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Analyzing adsorption data of erythrosine dye using principal component analysis

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ABSTRACT

Erythrosine or Acid Red 51 (C.I. 45430) is a common food dye used for coloring many food products including luncheon meat. Few adsorption studies conducted on erythrosine removal from solution and the tested adsorbents showed modest adsorption values for this dye. Pittsburgh commercial activated carbon showed a reasonable adsorption performance for erythrosine from solution with a maximum capacity of 89.3 mg/g at 40 °C and pH 7. The formation of a complete mono-layer was not established where the fraction of surface coverage was only 0.21. The equilibrium distribution value K_d was 6.51 L/g at 40 °C indicating the high affinity of erythrosine toward activated carbon. Adsorption of erythrosine was an endothermic process (ΔH_{ads} 31.6 kJ/mol) and spontaneous over the studied temperatures (293–313 K). By conducting 27 adsorption tests, the influence of six experimental variables (shaking time, pH, mass of adsorbent, initial dye content, ionic strength/NaCl concentration, and solution temperature) on dye adsorption was investigated. Using principal component analysis PCA, an empirical relationship was created for correlating K_d values with the studied variables and the relationship contains six linear terms, six non-linear terms and one interaction term of the variables. Analysis of adsorption data by PCA revealed that linear and non-linear terms of variables were more significant than interaction term for data modeling. Two sets were created for model building and validation. The developed model was effective for predicting K_d, the sums of square errors squared SSE values were 1.6 and 2.1 for calibration and validation sets, respectively. PCA predicted the best combination of the experimental variables that would give the highest possible K_d value, 20.3 L/g.

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1. Introduction

Erythrosine or Acid Red 51 (C.I. 45430, E127) is a xanthene class and water soluble synthetic dye that often used as a food colorant [1]. Beside application in drugs and cosmetics, erythrosine is applied for dying many food stuffs including biscuits, chocolate, luncheon meat, sweets, and chewing gums [2,3]. When excessively consumed, it can cause sensitivity to light, affecting thyroid hormone levels and lead to hyperthyroidism in some cases [1]. The maximum allowed level of erythrosine is 200 mg/kg in some food stuffs [2]. Monitoring and eliminating erythrosine is a necessary job due to its potential toxicity and pathogenicity [1,2].

The high toxicity of erythrosine was behind many environmental studies to remove this dye from water. Photochemical degradation using TiO_2 particles [4], biochemical degradation [5], and adsorption by activated carbon/natural adsorbents [2,6–10] were the most applicable procedures. Dyes removal by adsorption technique is often recommended due to the low-running-costs and no harmful by-products are generated as the case in other destructive procedures [2]. In fact, most food dyes are often present at trace levels (usually in μg or ng levels) in water streams which may retard their direct quantification by most instruments [11]. Accordingly, finding effective adsorbents/extractants for food dyes enrichment is necessary. Even though erythrosine is widely used in food industry and has a high toxicity, only few studies have considered its elimination/extraction from water [2,4–10]. Extent of erythrosine adsorption by natural adsorbents was not high and even activated carbon showed a modest affinity for erythrosine in comparison with other common pollutants. Hu and Srinivasan have prepared a number of activated carbons from coconut shells and palm seeds and tested them for removing phenol, methylene blue (C.I. 52015) and erythrosine from water/ethanol mixture [10]. The adsorption isotherms indicated that phenol and methylene blue have better adsorption compared to erythrosine dye which is attributed to the large structure and to the negative charge of dye molecules [10]. Bottom ash and de-oiled soya adsorbents are tested for removing erythrosine and the obtained capacities were within the range 9–22 mg/g [2]. Jian and Sikarwar also outlined the application of de-oiled mustard as a low-cost adsorbent for erythrosine uptake at a high concentration level (5×10^{-5} M) [6].

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Usually, adsorption studies are carried out under different experimental variables including adsorbent mass, solution pH, shaking time, ionic strength, temperature, and solute concentration [2,6]. The main reason of studying such a large number of variables is to locate the best conditions for best adsorption. In most reported adsorption studies, the influence of a variable on solute adsorption is investigated while maintaining the rest of variables at appropriate fixed levels which is known as univariate analysis. However, the individual and combined influence of all variables on solute adsorption would be studied using appropriate multivariate analysis (like principal component analysis and multilinear regression) and in this case one can find the best combination of these variables that end up with the best performance [12]. The nature of the relationship (i.e., linear or non-linear) between experimental variables and solute adsorption would be also detected using multivariate analysis. Application of multivariate analysis in optimizing chemical reactions, chemical analysis, clustering of objects, designing experimental procedures is outlined in the literature [12,13]. However, application of multivariate analysis in adsorption studies is rather limited [13] and not yet reported for erythrosine/activated carbon system.

In this work, the novel application of a commercial activated carbon for erythrosine removal from solution is addressed. Adsorption isotherms will be recorded at different temperatures to study the mechanism of dye interaction and obtaining thermodynamic parameters. Adsorption data will be treated with different models to evaluate favorability of dye adsorption and the degree of surface saturation. Influence of six experimental variables at different levels on erythrosine adsorption is investigated. The studied variables are shaking time, pH, adsorbent mass, dye content, NaCl concentration (or ionic strength), and solution temperature. The adsorption data will be subjected to principal component analysis, a popular multivariate analysis tool, to assess the influence of all variables on dye adsorption. The importance of linear, non-linear and interaction terms of variables for modeling adsorption data will be investigated and the best combination of the variables that would give the maximum adsorption will be ascertained using PCA. Using PCA, an empirical relationship will be proposed for prediction of erythrosine uptake from other adsorption variables.

2. Experimental

2.1. Chemicals and solvents

Activated carbon was purchased from Calgon company (Pittsburgh, Pennsylvania, USA). The adsorbent was used as received from the manufacturers without any treatment. The manufacturer analyses indicated that bulk density and porosity of the adsorbent were 0.64 g/cm^3 and 0.4, respectively. The provided elemental analysis (wt%) of the adsorbent was: C% = 86.5, O% = 6.5, and H% = 1.2. Erythrosine (C.I. 45430, Acid Red 51) is a xanthene class dye and purchased from Sigma® with purity more than 99.9% and density of 0.35 g/cm^3. Erythrosine is highly soluble in water (70 g/L) and shows high stabilities in neutral and basic solutions as provided by the manufacturer. The chemical structure of erythrosine is given in Fig. 1.

A 1000 mg/L standard solution of erythrosine was prepared by dissolving 1.000 g ($\pm$0.0001 g) of erythrosine in distilled water, diluted to one liter, and the final pH was adjusted to 7.0 using 0.01 M HCL. Diluted solutions were prepared from the earlier stock solution. All solutions were kept in a dark and cold place until the time of use. The other chemicals were of analytical grade and obtained from TEDIA (Ohio, USA) and all solutions were prepared using distilled water.
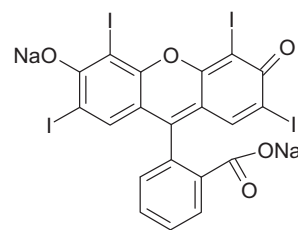

Fig. 1. Chemical structure of erythrosine.

2.2. Spectroscopic determination of erythrosine

Erythrosine was quantified using double-beam spectrophotometer (Cary 50 UV–vis spectrophotometer, Varian, USA) at λ_{max} 525 nm. Beer's law is obeyed over the concentration range 0.4–25.0 mg/L with a high degree of correlation, $r^2 = 0.9982$. The proposed method is fairly sensitive with 0.12 and 0.40 mg/L as detection limit ($3\sigma_{blank}$) and limit of quantification ($10\sigma_{blank}$), respectively. Fig. 2 shows the spectrum of erythrosine recorded at 20 °C and pH 7.0.

2.3. Erythrosine adsorption by activated carbon

2.3.1. Adsorption at different experimental variable using single-point adsorption test

Effect of different experimental variables on erythrosine adsorption was studied using single-point adsorption test as following; A fixed amount of dried activated carbon (particle diameter 300–500 μm) was agitated with 100 cm^3 of dye solution using thermostated mechanical shaker (GFL 1083 shaker, Germany). pH of dye solution was initially adjusted using either 0.01 M HCl or NaOH. After completion of shaking, the solution was carefully removed from the shaker and filtered using suitable filter paper. The optical absorbance of the clear solution was recorded at 525 nm and dye content was estimated using Beer's equation. Table 1 summarizes adsorption results at different experimental variables over different levels.

2.3.2. Adsorption isotherms using concentration variation method

Adsorption isotherms of erythrosine at different temperatures were recorded using concentration variation method. Eight solutions of erythrosine covering the concentration range 50–450 mg/L all at pH 7 were prepared in 250 cm^3 volumetric flask. For each
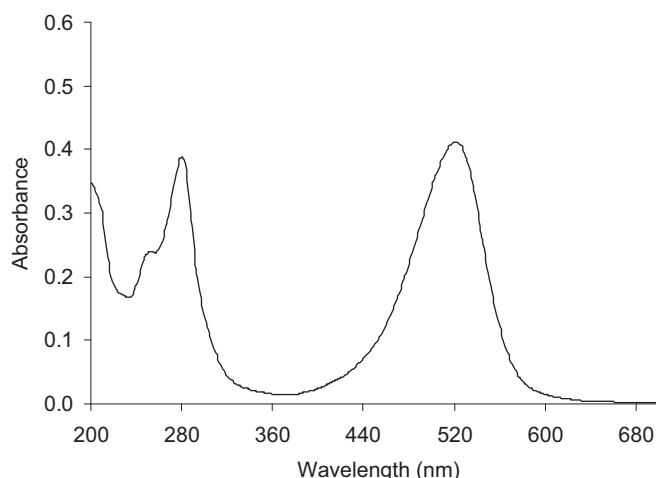

Fig. 2. Absorption spectrum of erythrosine.

Table 1
Effect of different experimental variables on erythrosine adsorption by activated carbon.

Exp. No.[a]	Variable and levels Shaking time (day)	K_d (L/g)[b]	Levels selected for other variables
1	1	0.84	AC mass 500 mg, pH 7, dye content
2	2	0.85	300 mg/L, Temp. 20 °C, NaCl 0.1 M.
3	3	0.96	
4	4	2.43	
5	6	2.70	
6	7	2.91	
pH			
7	3	2.89	AC mass 500 mg, dye content 300 mg/L,
8	7	2.33	Shaking time 4 days, Temp. 20 °C, NaCl
9	10	1.01	0.1 M.
10	12	0.92	
Mass of AC (mg)			
11	50	0	Dye content 300 mg/L, Shaking time 4
12	250	0.13	days, pH 7, Temp. 20 °C, NaCl 0.1 M.
13	500	2.39	
14	750	2.77	
15	950	2.95	
Dye content (mg/L)			
16	50	8.41	AC mass 500 mg, Shaking time 4 days, pH
17	150	3.27	7, Temp. 20 °C, NaCl 0.1 M.
18	250	2.27	
19	300	2.30	
20	450	1.58	
NaCl (M)			
21	0.1	2.41	Dye content 300 mg/L, AC mass 500 mg,
22	0.5	2.56	Shaking time 4 days, pH 7, Temp. 20 °C,
23	1.0	1.14	
24	3.0	0.28	
Temperature (°C)			
25	20	2.57	Dye content 300 mg/L, AC mass 500 mg,
26	30	5.44	Shaking time 4 days, pH 7, NaCl 0.1 M.
27	40	6.51	

[a] 20 experiments (unbolded numbers) were used for building calibration model, while 7 experiments (bolded numbers) were left for model validation.
[b] The reported K_d values were obtained as an average of there identical adsorption tests (RSD < 5% in al cases).

solution, 500 mg AC was added carefully and the solutions were closed and agitated for 4 days. Remaining concentration of the dye was determined as described in Section 2.3.1. The earlier procedure was carried out at 20, 30, and 40 °C to end up with three isotherms at three temperatures.

2.4. Multivariate analysis: principal component analysis

The individual and combined influence of the variables on dye adsorption was elucidated using principal component analysis, a popular tool of multivariate analysis. By conducting 27 adsorption experiments, the effect of shaking time, pH, mass of adsorbent, initial dye content, ionic strength/NaCl concentration, and solution temperature) on erythrosine adsorption by activated carbon was studied (see Table 1 for the levels of each variable). Initially, the adsorption data collected for dye adsorption (27 experiments and K_d values, see Table 1) were subjected to PCA for assessing the significance of the studied variables and relation between them and this was carried out by decomposing the adsorption matrix into its loading (variables) and score (experiments) vectors using the popular singular value decomposition technique [12]. The significant principal component factors were plotted for diagnostic purposes. The correlation between equilibrium distribution value K_d and the experimental variables was modeled including linear, non-linear (quadratic), and interaction terms for the variables. For calibration, twenty experiments were selected, while, seven experiments were kept for model validation. The calibration data is composed of a matrix **X** of dimension 20 × 14 and a response vector of dimension 20 × 1 (K_d in this case). The experimental conditions for calibration and validation sets are given in Table 1. In the first step, the matrix **X** along with the vector K_d were subjected to principal component analysis PCA for assessing the effect of linear, non-linear and

interaction terms of the variables on dye adsorption from solution. When the calibration sensor was obtained, K_d values were predicted for adsorption tests not included in the calibration model (i.e., validation set). PCA is a powerful statistical method that is often used for factor analysis, clustering of objects and also for modeling purposes [12]. PCA was carried out using as outlined in the literature [12] using version-7 Matlab®. The raw data were normalized to 100% prior to PCA analysis. More details on PCA will be given in section 3.6.

2.5. Adsorption parameters and models

The amount of adsorbed dye (q_e mg/g) and the equilibrium distribution value K_d were estimated as following [14]:

$$q_e = \frac{(C_0 - C_e) \times V}{\text{mass of adsorbent(g)}} \qquad (1)$$

And,

$$K_d = \frac{q_e}{C_e} \qquad (2)$$

where C_0, C_e, and V are the initial concentration (mg/L), equilibrium concentration (mg/L) and solution volume (L). K_d values higher than 1.0 L/g indicate the favorability of the adsorption process, i.e., solute prefers surface over solution. Adsorption isotherms were modeled using:

Langmuir's equation : $q_e = QK_LC_e/(1 + K_LC_e)$ (3)

Freundlich's equation : $q_e = K_F C_e^n$ (4)

Henry's equation : $q_e = K_H C_e$ (5)

In Langmuir's equation, Q_{max} (mg/g) is the amount of adsorbate at complete monolayer coverage and b (L mg^{-1}) is a constant correlates to the heat of adsorption [15,16]. In Freundlich's relation, K_F (mg^{1-n} g^{-1} L^n) represents adsorption capacity when dye equilibrium concentration equals to 1 and n reflects heterogeneity of the surface [15,16]. In Henry's equation, a constant partitioning is assumed during adsorption process. K_H is Henry's constant and is equal to K_d which is estimated from Eq. (2). In Henry's law, it is assumed that the number of active sites is much higher than the number of solute molecules to end up with a linear adsorption process. Nonlinear fitting methodology using data-solver which is available in Excel® was applied for modeling adsorption data and obtaining parameters of the isotherms. The assessment of the employed models for presenting dye adsorption isotherms was carried out by calculating the sum of square errors squared (SSE) and lower values of SSE indicate better fit to the model [16]. SSE is estimated from the formula: $\sum_{i=1}^{n}(q_{i,calc} - q_{i,pred})^2$, where $q_{i,calc}$, $q_{i,pred}$, and n represent the calculated q_e values, predicted q_e values and the number of isotherm points; respectively. The prediction power of PCA for predicting K_d from experimental variables would be also assessed using SSE criterion. The free energy of dye adsorption (ΔG_{ads}) was calculated from the common equation [17]:

$$\Delta G = -RT \ln K_L \tag{6}$$

where K_L is Langmuir constant obtained at a certain temperature; R is the ideal gas constant (8.314 J/mol K). The apparent enthalpy of adsorption $\Delta H_{ads.}$ and entropy of adsorption $\Delta S_{ads.}$ were estimated using Van't Hoff equation [18]:

$$\ln K_L = \frac{(\Delta S_{ads.}/R) - (\Delta H_{ads.}/R)}{T} \tag{7}$$

The values $\Delta H_{ads.}$ and $\Delta S_{ads.}$ were calculated from the slope and intercept of $\ln K_L - 1/T$ plot.

3. Results and discussion

3.1. Characteristics of activated carbon and erythrosine

Detailed chemical and physical analyses of the employed commercial activated carbon (Pittsburgh, Pennsylvania, USA) were reported by the Al-Degs et al. [15]. N_2-adsorption analysis indicated that AC has a large specific surface area 820 m^2/g which is expected for commercial activated carbons [15]. The employed adsorbent was microporous where micropore volume contributes to about 82% of the total pore volume. The average pore diameter of AC was 1.8 nm as obtained from Barrette–Joynere–Hanlenda (BJH) method [15]. Boehm titration method indicated that the activated carbon has both basic and acidic functional groups and basic groups (like ketonic, pyronic, and chromenic) were more abundant [15]. The density of surface functional groups was 0.54 group/nm^2. pH-drift method revealed that pH$_{pzc}$ (pH at point of zero charge) was 9.0 [15]. The large surface area and availability of many surface functional groups would make the selected activated carbon a potential adsorbent for toxic and hard to adsorb erythrosine dye. Acidity constants (K_a) of erythrosine is not reported in literature and not provided by the manufacture. The K_a of the dye was simply determined using simple potentiometric titration method as outlined in literature [19]. The K_a value was calculated by plotting the equilibrium pH against buffer intensity of the dye (MpH^{-1}) [19] and the K_a value was obtained from the maximum buffer intensity when the concentration of ionized and neutral dye species is equal [15,19]. The pK_a value of erythrosine is 5.3 and it is important to mention that the obtained acidity value is only an approximate estimation for acidity constant [19]. As shown in Fig. 1, erythrosine contains

large number of polar functional groups (6 C—O bonds and 4 C—I bonds/molecule) and two ionizable groups. The outlined physical and chemical properties would be helpful when discussing the adsorption behavior of erythrosine by activated carbon at different pH and NaCl concentration.

3.2. Effect of different experimental variables on dye adsorption

Before conducting adsorption isotherms, influence of different experimental variables on dye adsorption was investigated over reasonable ranges. The selection of the levels of variables was made so that a significant adsorption of the dye is achieved. It is known that the earlier variables are often selected when investigating adsorption properties of a certain adsorbent toward certain pollutant [2,6,15,17,18]. The values of K_d along with the experimental details for each test are summarized in Table 1.

The performance of the adsorbent is considered acceptable and the variables were in a good combination as long as K_d value is higher than unity. With few exceptions, all K_d values were higher than unity indicating the careful selection of the experimental variables for adsorption tests. As shown in Table 1, adsorption of erythrosine is a time dependent process and dye adsorption is gradually increased by the time. Under the studied experimental conditions, K_d value has been increased with time to stabilize at 2.91 L/g after seven days of shaking. In fact, shaking for 4 days would be an appropriate contact time in this case where a high distribution value is observed (2.43 L/g). A much lower contact time (100 min) was reported for erythrosine adsorption on de-oiled mustard [6]. A large decrease in erythrosine adsorption was reported in basic medium, the K_d value was reduced from 2.89 (at pH 3) to 0.92 (at pH 12). A similar observation was also reported for erythrosine adsorption by de-oiled mustard [6] and de-oiled soya [2]. The large reduction in dye adsorption at basic medium (at pH > 9) is highly attributed to electrostatic repulsion between negatively charged activated carbon (pH$_{pzc}$ = 9.0) and negatively charged dye molecules (pK_a = 5.3). The possible mechanisms of erythrosine adsorption are: (a) hydrogen bonding between oxygen-containing functional groups of erythrosine and polar surface groups of activated carbon such as carboxylic and phenolic groups and, (b) hydrophopic–hydrophopic interactions between the hydrophobic part of erythrosine and the hydrophobic surface of activated carbon [15]. Even though adsorption at pH 7 was not high as the case in pH 3, pH 7 was selected for the next experiments due to the high K_d value. Mass of adsorbent has a significant influence on dye removal from solution. No adsorption was observed at adsorbent dosage 50 mg while the best performance was observed at 950 mg where K_d value was 2.95 L/g. As the adsorbent mass increases, the number of active sites capable of attracting dye molecules increases and better adsorption would take place. For the next experiments, the dosage was maintained at 500 mg where a reasonable and high distribution value was reported and there is no urgent need to use higher masses of activated carbon. For an adsorption process, the rate of solute uptake related directly with initial concentration. Influence of initial dye concentration on adsorption was studied over the range 50–450 mg/L while keeping adsorbent mass at 500 mg. It is evident from Table 1 that K_d value was high at lower concentrations (at 50 and 150 mg/L) and then decreased by increasing dye concentration. The earlier observation is expected because at low solute concentration the adsorbed amount of dye would be much higher than the amount left in solution and a high K_d value is expected. Stable and high K_d values were observed over the concentration range (250–300 mg/L), therefore, dye concentration would be maintained at 300 mg/L. As shown in Table 1, adsorption of erythrosine from solution has been significantly decreased at higher NaCl concentration. A modest distribution value (0.28 g/L) was observed at 3.0 M NaCl solution. The mechanism of dye
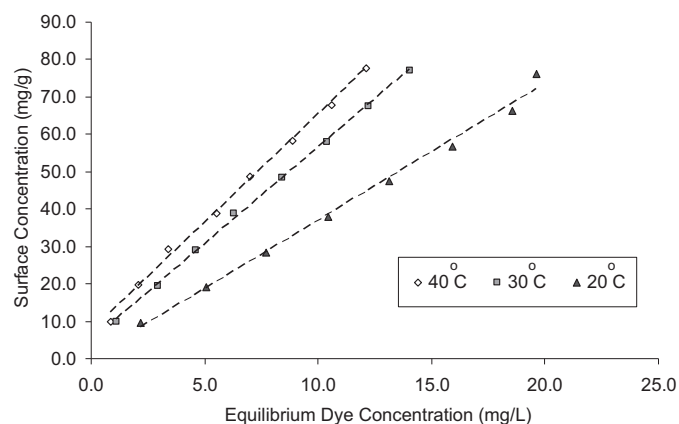
Fig. 3. E127 adsorption isotherms at different temperatures.

Table 2
Langmuir, Freundlich, and Henry isotherm constants for dye adsorption.

	20 °C	30 °C	40 °C
Langmuir isotherm			
Q_{max} (mg/g)	77.2	83.2	89.3
Q_{max} (mmol/g)	0.088	0.094	0.101
K_L (L mmol^{-1})	96.8	158.3	220.0
r^2	0.9052	0.9203	0.9214
θ[a]	0.18	0.19	0.21
SSE	820	632	602
Freundlich isotherm			
K_F	3.54	7.76	10.45
n	0.82	0.86	0.79
r^2	0.9936	0.9989	0.9973
SSE	25.2	6.4	11.2
Henry isotherm			
K_H (L/g)	3.68	5.61	6.64
r^2	0.9933	0.9991	0.9964
SSE	25.5	47.8	108.3

[a] Surface fraction of activated carbon occupied by dye molecules at saturation.

interaction with activated carbon would be deduced from the results of the earlier experiments. Effect of ionic strength on dye adsorption was studied at pH 7.0 and at this value the dye and activated carbon are differently charged (pH$_{pzc}$ = 9.0 of activated carbon and pK_a = 5.3 of erythrosine). Theoretically, if the electrostatic attractions between solute and adsorbent are attractive (like the situation in this case) then an increase of the ionic strength shall diminish erythrosine adsorption [20]. This convention was hold true in this study where the adsorption of negatively charged dye molecules on positively charged activated carbon has been decreased upon salt addition. It is important to mention that the absorption characteristics and λ_{max} of erythrosine were insensitive toward changes in pH and ionic strength of solution. The extent of adsorption is, in fact, depends on the temperature of the solid/liquid interface. The K_d values at 20, 30, and 40 °C where 2.57, 5.44, and 6.51 L/g, respectively. The earlier data indicated that erythrosine adsorption is an endothermic process and adsorption was high at 40 °C, however, in all experiments the temperature was maintained at 20 °C where K_d value was higher than 1.0 L/g which indicates a favorable uptake of erythrosine at this temperature. Similar observations regarding effect of temperature on erythrosine uptake were reported in the literature [2,6]. In the earlier discussion, univaraite analysis was used to see how K_d is varied with each variable while keeping other variables at certain levels, however, to see how K_d varied with all variables then multivariate analysis is needed. Moreover, the perfect combination between the variables that would give a high adsorption will be ascertained using multivariate analysis as will be shown in Section 3.5.

3.3. Adsorption isotherms

Adsorption isotherms of erythrosine were measured using concentration-variation method at different temperatures and the results are shown in Fig. 3.

From Fig. 3, the shapes of dye isotherms are "C1" according to Giles classification for isotherms [21]. In this isotherm, a constant distribution value is obtained over the tested concentration range, i.e. linear adsorption behavior. This behavior is attributed to the fact that the amount of added dye was relatively lower than the amount needed to fill the active sites of activated carbon. Adsorption data (8 points/isotherm) presented in Fig. 3 were modeled using Langmuir, Henry and Freundlich equations. The adsorption data were fitted to the earlier models using nonlinear fitting methodology. Parameters of the models, r^2 and the sum of square errors squared SSE values were all summarized in Table 2.

The assessment of the employed models for fitting isotherms was mainly based on the magnitude of SSE value, lower values of SSE indicate better fit to the isotherm. Adsorption isotherms

at all temperatures were satisfactorily modeled using Freundlich isotherm with SSE values 25.2, 6.4, 11.2 at 20, 30, and 40 °C, respectively. It seems that Langmuir isotherm has a limited application for the current system as indicated from the high SSE values. Freundlich model expected that dye adsorption was a favorable process over the tested concentration range (50–400 mg/L) and the surface of activated carbon was heterogeneous because the exponent n was less than unity in all cases [22,23]. Langmuir isotherm assumes that the surface has a limited number of active sites of identical energies and the adsorption of solute continues until the surface sites are occupied and the interaction between adsorbed molecules is neglected [15]. As shown in Table 2, the maximum adsorption values are 77.2, 83.2, and 89.3 mg/g at 20, 30 and 40 °C, respectively. In Langmuir model, K_L represents the equilibrium adsorption constant and higher values of K_L signify the favorability of adsorption process. By comparing K_L values, it can be concluded that adsorption of dye was more favorable at higher temperatures and the process is endothermic. A similar observation was reported in the literature for erythrosine adsorption [2,6]. The fraction of the carbon surface that is occupied by dye molecules (θ) can be calculated from the amount of dye adsorbed and the surface area occupied by one dye molecule (σ) using the following equation [22,24].

$$\theta = \frac{Q_{max} N \sigma 10^{-20}}{S_{BET}} \qquad (8)$$

where θ represents the fraction of the surface that is occupied by dye molecules at saturation, Q_{max} (mol g^{-1}) is the amount of dye adsorbed at saturation, σ (Å^2/molecule) is the surface area occupied by one molecule, N is the Avogadro's number (6.022 × 10^{23}), and S_{BET} is the specific surface area of the adsorbent. McClellan and Harnsberger had proposed an empirical relationship that could be used for the estimation of (σ) of organic molecules adsorbed on activated carbon [25]:

$$\sigma(\text{Å}^2/\text{molecule}) = 1.091 \times 10^{16} \left(\frac{MW}{\rho N}\right)^{2/3} \qquad (9)$$

where MW is the molar mass of solute and ρ is the density of adsorbate. The estimated value of σ was 280 Å^2/molecule and the values of θ at all temperatures were given in Table 2. The values of θ indicate that the formation of a complete molecular layer (i.e., θ = 1) was not achieved in this case and a large fraction of the surface remains unoccupied. The incomplete formation of monolayer may be attributed to: (a) the large size of dye molecules which could not get inside the micropores of the adsorbent, or (b) adsorption isotherms were carried out at low concentrations of dye and higher

Table 3
Energy parameters for erythrosine adsorption by activated carbon.[a]

Temperature (K)	$\Delta G_{ads.}$ (kJ/mol)	$\Delta H_{ads.}$ (kJ/mol)	$\Delta S_{ads.}$ (J/mol K)
293	−2.43	31.6	145.5
303	−2.51		
313	−2.60		

[a] Plotting $\ln K_L$ versus $1/T$ produced a straight line ($r^2 = 0.9911$) with slope and intercept of −3771.4 and 17.5, respectively.

concentrations would be needed to attain full surface coverage. It is interesting to notice that only 21% of active sites were filled at 40 °C ($\theta = 0.21$). The limited application of Langmuir isotherm to the current adsorption system would be attributed to the incomplete filling of adsorption sites which is necessary condition for this model.

3.4. Thermodynamic parameters

The obtained thermodynamic parameters are given in Table 3.

As indicated in Table 3, dye adsorption was a spontaneous process over the temperature range. Mittal and co-workers reported a negative ΔG_{ads} values for erythrosine adsorption, however, with higher magnitudes than those reported in this work [2]. ΔH_{ads} value as calculated from Eq. (7) was 31.6 kJ/mol indicating the endothermic nature of this process. Physisorption and chemisorption could be classified by the magnitude of the enthalpy value. Chemisorption bond strength is often fall within the range 84–420 kJ/mol and bond strength lower than 84 kJ/mol is typical for physisorption [26]. Based on that division, adsorption of erythrosine on activated carbon is mainly a physical adsorption process. The enthalpy of adsorption of organic molecules from aqueous solution on activated carbon usually within 8–65 kJ/mol[27] and the reported value for erythrosine was within this range. It is generally expected that adsorption processes (either from gas or liquid phases) are exothermic as adsorption is a bond formation process[26,27]. The endothermic adsorption of erythrosine on activated carbon seems to be uncommon behavior. Several authors have reported an endothermic adsorption of many dyes on different types of adsorbents [2,6,15,18,28]. As shown in Table 3, the entropy value of adsorption process was 145.5 J mol^{-1} K^{-1}. This is also uncommon behavior because adsorption of dye molecules on carbon surface should be accompanied with a decrease in the entropy of the system. The liberation of previously adsorbed water molecules upon dye adsorption may account for the increase in entropy of adsorption systems [28].

3.5. PCA analysis of adsorption data

PCA was applied to the raw adsorption data given in Table 1 to view the interrelation among the studied variables and their influence on dye adsorption. Before analysis, the data were normalized to 100% as mentioned earlier. PCA was carried out on a data matrix of dimension 27 × 7 where 27 is the number of experiments and 7 is the number of variables (6) plus K_d. After decomposing adsorption matrix, the obtained eignvalues (which account for principal components PC) were 3056, 1430, 170, 26, 20, 14, and 3. The earlier values indicated that adsorption data could be satisfactorily presented using only two principal components PC which captured 95% of variances in the original adsorption data. Accordingly, the first two loading vectors and score vectors were generated. The plots of score and loading vectors for the first principal component PC1 and the second principal component PC2 are shown in Fig. 4.

Fig. 4A shows the loadings (loadings account for variables) plot and this plot indicated that NaCl variable has a high positive score on PC1 and a high negative score on PC2. Moreover, it seems this
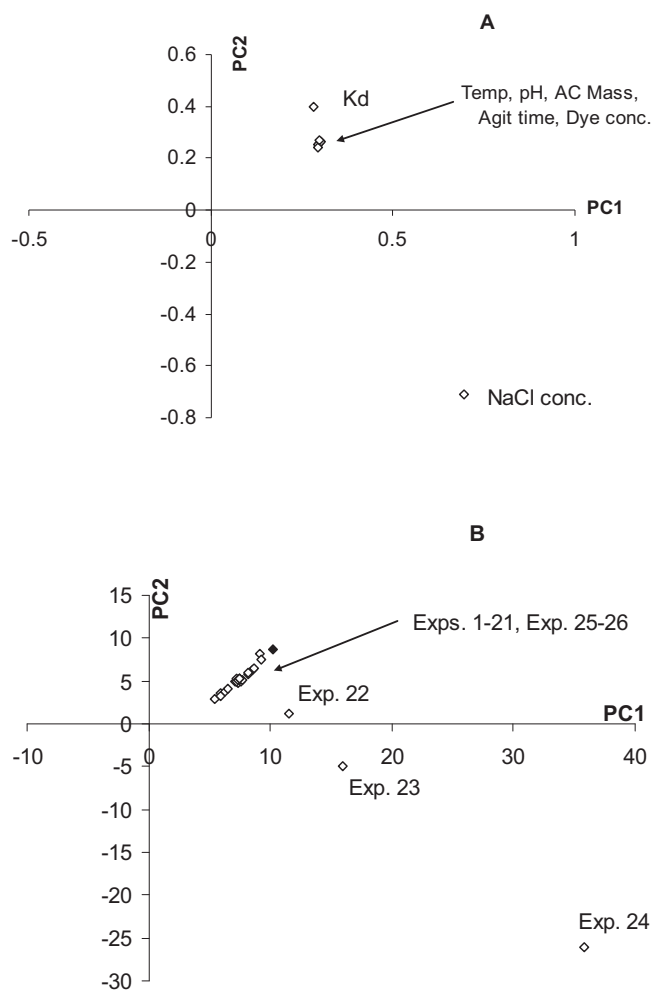
Fig. 4. PC loadings (A) and scores (B) plots obtained form adsorption data.

variable is work against our target, K_d which is appeared far away from the position of this variable (Fig. 4A). The interested part in Fig. 4 is that the positions of the rest of variables (pH, AC mass, etc.) are almost the same and not far from the position of K_d and this reflected that the levels of these variables were properly selected to give favorable dye uptake. The position of temperature variable should be away from these variables as this variable is significantly affect dye adsorption (see Table 1). The main conclusion obtained from Fig. 4A is that a favorable dye adsorption (i.e., high K_d value) is obtained at high AC mass, high solution temperature, high pH, high dye concentration, high agitation time, and low NaCl content. In fact, the earlier conclusion is partially correct because K_d is reduced at high pH and high dye concentration.

One of the interesting features of PCA is its ability to cluster objects/experiments of similar behaviors or structures; moreover, PCA can easily detect outlier if present in the tested objects/experiments [12]. Fig. 4B indicated that experiments 1–21 and 25–26 are making a cluster while experiments 22–24 significantly deviate from the earlier cluster. In fact, the main reason behind this deviation is that the content of NaCl in these experiments (Exp. 22–24) was high.

3.6. Prediction of K_d from experimental variables using PCA

The design matrix is very important before carrying out PCA and this design contains the values of the experimental variables of adsorption tests. It is possible to correlate the independent

experimental variables (i.e., shaking time, AC mass, pH ..., etc.) with the dependent K_d values according to the following mathematical relationship:

$$K_d = b_0 + b_1(\text{Shak Tim}) + b_2(\text{pH}) + b_3(\text{AC Mass}) + b_4(\text{Dye Conc})$$

$$+ b_5(\text{NaCl Conc}) + b_6(\text{Temp}) + b_7(\text{Shak Tim})^2 + b_8(\text{pH})^2$$

$$+ b_9(\text{AC Mass})^2 + b_{10}(\text{Dye Conc})^2 + b_{11}(\text{NaCl Conc})^2 + b_{12}(\text{Temp})^2$$

$$+ b_{13}(\text{Shak Tim})(\text{pH})(\text{AC Mass})(\text{Dye Conc})(\text{NaCl Conc})(\text{Temp}) \quad (10)$$

Eq. (10) is simply presented as:

$$K_d = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_5 x_5 + b_6 x_6 + b_7 x_1^2 + b_8 x_2^2$$

$$+ b_9 x_3^2 + b_{10} x_4^2 + b_{11} x_5^2 + b_{12} x_6^2 + b_{13} x_1 x_2 x_3 x_4 x_5 x_6 \quad (11)$$

where x_1, x_2, x_3, x_4, x_5, and x_6 represent shaking time, pH, mass of AC, dye concentration, NaCl content, and solution temperature, respectively. b_0 represents the intercept and it is usually set at 1.0 before running numerical analysis or even removed if the original data were mean-centered [12]. b_1 to b_6 are the coefficients of linear terms of the variables (x_1–x_6) and these terms are important because they allow for a direct relationship between K_d and a given variable. b_7–b_{12} are the coefficients of nonlinear (or quadratic) terms of the variables (x_1^2–x_6^2) and these terms are of great importance for balancing nonlinear relationship between K_d and the variables. It is possible that the relationship between K_d and one or more of the variables is nonlinear, then, the earlier coefficients are important in modeling Eq. (11). Finally, b_{13} represents the interaction term ($x_1 x_2 x_3 x_4 x_5 x_6$) of the variables and this term is important in adsorption studies because the interaction influence between the variables on K_d if often dependent. It is expected that the linear terms of the variables will be of great importance for modeling adsorption data compare to the other terms and this is anticipated from the high correlation between K_d and the studied variables as discussed in Section 3.2. As shown in Eq. (11), there are 14 coefficients in Eq. (11) and finding these coefficients is carried out using matrix operations that is available in many softwares like Excel® or Matlab®. For building the calibration model, twenty experiments were selected and seven experiments were left for model validation. Table 1 shows the experiments that selected for model building and those selected for model validation. The normalized values of data matrix and the response vector K_d used for model training are shown in Table 4. In this case, the data matrix has the dimension 20×14 (20 experiments and 14 coefficients of the model) and response vector of 20×1 dimension (i.e., K_d values for the 20 experiments).

The raw data were normalized to 100 (i.e., the sum of each column in the matrix is 100 so that all variables are of similar scale) before doing numerical analysis. Scaling the columns in Table 4 was carried out by diving each value in the column by the sum of all values and then multiply by 100.

The relationship between response vector K_d and the data matrix $\mathbf{X}$ is expressed as:

$$K_d = \mathbf{X}.b \quad (12)$$

where vector b (dimension 14×1) contains the values of the 14 coefficients and this is obtained using principal component algorithm as following [12]:

$$b = (\mathbf{U^t U})^{-1} \mathbf{U}^t K_d \quad (13)$$

where $\mathbf{U}$ is the score matrix of dimension 20×14 obtained by PCA algorithm [12]. t stands for matrix transpose. Prediction of K_d values from data matrix $\mathbf{X}$ or from the data matrix of the validation set is achieved using the following equation [12]:
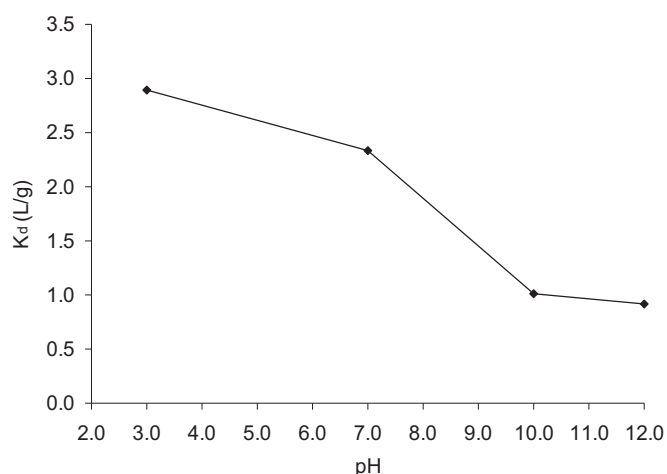
$$K_d = \mathbf{X^t V} b \quad (14)$$

Fig. 5. Effect of solution pH on dye adsorption.

where $\mathbf{V}$ is the loading matrix of size 20×14 obtained by PCA algorithm [12]. SSE criterion is used here to evaluate the degree of closeness between experimental K_d values and those obtained from Eq. (14). The values of the coefficients are given in Table 5.

The significance of linear, non-linear, and interaction of variables in modeling adsorption data would be deduced from the magnitudes of the coefficients (b_1–b_{13}). The larger the coefficient, the greater its significance. It seems that b_0 is insignificant for presenting adsorption data and could be removed from Eq. (11). On the other side, linear terms (x_1–x_6) are of great importance and the sings of their coefficients proved the positive and negative linear relationship between K_d and the variables as discussed earlier. For example, the earlier analysis indicated that K_d values decrease as pH increase and this indicated from the negative value of b_2 as shown in Table 5. PCA results indicated that initial dye concentration is more significant on dye adsorption compare to solution pH and NaCl content as indicated from the magnitudes of the coefficients of these variables. The earlier conclusion cannot be deduced from univariate analysis of adsorption data. Solution temperature has a significant positive influence on dye adsorption as indicated from b_6 value (0.358). The small and negative sign of b_3 indicated that increasing mass of AC in large amounts has a slight influence on dye adsorption.

The interested part in PCA is the high magnitudes of the coefficients of non-linear terms (b_7–b_{12}) and the results clearly reflected the presence of non-linear relationship between the studied variables and dye adsorption. The non-linear relationships could not be detected using univariate analysis because we observed the general relationship between K_d and each variable, however, the nature of the relationship between K_d and any tested variable would be investigated by plotting K_d against that variable. Fig. 5 shows the relationship between K_d and pH and this variable was selected among the others due to its importance on adsorption process.

As shown in Fig. 4, the general observation is that as pH increases, dye adsorption decreases and the best pH for adsorption is 3.0. In fact, the relationship between K_d and pH is linear over the range 3–7 and then turned non-linear over the range 7–12 as indicated in Fig. 4. The coefficient of non-linear term of pH (b_8) is 4-times higher than the coefficient of linear term of this variable (b_2) indicating the importance of non-linear terms for modeling adsorption data. The presence of both linear and non-linear relationships between K_d and pH would be simply explained as following. At pH range 3–7, the surface of adsorbent and adsorbate molecules are differently charged making adsorption favorable and linear over this range, while at the basic range 7–12 dye molecules ionize to have a negative charge making adsorption process less favorable

Table 4
Components of data matrix **X** and response vector K_d for the calibration set (20 experiments) use in principal component analysis.[a]

intercept	x_1	x_2	x_3	x_4	x_5	x_6	x_1^2	x_2^2	x_3^2	x_4^2	x_5^2	x_6^2	$x_1x_2x_3x_4x_5x_6$	K_d
5.00	1.23	4.86	4.88	5.08	1.89	4.76	0.28	4.51	4.37	4.93	0.11	4.35	0.02	0.84
5.00	3.70	4.86	4.88	5.08	1.89	4.76	2.56	4.51	4.37	4.93	0.11	4.35	0.66	0.96
5.00	4.94	4.86	4.88	5.08	1.89	4.76	4.56	4.51	4.37	4.93	0.11	4.35	1.55	2.43
5.00	7.41	4.86	4.88	5.08	1.89	4.76	10.26	4.51	4.37	4.93	0.11	4.35	5.24	2.70
5.00	**8.64**	4.86	4.88	5.08	1.89	4.76	**13.96**	4.51	4.37	4.93	0.11	4.35	8.33	2.91
5.00	4.94	2.08	4.88	5.08	1.89	4.76	4.56	0.83	4.37	4.93	0.11	4.35	0.12	2.89
5.00	4.94	6.94	4.88	5.08	1.89	4.76	4.56	9.21	4.37	4.93	0.11	4.35	4.53	1.01
5.00	4.94	**8.33**	4.88	5.08	1.89	4.76	4.56	**13.26**	4.37	4.93	0.11	4.35	7.83	0.92
5.00	4.94	4.86	0.49	5.08	1.89	4.76	4.56	4.51	0.04	4.93	0.11	4.35	0.16	0
5.00	4.94	4.86	4.88	5.08	1.89	4.76	4.56	4.51	4.37	4.93	0.11	4.35	1.55	2.39
5.00	4.94	4.86	7.32	5.08	1.89	4.76	4.56	4.51	9.84	4.93	0.11	4.35	2.33	2.77
5.00	4.94	4.86	**9.27**	5.08	1.89	4.76	4.56	4.51	**15.78**	4.93	0.11	4.35	2.95	2.95
5.00	4.94	4.86	4.88	0.85	1.89	4.76	4.56	4.51	4.37	0.14	0.11	4.35	0.26	8.41
5.00	4.94	4.86	4.88	5.08	1.89	4.76	4.56	4.51	4.37	4.93	0.11	4.35	1.55	2.3
5.00	4.94	4.86	4.88	**7.63**	1.89	4.76	4.56	4.51	4.37	**11.10**	0.11	4.35	2.33	1.58
5.00	4.94	4.86	4.88	5.08	1.89	4.76	4.56	4.51	4.37	4.93	0.11	4.35	1.55	2.41
5.00	4.94	4.86	4.88	5.08	9.43	4.76	4.56	4.51	4.37	4.93	2.65	4.35	7.77	2.56
5.00	4.94	4.86	4.88	5.08	**56.60**	4.76	4.56	4.51	4.37	4.93	**95.44**	4.35	46.61	0.28
5.00	4.94	4.86	4.88	5.08	1.89	4.76	4.56	4.51	4.37	4.93	0.11	4.35	1.55	2.57
5.00	4.94	4.86	4.88	5.08	1.89	**9.52**	4.56	4.51	4.37	4.93	0.11	**17.39**	3.11	6.51
Data matrix (20 × 14)														

The bold numbers indicated the upper limit for the studied variables.

[a] The raw data were normalized to 100 before running PAC.

and non-linear over this range as shown in Fig. 4. As shown in Table 5, the coefficient of non-linear term of shaking time (b_7) is high compare to the coefficient of linear term of this variable (b_1) indicating the presence of non-linear relationship between K_d and shaking time. The K_d-shaking time plot (not shown) indicated that the relationship was linear over the time period 1–2 days and then become non-linear over the time period 2–7 days. The explanation of the shift from linear to non-linear relationship is that dye adsorption is favorable and linear at early stages of interaction where the density of vacant active sites is high and by the time active sites get filled and further adsorption become less favorable and the relationship become non-linear. For all variables, the coefficients of non-linear terms are significantly higher than linear terms and this necessitate including non-linear terms in Eq. (11) for modeling adsorption data.

Finally, PCA analysis also indicated the significance of interaction term with a high coefficient (5.667). It should be mentioned that not all terms would be significant for modeling adsorption data and t-test would be applied in this case to assess the importance of the coefficients to be included in Eq. (11). Student's t-test was used as a statistical indicator provided that more experiments (20 experiments) were performed than number of required coefficients

Table 5
Values of coefficients as obtained by PCA and the significance t-test results.[a]

Variables and terms	Coefficient	v	t
Intercept	b_0 (0.031)	1×10^{-5}	10.89
Shak. Tim. (x_1)	b_1 (0.221)	1.1	0.23
pH (x_2)	b_2 (−0.192)	0.54	0.29
AC mass (x_3)	b_3 (−0.122)	1.24	0.12
Dye conc. (x_4)	b_4 (−0.470)	0.72	0.62
NaCl conc. (x_5)	b_5 (−0.380)	74.3	0.05
Temp. (x_6)	b_6 (0.358)	0.66	0.49
(Shak. Tim.)^2 (x_1^2)	b_7 (0.522)	3.8	0.30
(pH)^2 (x_2^2)	b_8 (0.812)	2.6	0.56
(AC mass)^2 (x_3^2)	b_9 (2.841)	4.95	1.42
(Dye conc.)^2 (x_4^2)	b_{10} (−1.492)	1.84	1.22
(NaCl conc.)^2 (x_5^2)	b_{11} (−2.112)	288	0.14
(Temp.)^2 (x_6^2)	b_{12} (−5.452)	4.4	2.89
All ($x_1x_2x_3x_4x_5x_6$)	b_{13} (5.742)	58.6	0.83

[a] Tabulated two-paired t value is 4.3 at 2 degrees of freedom and 95% confidence level. 20 experiments, 14 coefficients and 4 replicate (2 degree of freedom).

(14 coefficients). The significance t-test was carried out as following [12,29]: (a) the square covariance matrix was calculated and the variances v were taken as the diagonal values of this matrix, (b) SSE value was calculated from experimental and predicted values as outlined earlier, (c) determination of the mean of ESS (s) by dividing SSE by degrees of freedom which equals to $N–P–R$, where N is number of experiments (20), P is the number of coefficients (14), and R number of replicates (4), and (d) estimation of t-value: $t = b/(sv)^{1/2}$ and compare this with a selected two-tailed t value 4.3 which collected at 2 degrees of freedom and 95% confidence level. The statistical results are summarized in Table 5. Except for b_0, the calculated t values were lower than t_{table*} value and this indicate that linear, non-linear and interaction terms of the variables necessary for modeling adsorption data.

Assessment of the prediction power of Eq. (11) and the significance of different terms were made by predicting K_d values, however, under different circumstances as summarized in Table 6. Moreover, the prediction power of PCA was evaluated for the calibration/training set and also for the validation set (7 experiments) which do not involved in model creation.

The results presented in Table 6 indicated that non-linear terms are so significant for modeling adsorption data where SSE value has been reduced from 9.3 to 1.6 (calibration set) after adding these terms to Eq. (11). On the other hand, SSE value was slightly increased (from 1.6 to 3.3) when interaction term was included in PCA analysis for K_d prediction for calibration set. Relatively speaking, higher SSE values were obtained for K_d prediction in validation set at all conditions of regression, however, the performance of the developed model is acceptable for predicting K_d in new experiments. Fig. 6A shows the plot between calculated and predicted

Table 6
Performance of PCA for K_d prediction in the calibration and validation sets under different conditions.[a]

Terms included in the model (Eq. (11))	SSE (calibration set)	SSE (validation set)
Linear terms	9.3	12.2
Linear and non-linear terms	1.6	2.1
Linear, non-linear, and interaction terms	3.3	4.1

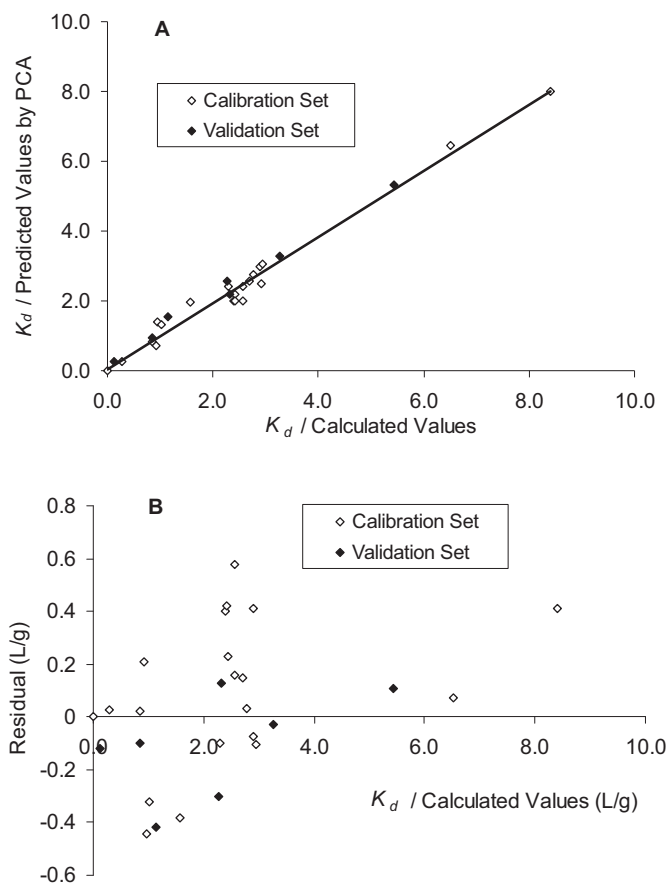[a] Intercept (b_0 value) was removed before running PCA in all cases.

Fig. 6. Calculated K_d values against predicted ones (A) and residual distribution plot (B).

K_d values where only linear and non-linear terms included in the analysis. Fig. 6B showed the residual plot for both sets. It should be mentioned that the intercept (b_0) was removed from Eq. (11) in all regressions as it has a small magnitude compared to the other coefficients.

As indicated in Fig. 6A, the prediction power of Eq. (11) is acceptable with good correlation coefficients of 0.9811 (for calibration set) and 0.9456 (for validation set) which reflects the high credibility of the derived empirical equation for predicting K_d values even in the tests not involved in model building. It seems that no interaction between the variables where each variable independently affect dye adsorption. Because the interaction term was insignificant for presenting data then one can conclude that the optimum pH is 3.0 weather adsorption test carried out at 20 or 40 °C or at 50 or 450 mg/L. Furthermore, the optimum temperature for adsorption is 40 °C weather solution pH is 3 or 12, i.e., there is no interaction effect between the variables on dye adsorption. The earlier conclusions could not be formulated based on univariate analysis of adsorption data and multivariate analysis was necessary in this case.

In fact, the developed model contains large number of parameters and this seems to be necessary to model complex adsorption data which based on a large number of variables. Many attempts were made to model the adsorption data using few parameters, however, a poor prediction for K_d was often obtained. Using PCA, Álvarez-Uriarte et al. have modeled organic matter adsorption by fourteen activated carbons using few number of parameters (pore volume, Iron and oxygen content of the carbons) [13]. In the earlier work, nine samples were included in model building and five samples were left for external validation [13].

3.7. Prediction of the best combination of experimental variables using PCA

An important question that would one asks is: what is the perfect combination of the variables that would end up with maximum adsorption or maximum K_d value? In fact, PCA was used to find the perfect mach of the variables that would give the maximum adsorption of dye (i.e., the maximum K_d value). This was simply achieved by collecting the maximum values of linear and non-linear terms (the bolded values in Table 4) in a vector of dimension 1×14 and use Eq. (14) to predict K_d values at these extreme conditions. The result showed that the maximum value of K_d is 20.3 L/g and this value would be achieved at the following conditions: shaking time 7.0 days, pH 12, dye content 450 mg/L, mass of AC 950 mg, NaCl concentration 3.0 M, and temperature 40 °C. The obtained combination of the variables seems to be reasonable and capable to achieve the maximum dye adsorption; however, it was interesting to notice that the optimum levels of pH and NaCl are 12 and 3.0 M, respectively. As shown in Table 1, the maximum K_d value was 8.41 L/g and this reflected that the design of the experiments could be further adjusted for getting better adsorption results.

4. Conclusions

Generally speaking, adsorption of erythrosine by activated carbon is acceptable with a maximum capacity of 89.3 mg/g at 40 °C and pH 7. The reported adsorption capacity is modest when compared to adsorption capacity of positively charged methylene blue (C.I. 52015). The modest adsorption of erythrosine is mainly attributed to its large molecular structure and its negative charge. Thermodynamic parameters reflected that adsorption of erythrosine is an endothermic process with ΔH_{ads} of 31.6 kJ/mol and was spontaneous over the studied temperatures (293–313 K). Using PCA, a useful empirical relationship including six linear terms and six non-linear terms of the variables for predicting K_d values. K_d values were predicted from experimental variables with an acceptable margin or error. Using PCA, the best combination of the experimental variables that would give the maximum adsorption were ascertained: shaking time 7 days, pH 12, mass of adsorbent 950 mg, initial dye content 450 mg/L, NaCl concentration 3.0 M, and solution temperature 40 °C. Multivariate analysis of adsorption data is necessary for assessing the perfect combination of the experimental variables to get the best performance of the adsorbent.

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