention is needed for solute quantification due to intense spectral overlapping. Few studies have been reported which extended from direct spectrophotometric quantification [1,13] to more advanced spectrophotometric ones [14,15]. The proper selection of the analytical method is reliant on the degree of spectral overlap between dyes. Therefore, this study was aimed to investigate the difficulties accompanied with multi-dye adsorption from solution.

The most adopted analytical methods used for dyes quantification are high-performance liquid chromatography, liquid chromatography/mass spectrometry (LCMS), capillary electrophoresis, and gas chromatography [16]. In fact, dyes quantification based on chromatographic procedures is a laborious work and takes much more time where solutes separation is necessary before detection [16,17]. In case of intense spectral overlap or complex matrices, multivariate calibration methods including multilinear regression (MLR), principal component regression (PCR), and partial least squares (PLS) have been effectively applied for dyes quantification [4,16–18]. The main advantage of multivariate calibration methods is to minimize or eliminate sample preparation and to avoid applying tedious chromatographic methods [4,16,17]. In multi-dye adsorption, evaluating dyes competition for active sites is very important. The prediction and also modeling multi-component adsorption equilibrium are also important issues and very helpful for understanding adsorption in multi-solute systems. In fact, limited studies have considered the application of multivariate calibration for studying competitive adsorption of food dyes. To the best of our knowledge, using multivariate calibration for studying competitive adsorption of SY, AR, TA, and BB by natural wood is not reported (the dyes showed intense spectral overlapping).

In this work, adsorption of four food dyes from single and multi-solute solutions is studied with the aid of multivariate calibration. The tested dyes have intense spectral overlapping which gives more value for multivariate calibration for dyes quantification in the mixture, and in the same time, avoiding labours chromatographic methods. Microwave-heated pine wood is used as solid medium for dyes removal from solution. Multivariate calibration methods including multilinear regression (MLR), PCR, PLS, and net-analyte signal processing with PLS1 (NAP-PLS) are applied for dyes quantification in the mixture. Adsorption data were presented with different adsorption models so as to get a better idea regarding competitive adsorption of dyes and the nature of solute–solute and solute–adsorbent interactions. This research is, in fact, an extension of our previous work on utilizing microwave-heated pine wood for dyes removal from solution [2].

2. Materials and methods

2.1. Pine wood flakes and microwave activation

Pine wood was collected as flakes of dimension (2×2 cm) from a local carpentry. The sample (4.0 kg) was washed with distilled water and dried at 105°C for 24 h. Heat treatment by microwaves was outlined in the literature [2] and a short summary is provided herein. Microwave heating was carried out using a domestic microwave oven (SAMSUNG, triple distribution system, Japan) operating at 2.45 GHz. About 4.0 gram sample was placed on a quartz dish. The dish was carefully was exposed to microwaves (600 W) for 8.0 min. The earlier activation conditions were the optimum activation conditions. For better activation results, wood flakes were soaked in 0.01 M H_2SO_4 for 1.0 h, filtered, and then irradiated with microwaves. Upon completion of treatment, the hot sample was removed and placed in the desiccators before running adsorption tests. Textural characteristics including specific surface area, total pore volume, and average pore diameter were determined using standard N_2 -adsorption techniques (Nova 4200e, Surface Area and Pore Size Analyzer) [2,19]. Total acidity and basicity of the adsorbent were measured using standard Boehm's titrations [2,19]. pH_{zpc} (pH at zero point of charge) was estimated using pH-drift method [2,19].

2.2. Food dyes

Four common food dyes with a high industrial application were purchased from Sigma[®] with variable purities (60–100%): Allura Red, Sunset Yellow,

Tartrazine, and Brilliant Black. The structures of dyes with corresponding pK_a values are depicted in Table 1.

For each dye, a standard solution was prepared and used to prepare other diluted solutions. Different phosphate buffers (pH 2.0, 6.0, and 12.0) were freshly prepared and used to fix pH for dye solutions. The following solutions were used to prepare buffers: NaOH (0.05 mol L^{-1}), HCl (0.05 mol L^{-1}), H_3PO_4 (0.05 mol L^{-1}), NaH_2PO_4 (0.05 mol L^{-1}), and Na_2HPO_4 (0.05 mol L^{-1}). The final pH of each buffer was checked and re-adjusted if necessary. It is already known that the tested dyes have unwanted consequences when consumed in large excess [5] and consider as common pollutants [7,8].

2.3. Effect of pH and mass of adsorbent on dyes adsorption from single-solute solution

Generally, adsorption tests were carried out as following: To a 100 mL solution of 100.0 mg L^{-1} dye in 250 mL volumetric flask, a certain amount of dried adsorbent is added. The mixture was closed and agitated for 24 h (equilibrium time) at 25°C using thermostated mechanical shaker. After 24 h, the remaining

concentration was measured using UV-vis spectrophotometer (Cary 3E UV-vis spectrophotometer, Varian, Australia). Four calibration graphs were provided for each dye. Effect of solution pH (2.0, 6.0, and 12.0) and mass of adsorbent (0.5, 1.0, 1.5, and 2.0 g) on dyes adsorption were studied following the outlined procedure. Initial and final pH of adsorption solutions were measured using a digital pH meter (Weilheim, Germany) combined with glass electrode with an accuracy of ± 0.01 unit. At each pH, a separate calibration equation was provided for each dye. Retention or adsorption value at equilibrium q_e (mg g^{-1}) and dye removal % were estimated as [2]:

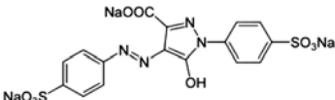
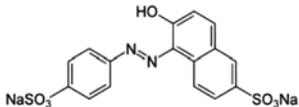
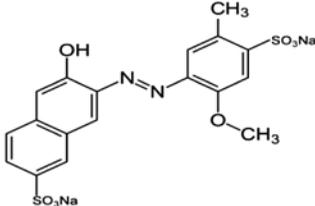
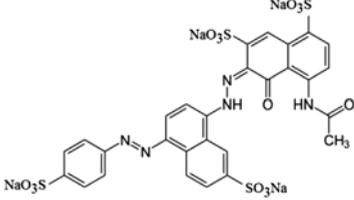
$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

and

$$\text{Dye removal \%} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where C_o , C_e , q_e , V , and m are initial dye concentration (mg L^{-1}), equilibrium dye concentration (mg L^{-1}), surface dye concentration (mg g^{-1}), volume of solution

Table 1
Chemical properties of studied food dyes^a

Dye/short name	Structural formula (Na-form)	pK_a (13)	CAS no.
Tartrazine TA		9.4	1934-21-0
Sunset Yellow SY		10.4	2783-94-0
Allura Red AR		11.4	25956-17-0
Brilliant Black BB		6.4	2519-30-4

^aAll dyes were of food quality and purchased from Sigma[®] with the following purities 100, 90, 80, and 60 for tartrazine, Sunset Yellow, Allura Red, and Brilliant Black, respectively.

(mL), and mass of adsorbent (g), respectively. In certain cases, dilution was necessary before UV scanning to get accurate readings.

2.4. Adsorption from multi-solute solution and competitive adsorption

For multi-solute adsorption, the earlier experimental protocol was repeated, however, using mixture of dyes over the range 10–100 mg/L. Ten solutions were prepared and the concentrations of four dyes were 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg L⁻¹. For example, 10 mg L⁻¹ of each dye was used to prepare solution number 1 and so on. It was not possible to measure dyes in the mixtures by simple spectrometry due to intense spectral overlapping, accordingly, multivariate calibration was necessary in this complex system. Multivariate calibration was applied to find individual dye content in multi-solute solutions as outlined in the following section. Finally, adsorption isotherms of dyes were plotted and the data were presented by different models. Two common isotherms were used to correlate adsorption data of the single and the multi-solute systems, namely Langmuir and Freundlich equations. Langmuir equation which is valid for monolayer adsorption cases, equal energy active sites, and no solute–solute interactions is represented as following [20]:

$$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (3)$$

where Q_{\max} (mg g⁻¹) is the amount adsorbed at complete monolayer coverage. K_L (L/mg) is Langmuir parameter taken as equilibrium constant (Allen et al.). The empirical Freundlich model which is based on adsorption by heterogeneous surface takes the form [20]:

$$q_e = K_F C_e^n \quad (4)$$

where K_F (mg/L) and n are equilibrium constant indicative of relative adsorption capacity and model exponent which characterize quasi-Gaussian energetic heterogeneity of the surface. A favorable uptake of dye is indicated by higher n value (1–10) [19,20].

The closeness between actual and predicted adsorption values q_e was assessed by finding the prediction error sum of squares Press which was estimated as [4]:

$$\text{Press} = \sum_{i=1}^n (q_{e,\text{exp}} - q_{e,\text{pred}})^2 \quad (5)$$

where $q_{e,\text{exp}}$, $q_{e,\text{pred}}$, and n are experimental adsorption value, model-predicted adsorption value, and number of experiments, respectively.

Another important parameter that should also be estimated in order to evaluate the extent of the competition between dyes is the competition factor (CF) [2]:

$$\text{CF} = \frac{Q_{\max\text{-mixture}}}{Q_{\max\text{-single-solute}}} \quad (6)$$

where $Q_{\max\text{-mixture}}$ and $Q_{\max\text{-single-solute}}$ are the maximum adsorption values obtained from the multi-solute and single-solute isotherms; respectively. Positive competition is encountered if the CF is more than unity and the adsorption is enhanced by the other competing solutes. Adsorption of no competition is encountered if CF = 1.0. The common case is CF < 1 which indicates that adsorption of the solute is reduced due to competition with other solute(s) [2,21].

2.5. Collection of spectral data and numerical calculations by MVC1[®] program

Initially, two sets were prepared. Calibration set which contains 10 mixtures of dyes. For each dye, the concentration range was: 1–10 mg L⁻¹. Validation set which composed of five mixtures of dyes and this synthetic set was used to check the performance of the model. The level of dyes in validation set was comparable to that used in calibration set. For each mixture, a spectrum containing 75 points was recorded at pH 2.0, 6.0, and 12.0 and over the range 330–700 nm at interval of 5.0 nm. The collected spectral data were subjected to different algorithms in order to find content of dyes in the mixture. The theoretical backgrounds of adopted algorithms: multilinear regression MLR, PCR, PLS, net-analyte processing/PLS NAP/PLS are discussed elsewhere [22,23]. Recently, an advanced program called MVC1 was launched to run MLR, PCR, PLS, and NAP/PLS algorithms which performed under MATLAB[®] [22]. The program is easily accessed and has many options including data processing, cross-validation technique, wavelength selection, and outlier's detection [22]. The concept of net-analyte signal is available in MVC1 which is necessary to estimate figures of merit of the proposed analytical method.

3. Results and discussion

3.1. Extent of spectral overlapping between dyes and importance of multivariate calibration

It was necessary to have a look on the spectral behavior of dyes and to check the possibility of

applying other simple spectroscopic methods for dyes quantification in mixture. The spectra of dyes at pH 2 are given in Fig. 1.

As indicated in Fig. 1, spectra of dyes have an intense spectral overlapping. The highest overlap (70–100%) was between SY, AR, and BB and this retard the application of simple spectrometry for quantification. The spectral overlap between TA and SY was also significant. To overcome the earlier analytical dilemma, two options are considered: (A) applying liquid chromatography for solutes separation prior to detection, and (B) applying multivariate calibration method. In this study, adoption of multivariate calibration for dyes quantification seems to be a reasonable solution taking into account the high running cost of liquid chromatography.

3.2. Multivariate calibration for dyes quantification

To predict dyes in the mixture, different models were used MLR, PLS-1, PCR, and PLSNAP/PLS. A short summary on multivariate calibration is provided. Multivariate calibration is an efficient tool for developing a quantitative relationship between several predictor variables in matrix X (spectral measurements in this work) and a property of interest in vector y (the independent variable or dye content in this work). Mathematically, the relationship between X and y is given as [24]: $y = Xb$, where y , X , and b are dye 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 estimating dye content in mew

solutions. MLR, PLS-1, PCR, and PLS NAP/PLS are efficient numerical tools to find b which is necessary to predict dye in unknown solution. All numerical calculations were carried out using MVC1 program [22]. The following general procedure was adopted to run the models: (a) training the model using calibration set, (b) testing the model by dyes prediction in validations set, and (c) predicting dyes content in adsorption solution.

The studied dyes are weak acids and have acid–base equilibria in solution. Accordingly, the performance of multivariate calibration for dyes quantification under different acidity conditions was studied. Prediction of dyes level in validations set at different pH was assessed by estimating correlation coefficients r^2 and relative error of predictions REP%. The earlier parameters were estimated from nominal and predicted concentrations. Correlation coefficients r^2 was estimated as [4]:

$$r^2 = 1 - \left(\frac{\sum_{i=1}^n (C_{i,\text{pred}} - C_{i,\text{act}})^2}{\sum_{i=1}^n (C_{i,\text{act}} - \bar{C})^2} \right)^2 \quad (7)$$

On the other hand, relative error of prediction REP% was estimated as [4]:

$$\text{REP}\% = 100 \times \left(\frac{\sum_{i=1}^n (C_{i,\text{pred}} - C_{i,\text{act}})^2}{\sum_{i=1}^n (C_{i,\text{act}})^2} \right)^{1/2} \quad (8)$$

where n , $C_{i,\text{pred}}$, $C_{i,\text{act}}$, and \bar{C} are the number of samples in validation set, predicted concentration

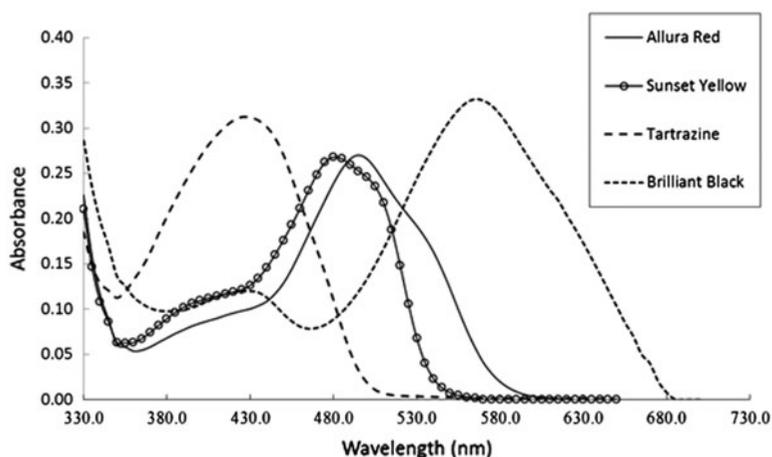


Fig. 1. Spectra of food dyes at 8.0 mg L^{-1} and pH 2.0.

(mg L⁻¹), actual concentration (mg L⁻¹), and the average dye concentrations in the set (mg L⁻¹). The overall results for dyes prediction at different pHs are given in Table 2.

As indicated in Table 2, MLR was not effective as other algorithms. However, the model was able to predict TA in the mixture with acceptable recoveries (to some extent) even in the presence of intense overlapping with AR and SY. The final REP% over pH was in the range 13.6–14.2. The best results were observed when using PLS. The method outperformed other algorithms for TA prediction with mean recoveries 96.2–103.6% and REP% 2.3–6.9. The model was effective for dye prediction at pH values of 2.0, 6.0, and 12.0 with PLS variables of 5, 6 and 5; respectively. Fig. 2 depicts the Press-latent variable obtained at pH 2.

As indicated in Fig. 2, the Press value was significantly reduced at 5; indicating the optimum prediction of TA using 5 variables which would account for the rest of dyes. Using more number of variables would

produce over fitting problem. The interesting point in Table 2 is that pH 2.0 is the best value for running all algorithms. The good performance at pH 2.0 may be attributed to the better light absorption of dyes compared to other pH. PCR also manifested a good analytical performance where TA was quantified using 5 factors at all pHs. The accuracy was acceptable with mean recoveries of 99.5–103.4. The best results were reported at pH 2.0 with REP% of 2.4. As noticed earlier, the best prediction was accomplished at pH 2.0 with r^2 and REP% of 0.9933 and 2.1, respectively. It seems that NAS-filtering of signals has improved performance of PLS-1 as indicated in Table 2. For example, REP% of 2.2 was reported at pH 2.0 using NAP-PLS-1. The earlier model predicted TA at all pH with acceptable accuracy 98.3–102.4. As was the case in TA, BB was predicted by different algorithms at all pH. The final prediction results along with other statistical parameters are also summarized in Table 2. MLR was found applicable for BB prediction at all pH with reasonable recoveries 113.6–115.5% and REP% 12.6–14.0.

Table 2

Prediction of Tartrazine, brilliant black, Sunset Yellow and Allura Red in validation samples at different pH values

Method	Statistical indicators	Validation set TA			Validation set BB			Validation set SY			Validation set AR		
		pH 2.0	pH 6.0	pH 12.0	pH 2.0	pH 6.0	pH 12.0	pH 2.0	pH 6.0	pH 12.0	pH 2.0	pH 6.0	pH 12.0
MLR	Mean Recovery ^a	112.6	113.5	111.2	113.6	115.5	114.2	Not applicable			Not applicable		
	REP% ^b	13.6	14.2	13.7	12.6	14.0	12.9						
	r^{2c}	0.8954	0.8845	0.8845	0.8532	0.8943	0.8511						
PLS	Mean Recovery ^a	103.6	97.9	96.2	101.5	97.4	99.4	102.6	104.3	98.8	91.2	102.3	88.3
	REP% ^b	2.3	4.9	6.9	3.1	5.2	8.3	4.1	3.6	5.1	8.3	7.2	11.2
	r^{2c}	0.9969	0.9855	0.9711	0.9964	0.9763	0.9684	0.9795	0.9529	0.9699	0.9757	0.9821	0.9567
	A ^d	5	6	5	5	5	4	7	8	7	8	9	8
PCR	Mean Recovery ^a	103.4	99.5	101.2	100.9	98.3	97.7	101.3	103.2	100.8	93.2	99.2	92.0
	REP% ^b	2.4	4.1	7.9	3.5	5.6	8.1	4.2	3.7	5.0	8.1	6.9	10.8
	r^{2c}	0.9957	0.9887	0.9622	0.9894	0.9754	0.9645	0.9891	0.9366	0.9722	0.9692	0.9788	0.9545
	A ^d	5	5	5	5	5	5	7	7	7	9	9	9
NAP/ PLS-1	Mean Recovery ^a	101.6	98.3	102.4	100.3	98.1	98.8	98.7	103.3	104.5	95.3	101.8	92.7
	REP% ^b	2.2	4.4	6.4	3.5	5.6	8.2	4.8	4.1	5.6	8.1	6.9	9.8
	r^{2c}	0.9981	0.9798	0.9686	0.9981	0.9772	0.9654	0.9813	0.9611	0.9527	0.9766	0.9876	0.9508
	A ^d	4	4	4	4	4	3	6	7	7	7	7	7
	A _{ext} ^e	1	1	1	1	1	1	1	1	1	1	1	1

^aMean recovery of the dye in validation set (see Table 3).

^bREP%: relative error of prediction.

^c r^2 : correlation coefficient between predicted and measured concentrations in validation set.

^dA is the optimum PLS-1 factors obtained by Haaland and Thomas method [22,23].

^eA_{ext} is the extracted NAS factors employed in data-pre-processing (matrix of absorbances) [22,23].

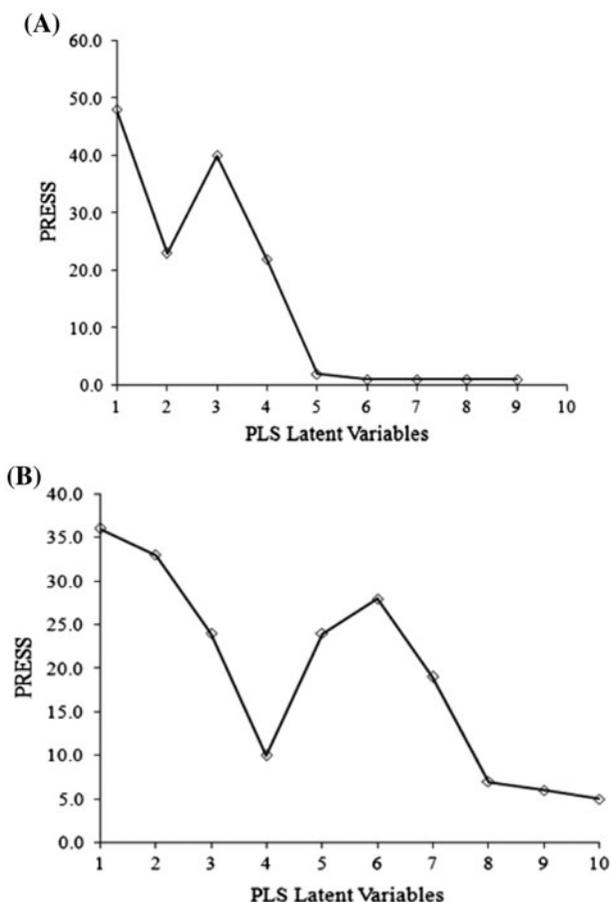


Fig. 2. Press–latent variables for PLS modeling: (A) Tartrazine at pH 2.0 and (B) Allura Red at pH 12.0.

The concentration of BB was determined in the presence of other dyes with an excellent recovery using PLS. The model predicted BB using 5, 5, and 4 variables at pH 2.0, 6.0, and 12.0, respectively. In fact, the best result was observed at pH 2.0 with REP% of 3.1. The excellent performance of PLS for dyes quantification in mixture was reported in the literature [4,17]. PCR showed a good analytical performance for BB prediction using five factors at all pH. The accuracy was reasonable with mean recoveries 97.7–100.9 and REP% 3.5–8.1. The best results were reported at pH 2.0 with REP% value of 3.5. As reported in the earlier methods, the best prediction was achieved at pH 2.0 with r^2 and REP% values of 0.9933 and 3.3; respectively. NAS-filtering did not improve the calibration performance of PLS as indicated in Table 2. For example, REP% values (at pH 2.0) were 3.1 and 3.5 before and after NAS-filtering, respectively. The main conclusion is that BB can be predicted with good accuracy even in the presence of other dyes.

Unlike the earlier dye, SY had an intense spectral overlapping with AR which may affect their accurate prediction by multivariate calibration. Although the spectral overlapping between SY and AR is high, PLS showed an excellent performance to predict both dyes with low REP% values. Due to the intense overlapping, more PLS variables were needed to predict AR and SY compared to BB and TA. For SY, numbers of the PLS variables were 7, 8, and 7 at pH 2.0, 6.0, and 12.0, respectively. The higher number of variables would reflect the nonlinearity in the current system. In general, PLS was more effective to predict SY at all pH with final REP% 3.6–4.1. With seven factors, PCR predicted SY with REP% values of 3.7–5.0 over all pH. NAP-PLS-1 showed a comparable performance with PLS, and this may prove that NAS-pre-processing was not effective in this case. In NAP-PLS, numbers of PLS factors were 6, 7, and 7 at pH 2.0, 6.0, and 12.0, respectively, while one NAS factor was used in all cases. Reasonable REP% values were reported 4.1–5.6. In general, all models were effective for SY prediction but at pH 2.0 and 6.0.

Unlike TA and BB, AR has an intense overlapping with SY which may need advanced calibration methods. The intense overlapping was badly reflected on MLR as it was invalid to predict AR in the mixture. PLS was excellent for AR prediction at all pH as obvious in Table 2. As expected, PLS was the winner for dyes prediction in the mixture. The performance of PLS was acceptable with mean recovery and REP% of 88.3–102.3 and 7.2–11.2, respectively. Numbers of PLS-1 latent variables were 8, 9, and 8 at pH 2.0, 6.0, and 12.0, respectively. Press-PLS variables plot that obtained for AR is shown in Fig. 2. As indicated in Fig. 2, an unusual plot is generated and the optimum number of variables was 8 based on the leave-one-out rule. For PCR, the model was effective for dye prediction using 9 factors at all pH with reasonable REP% 6.9–10.8. NAS-pre-processing of spectral data prior to PLS calibration improved modeling as indicated in Table 2, with final REP% of 6.9–9.8. For NAS-PLS, 7 variables were included along with one NAS factor in pre-processing. In fact, the better results were obtained at pH 2.0 and 4.0 for dye prediction by all methods. Based on the earlier results, dyes would be quantified in mixture and over the range (1–10 mg L⁻¹) using PLS.

3.3. Figures of merit for dyes quantification

Figures of merit including detection limit DL, quantification limit QL, sensitivity, selectivity, and dynamic range (DR) are estimated by MVC1 using a

special routine-based net-analyte concept. Table 3 summarizes the estimated figures of merit at pH 2.0. The standard deviation in absorbance readings was taken as ± 0.0001 .

As indicated in Table 3, dyes were accurately quantified in mixture without the need for any advance separation-based methods. The method showed an excellent accuracy (98.7–103.6) and acceptable inter and intra-day precision ($<10\%$) for dyes quantification. The proposed multivariate calibration method was more sensitive and selective for TA and BB compared to SY and AR. The best sensitivity and selectivity were reported for TA with values of 0.67 and 0.25; respectively. The dyes are quantified down to 0.24, 0.29, 0.4, and 0.5 for AR, SY, TA, and BB, respectively. The analytical range is also provided in Table 3. In fact the better detection of TA and BB compared to the AR and SY is attributed to the intense spectral overlapping in the later couple and this negatively affected the spectral modeling.

3.4. Variables controlling dyes adsorption by pine-wood

Adsorption of food dyes was studied at different experimental factors including pH, adsorbent mass, and dye concentration. Moreover, competitive adsorption of dyes was studied with multivariate calibration.

3.4.1. Effect of solution pH on dyes removal: Mechanisms of dyes removal from solution

Studying dyes adsorption at different pH would have a strong correlation with the nature of controlling mechanism, either electrostatic or non-electrostatic interaction or mechanism. Removal of dyes

from solution was studied at pH 2.0, 6.0, and 12.0 at 100 mg L^{-1} , liquid-to-solid ratio 100 ml/g , and shaking time 24 h. Both single and multi-solute systems were considered in pH study. The results are presented in Fig. 3

As shown in Fig. 3(A), the best pH for dyes removal was pH 2.0 with a systematic reduction at higher pH. The adsorption trend of dyes (single-solute system) decreased in the following order: $\text{SY} < \text{AR} < \text{TA} < \text{BB}$. The maximum removal values for single-solute systems were 83, 61, 43, and 36% for SY, AR, TA, and BB, respectively.

Physicochemical analysis of the adsorbent indicated that it has a high specific surface area of $174.6 \text{ m}^2 \text{ g}^{-1}$, total pore volume of $0.082 \text{ cm}^3 \text{ g}^{-1}$, average pore diameter of 0.87 nm, total acidic groups of 0.38 mmol g^{-1} , and total basic groups of 0.23 mmol g^{-1} . pH of zero point of charge was estimated and found to be 6.3. At this stage, the natural adsorption mechanism would be ascertained from pH study. pH_{zpc} of the heated-pine wood was 6.3 while pK_{a} of dyes was within the range 6.4–11.4 (Table 1). Accordingly, at pH 2.0 the dyes and pine wood are positively charged and this should reduce electrostatic adsorption, which was not the case in the current system. Moreover, at pH 12.0 both dyes and pine are negatively charged which reduced the dyes removal and this was achieved in the current case. It was highly possible that OH^- ions were favorably removed over dyes at pH 12.0. In addition, H-bonding and hydrophobic-hydrophobic interactions may involve at pH 2.0 but not electrostatic mechanism. Adsorption behavior of dye mixture is shown in Fig. 3(B) and indicated that dyes compete with each other toward active sites. For all dyes, removing from single-solute solution was

Table 3
Figures of merit of proposed MVC method for dyes determination at pH 2

Figures of merit	AR	SY	TA	BB
Accuracy (mean recovery, $n = 4$) ^a	99.4	103.6	100.4	98.7
Inter-day Precision (RSD, $n = 4$) ^a	11.4	6.2	7.2	8.3
Inter-day precision (RSD, $n = 4$) ^a	10.9	5.9	6.8	9.1
Sensitivity ^b	0.14	0.22	0.67	0.63
Selectivity ^b	0.043	0.093	0.25	0.16
Detection limit (mg L^{-1}) ^c	0.24	0.29	0.11	0.15
Quantification limit (mg L^{-1}) ^c	0.80	0.96	0.40	0.50
Dynamic range (mg L^{-1})	0.8–10.0	1.0–10.0	0.4–10.0	0.5–10.0

^aDyes were determined in a mixture containing 3.0 mg L^{-1} each. Dyes were determined within the same day and over three successive days.

^bBased on net-analyte signal calculations.

^cDL and QL were estimated based on the convention that signal-to-noise ratio equal to 3 and 10, respectively.

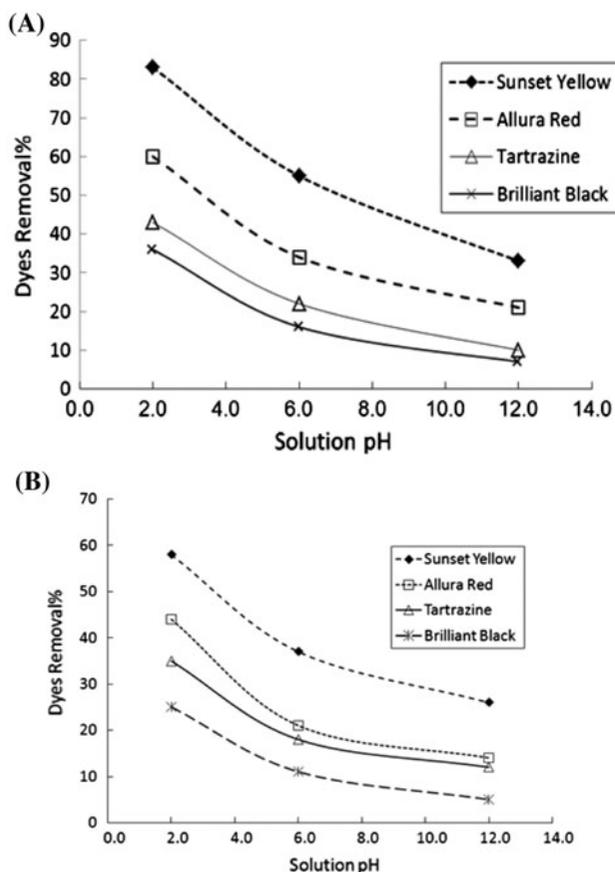


Fig. 3. Effect of solution pH on dyes adsorption: (A) single-solute solution and (B) multi-solute solution (competitive adsorption). L/S ratio 100 ml/g and dye content 100 mg/L.

significantly higher compared to the mixture. Again, the maximum removal of dyes from solution was also noticed at pH 2.0 with the following trend: SY (58%) > AR (43%) > TA (34%) > BB (23%). A high reduction in dyes removal was observed in mixture (25% reduction in all cases) and this reflected the high competition between dyes. CF for dyes will be estimated from equilibrium studies as will be discussed soon.

3.4.2. Effect of adsorbent dosage on dyes adsorption

Probably, liquid-to-solid ratio is one of the most important parameters to be optimized before conducting adsorption isotherms. Effect of mass on dyes removal from solution and retention or adsorption value is investigated using single-solute solution only and the final results are shown in Fig. 4.

For all dyes, higher dye removal from solution was observed at higher masses of pine wood. The higher removal was attributed to the higher number

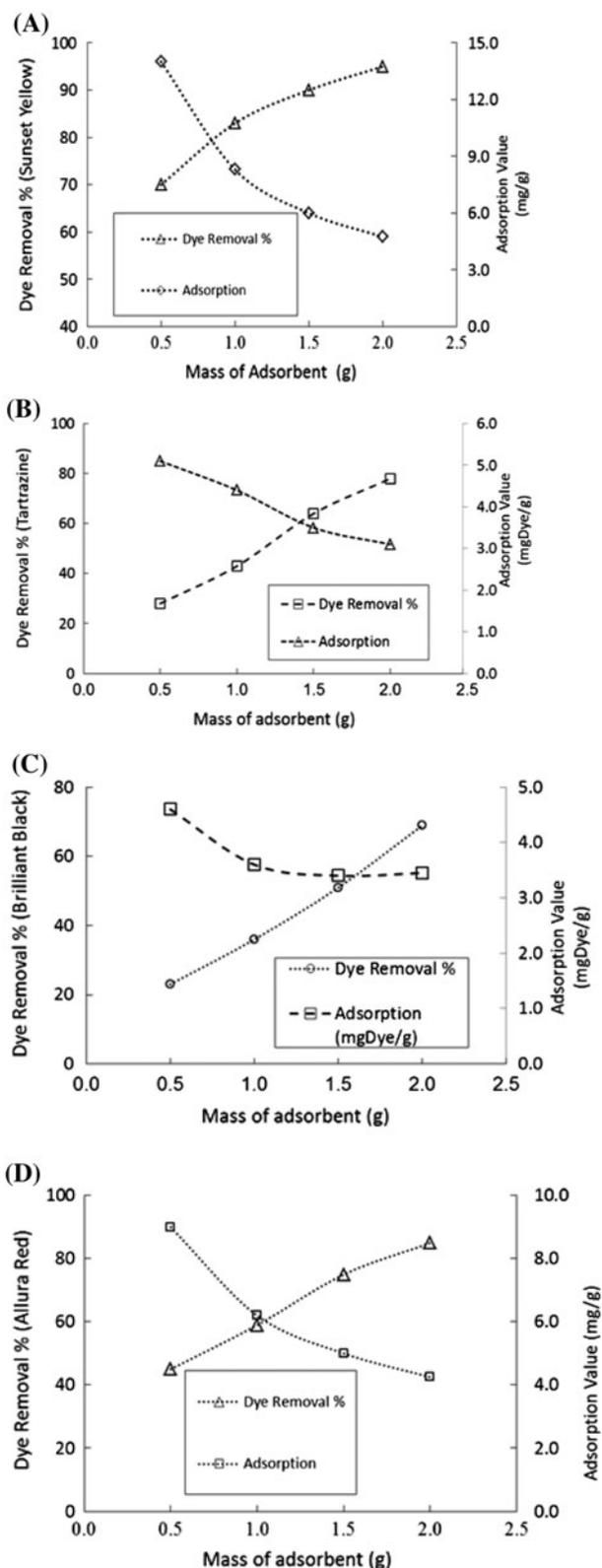


Fig. 4. Effect of mass on dyes removal from single-solute solution (dye content 100 mg L⁻¹ and pH 2): (A) Sunset Yellow, (B) Tartrazine, (C) Brilliant Black, and (D) Allura Red.

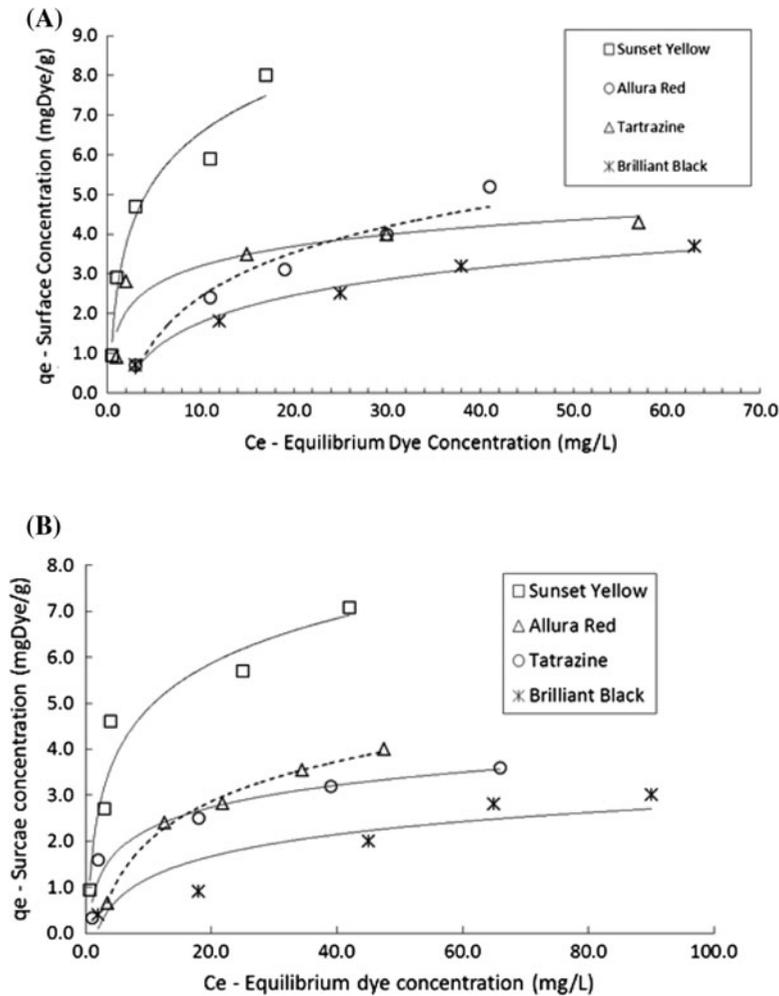


Fig. 5. Adsorption isotherms of dyes (volume 100 mL, pH 2.0, concentration 10–100 mg L⁻¹ and 25°C): (A) single-dye isotherms and (B) multi-dye isotherms. Lines present Langmuir modeling.

of active sites available for adsorption. For SY (Fig. 4(A)), the removal increased from 70 to 95% upon increasing the mass from 0.5 to 2.0 gram, respectively. On the other hand, the adsorption/retention value of SY reduced from 14.0 to 5.3 mg g⁻¹ upon increasing the mass from 0.5 to 2.0 g, respectively. The removal significantly increased from 25 to 80% upon increasing the mass from 0.5 to 2.0 g, respectively. According to Fig. 4, the dyes adsorption decreased in the following order at (0.5 g dosage): SY (Fig. 4(A)) > AR (Fig. 4(D)) > TA (Fig. 4(B)) > BB (Fig. 4(C)). The maximum removal and adsorption were observed for SY, 95% and 14.0 mg g⁻¹, respectively. The maximum removal was observed at 2.0 g while maximum adsorption was reported at 0.5 g. The point of intersections between %removal and adsorption (Fig. 4) is often taken as a balance point between adsorption on the surface and removal from solution [25]. The opti-

imum mass for the test is taken from the intersection point. Accordingly, adsorption or removal of SY, AR, TA, and BB should be studied at 0.8, 1.0, 1.3, and 1.5 g, respectively. The earlier values indicated that more mass is needed for BB than SY.

3.5. Dyes adsorption from single and multi-solute solutions: competitive adsorption

Adsorption behavior of the food dyes from single and multi-solute solutions is studied. The resulted isotherms for both systems are depicted in Fig. 5. The results of the CF and Press values are all provided in Table 4.

For single-dye solution (Fig. 5(A)), typical L2-isotherm was observed for dyes according to Giles classification [26]. This reflected that the removal of dyes from solution by heated pine wood was attained by

Table 4
Langmuir/Freundlich parameters and CFs estimated from different adsorption systems

Dye	Langmuir model					Freundlich model				CF ^b
	Q _{max} (mg/g)	Q _{max} (mmol/g)	K _L	R ²	Press ^a	K _F	n	R ²	Press	
<i>Single-dye adsorption systems</i>										
SY	9.2	0.020	172	0.9547	2.3	2.03	0.55	0.8562	7.3	
AR	7.3	0.015	153	0.9453	4.2	0.33	0.74	0.9859	1.1	
TA	4.4	0.009	26	0.9971	0.9	0.50	0.56	0.9423	2.4	
BB	3.9	0.004	24	0.9924	0.7	0.41	0.54	0.9645	2.8	
<i>Multi-dye adsorption system</i>										
SY	7.1	0.015	178	0.8967	7.4	1.56	0.44	0.8562	17.2	0.77
AR	4.8	0.010	159	0.8834	8.3	0.27	0.38	0.9150	15.2	0.66
TA	3.4	0.007	57	0.9567	2.5	0.21	0.38	0.8941	13.8	0.77
BB	2.5	0.003	41	0.9849	2.9	0.23	0.29	0.9076	12.9	0.64

^aEstimated from Eq. (5).

^bEstimated from Eq. (6).

the formation of monolayer layer on the surface [26]. L2 isotherm indicated high affinity between polar dye molecule and pine wood at lower concentration and then the surface becomes saturated at higher concentrations. L2 isotherm is often reported for heavy metals and charged dyes adsorption with a weak competition with water molecules [2,26]. As shown in Fig. 5(B), the shapes of isotherms (for multi-solute system) are L2 and similar to single-solute isotherm which is not usually reported. The stable isotherms are attributed to lower competition between dyes. In fact, the extent of competition would increase at higher concentrations and should negatively affect the shapes of isotherms.

As shown in Table 4, Langmuir isotherm showed a better presentation for dyes adsorption in single and multi-solute systems. The model was also more applicable for single-dye solution in comparison with multi-solute solution as anticipated from the lower Press values. For single-solute system, Press values ranged from 0.7 to 4.2, however, higher values were obtained for multi-solute system 2.5–7.4. In general, the model was effective for modeling dyes adsorption from single and mixture of dyes. The applicability of Langmuir model for modeling dyes adsorption would indicate the following points: (a) limited number of active sites was available on the surface, (b) adsorption of dyes continued until surface saturation and, (c) interaction between adsorbed molecules was neglected. The maximum adsorption capacity of the dyes was 9.2, 7.3, 4.4, and 3.9 mg g⁻¹ for SY, AR, TA, and BB, respectively, at pH 2.0 and 25°C. The favorable uptake of SY and AR was indicated from the high K_L value, 172 and 153, respectively. For the multi-so-

lute system, the maximum adsorption values were 7.1, 4.8, 3.4, and 2.5 mg g⁻¹ for SY, AR, TA, and BB, respectively. The estimated energy parameters were 178, 159, 57, and 41 for SY, AR, TA, and BB, respectively. It is interesting to notice that the values of K_L were comparable (±2%) in both systems and this is expected as K_L is a temperature-dependent parameter. Freundlich's isotherm showed a higher applicability for modeling single-dye system with Press 1.1–7.3 compared to 12.9–17.2 for multi-dye system. The earlier conclusion confirmed that the model had limited application for modeling competitive adsorption systems. In all cases, the exponent *n* was always lower than 1.0; indicating the favorable adsorption process for dyes and the high heterogeneity of pine wood [20,21].

The degree of competition between dyes was assessed by estimating CF. As shown in Table 4, a negative competition between dyes was involved as CF values are less than unity in all cases. With a CF of 0.77, SY was the least affected among dyes, however, the most affected dye was BB with CF 0.64. The high CF value of SY compared with other dyes is attributed to the high affinity compared to the rest of dyes.

4. Conclusions

The main conclusions that drawn from this work are: (a) competitive adsorption of SY, AR, TA, and BB by heated pine wood is simply studied using multivariate calibration, (b) the dyes are simultaneously determined with reasonable detection limits using multivariate calibration, (c) PLS and PCR are suitable algorithms for handling the intense spectral overlap-

ping between dyes, (d) multivariate calibration is a good substitute for laborious chromatographic/electrophoresis instruments for studying complex adsorption systems, (e) pine wood is capable of adsorbing mixture of dyes with capacities of 7.1, 4.8, 3.4, and 2.5 mg g⁻¹ for SY, AR, TA, and BB, respectively, and (f) CFs indicated that the most affected dye was BB, while TA and SY were the least affected in mixture adsorption.

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