

# Adsorption of basic dyes from single and binary component systems onto bentonite: Simultaneous analysis of Basic Red 46 and Basic Yellow 28 by first order derivative spectrophotometric analysis method

Meral Turabik\*

*University of Mersin, Higher Vocational School of Technical Science, Chemical Prog., Çiftlikköy-Mersin, Turkey*

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## Abstract

The present study deals with the simultaneous analysis and adsorption of Basic Yellow 28 and Basic Red 46 dyes in binary mixture onto bentonite. First order derivative spectrophotometric method was used for simultaneous analysis of BY28 and BR46 in binary mixtures. The adsorption experiments were carried out in a batch system. The mono- and multi-component Langmuir and Freundlich isotherm models were applied to experimental data and the isotherm constants were calculated for BY28 and BR46 dyes. The monolayer coverage capacities of bentonite for BY28 and BR46 dyes in single solution system were found as 256.4 mg/g and 333.3 mg/g, respectively. It was observed that the equilibrium uptake amounts of BY28 and BR46 dyes in binary mixture onto bentonite decreased considerably with increasing concentrations of the other dye resulting in their antagonistic effect. The adsorption equilibrium data fitted more adequately to mono-component Langmuir isotherm model than mono-component Freundlich isotherm model, while the extended Freundlich isotherm model adequately predicted the multi-component adsorption equilibrium data at moderate ranges of concentration. Thermodynamic parameters showed that adsorption of BR46 and BY28 was endothermic and spontaneous in nature.

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## 1. Introduction

Dyes and pigments are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing. Wastewater streams from the textile dyeing operation contain unused dyes (about 8–20% of the total pollution load due to incomplete exhaustion of the dye) and auxiliary chemicals along with large amounts of water [1]. The presence of dyes in water reduces light penetration and has a derogatory effect on photosynthesis. There are many structural varieties, such as acidic, basic, disperse, azo, diazo, anthraquinone based and metal complex dyes [2]. Cationic dyes, commonly known as basic dyes, are widely used in acrylic, nylon, silk, and wool dyeing [3]. Due to the complex chemical structure of these dyes, they are resistant to breakdown by chemical, physical and bio-

logical treatments. Furthermore, any degradation by physical, chemical or biological treatments may produce small amount of toxic and carcinogenic products [3,4].

The conventional methods for treating dye-containing wastewaters are coagulation and flocculation, reverse osmosis, electroflotation, membrane filtration, irradiation and ozonation and active carbon adsorption [5,6]. The most popular of these technologies is activated carbon adsorption and widely used but it is expensive. In recent years, clays have been accepted as one of the appropriate low-cost adsorbents for the removal of dyes from dye wastewater. Clay materials have been increasingly gaining attention because they are cheaper than activated carbons. Various studies have been reported where clays were shown as effective adsorbents for textile dyes [3,7–12].

In recent years, considerable information has been collected for the adsorption of single component dyes by various adsorbents, many industrial situations involve the discharge of effluents that contain a mixture of several dyes, and limited data is available on multi-component dye adsorption [1].

\* Tel.: +90 324 361 00 01x6771; fax: +90 324 361 00 43.

E-mail address: [mturabik@mersin.edu.tr](mailto:mturabik@mersin.edu.tr).

### Nomenclature

$C_{eq,i}$	unadsorbed dye concentration of each component at equilibrium (mg/L)
$C_{0,i}$	initial dye concentration of each component (mg/L)
$D$	absorbance value of each dye at the first order derivative wavelength
$\Delta G^\circ$	free energy change (kJ/mol)
$\Delta H$	enthalpy change (kJ/mol)
$K_{a,i}$	individual Langmuir isotherm constant of each component (L/mg)
$K_{F,i}$	individual Freundlich isotherm constant of each component
$n_i$	individual Freundlich isotherm constant of each component
$q_{eq,cal}$	calculated value of the adsorbed dye amount per unit weight of adsorbent at equilibrium (mg/g)
$q_{eq,i}$	adsorbed dye amount of each component per unit weight of adsorbent at equilibrium (mg/g)
$q_{max}$	maximum amount of the dye per unit weight of adsorbent to form a complete monolayer on the surface bound at high $C_{eq}$ (mg/g)
$R^2$	correlation coefficient
$\Delta S^\circ$	entropy change (J/mol K)
$T$	temperature ( $^\circ\text{C}$ )
$V$	volume of dye-containing solution (L)
$w$	mass of the adsorbent (g)
$x_i, y_i, z_i$	extended Freundlich isotherm constants of each component
<i>Greek letters</i>	
$\eta_i$	modified Langmuir isotherm constant of each component
$\lambda$	wavelength (nm)
$\epsilon$	percentage error (%)

Also, the simultaneous analysis of multi-component dye mixtures is very complex problem in analytical chemistry due to the spectral interferences, which results in widely overlapped absorption bands. Derivative spectrophotometry is an analytical technique of great utility for resolving mixtures with overlapping spectra [13,14]. The derivatisation of zero order spectrum can lead to separation of overlapped signals, reduces the effect of spectral background interferences caused by presence of other compounds in a sample [15,16].

The present paper concerns with the simultaneous analysis of the Basic Yellow 28 (BY28) and Basic Red 46 (BR46) dyes using the first order derivative spectrophotometric method, and adsorption of BY28 and BR46 dyes in single and binary mixture onto bentonite. Bentonite is a clay consisting essentially of smectite mineral of the montmorillonite group [17]. The adsorption was studied in a batch system and various mono- and multi-component isotherm models were applied to the experimental data to determine bentonite adsorption capacity.

## 2. Equilibrium of adsorption

Equilibrium adsorption isotherms play an important role in the predictive modelling that is used for the analysis and design of adsorption systems. The Langmuir and Freundlich isotherm models are the most frequently used isotherm models in the literature describing the non-linear equilibrium between adsorbed pollutant on the adsorbent and pollutant in solution at a constant temperature. These models are simple, give a good description of experimental behaviour in a large range of operating conditions and recharacterized by a limited number of adjustable parameters [18]. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface [19];

$$q_{eq} = \frac{q_{max} K_a C_{eq}}{1 + K_a C_{eq}} \quad (1)$$

The Freundlich isotherm theory assumes that a monolayer adsorption by the adsorbent with a heterogeneous energy distribution of active sites [20];

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2)$$

When several components are present, interference and competition phenomena for adsorption sites occur and lead to a more complex mathematical formulation of the equilibrium. Individual adsorption constants may not define exactly the multi-component adsorption behaviour of dye mixtures [21]. Various multi-component isotherm equations have been developed by various researchers. The modified Langmuir [22] and extended Freundlich [21,22] isotherm models were applied to equilibrium data as multi-component isotherm models for the adsorption of BY28 and BR46 onto bentonite.

The modified Langmuir isotherm model is written as,

$$q_{eq,i} = \frac{q_{i,max} K_{a,i} (C_{eq,i}/\eta_i)}{1 + \sum_{j=1}^N K_{a,j} (C_{eq,j}/\eta_j)} \quad (3)$$

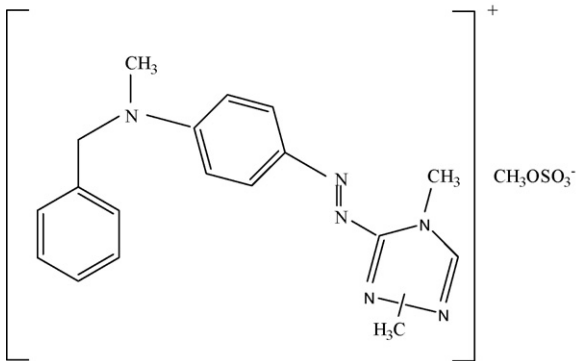
where  $q_{i,max}$  and  $K_{a,i}$  are derived from the corresponding individual Langmuir isotherm equations. An interaction term,  $\eta_i$  is the Langmuir correction coefficient of the  $i$  component where estimated from competitive adsorption data.  $\eta_i$  is characteristic of each species and depends on the concentration of the other components.

The empirical extended form of the Freundlich isotherm model restricted to binary mixtures, and this isotherm model contains six parameters ( $x_1; y_1; z_1$  and  $x_2; y_2; z_2$ ) which are the extended Freundlich adsorption constants of the first and second components in binary mixture. This model can be given by Eqs. (4) and (5) for each component of binary mixture.

$$q_{eq1} = \frac{K_{F1} C_{eq1}^{1/(n_1+x_1)}}{C_{eq1}^{x_1+y_1} C_{eq2}^{z_1}} \quad (4)$$

$$q_{eq2} = \frac{K_{F2} C_{eq2}^{1/(n_2+x_2)}}{C_{eq2}^{x_2+y_2} C_{eq1}^{z_2}} \quad (5)$$

Basic Red 46 (BR46) Astrazon Rot FBL 200 %; MW: 357.5 g/mol



Basic Yellow 28 (BY 28) Astrazon Goldgelb GL-E 400 % ; MW: 433 g/mol

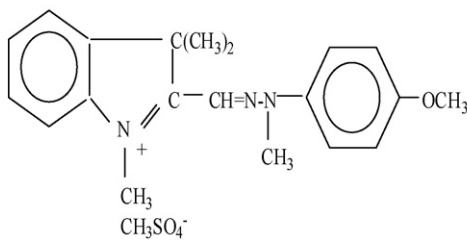


Fig. 1. Structure of the basic dyes.

where  $K_{F1}$ ,  $K_{F2}$  and  $n_1$  and  $n_2$  are derived from the corresponding individual Freundlich isotherm equations.

### 3. Material and methods

#### 3.1. Material

Basic Red 46 (BR46) and Basic Yellow 28 (BY28) were supplied by DyStar firm with commercial names Astrazone Rot FBL and Astrazone Goldgelb GL-E. The characteristics and structure of these basic dyes were presented in Fig. 1.

The bentonite used as an adsorbent was supplied from Ordu, Turkey. It was crushed, ground and sieved through a 45- $\mu$ m sieve and dried at 120 °C in an oven for 24 h before using in the experiments. The dried bentonite sample was stored in an air-tight plastic container for using in further experiments. The chemical composition of bentonite was given in Table 1. The X-ray diffractogram of bentonite was also determined using Rigaku Rint Series with Cu K $\alpha$  radiation. The mineral phases of bentonite were identified as montmorillonite ( $2\theta = 5.88^\circ$ ) and cristobalite ( $2\theta = 21.48^\circ$ ) (Fig. 2). The specific surface area and cation exchange capacity (CEC) of bentonite were 72.5 m<sup>2</sup>/g and 99.2 meq/100 g, respectively [23].

Table 1  
Chemical composition of the bentonite

Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI <sup>a</sup>
Weight (%)	72.07	14.54	1.19	1.06	3.57	1.04	0.59	0.08	0.02	5.84

<sup>a</sup> LOI: Loss ignition of bentonite.

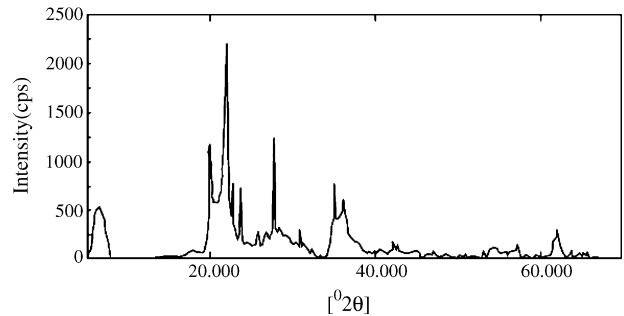


Fig. 2. The X-ray diffractogram of the bentonite.

#### 3.2. Preparation of dye solutions

The stock solutions of Basic Yellow 28 and Basic Red 46 dyes were prepared in 1.0 g/L concentration. The experimental solutions were prepared by diluting the stock solution with distilled water when necessary. The test solutions containing desired combinations of BY28 and BR46 were prepared by diluting 1.0 g/L of stock solutions of BY28 and BR46 and mixing them in the test medium. The initial pH of each solution was adjusted to the required value with concentrated H<sub>2</sub>SO<sub>4</sub> or NaOH solutions before mixing with bentonite.

#### 3.3. Batch adsorption studies

The 0.10 g of bentonite was mixed with 100 mL of solution containing a known concentration of BY28 and BR46 dyes in single solution or in binary mixture of these components in an Erlenmeyer flask. The flasks were agitated on a shaker at constant temperature for 2 h ample time for adsorption equilibrium. Samples (3 mL) of adsorption medium were taken before mixing the adsorbent and dye bearing solutions, and then at the end of 2 h, they were centrifuged at 3500 rpm for 15 min. The dye remaining in supernatant was analysed.

The adsorbed amount of each dye per unit weight of adsorbent at equilibrium,  $q_{eq,i}$  (mg dye/g adsorbent) can be calculated by using Eq. (6):

$$q_{eq,i} = \frac{(C_{0,i} - C_{eq,i})V}{w} \quad (6)$$

where  $V$  is the volume of dye-containing solution (L) and  $w$  is the mass of the adsorbent (g).

The individual adsorption yield ( $Ad_i$ , %) and the total adsorption yield ( $Ad_{Tot}$ , %) can be calculated by using the following expressions:

$$Ad_i (\%) = \frac{C_{0,i} - C_{eq,i}}{C_{0,i}} \times 100 \quad (7)$$

$$Ad_{Tot}(\%) = \frac{\sum(C_{0,i} - C_{eq,i})}{\sum C_{0,i}} \times 100 \quad (8)$$

### 3.4. Dye analysis

Shimadzu UV-160A spectrophotometer was used for analysis of the studied dyes. The zero order spectrophotometry and first order derivative spectrophotometry were used for the analysis of dyes remaining in single solution and binary mixture, respectively. The first derivative spectra of the studied dyes were recorded in 1 cm quartz cells at a scan speed of 1000 nm/min and a fixed slit width of 2 nm.

## 4. Results and discussion

This study consists of two main parts: the first part is the simultaneous analysis of BY28 and BR46 dyes in binary mixture, and the second is the adsorption of these basic dyes in single and binary mixture onto bentonite.

### 4.1. The analysis of BY28 and BR46 in single solutions

The zero order absorption spectra of BY28 and BR46 were used for the analysis of dyes in single dye solutions. The single solutions of BY28 and BR46 containing 10 mg/L of dyes were prepared and the zero order absorption spectra of these solutions were recorded between 300 and 700 nm and given in Fig. 3. As can be seen from Fig. 3, maximum wavelength ( $\lambda_{max}$ ) of BY28 and BR46 were determined as 437 nm and 529 nm, respectively. The calibration curves were prepared at  $\lambda_{max}$  of each dye.

### 4.2. The simultaneous analysis of BY28 and BR46 in binary mixtures

For the simultaneous analysis of BY28 and BR46 dyes in binary mixture, the binary mixture of these dyes containing 10 mg/L of initial BY28 and BR46 concentration were prepared and zero order absorption spectra were recorded (Fig. 3). As can be seen from Fig. 3, the absorption spectrum of BY28

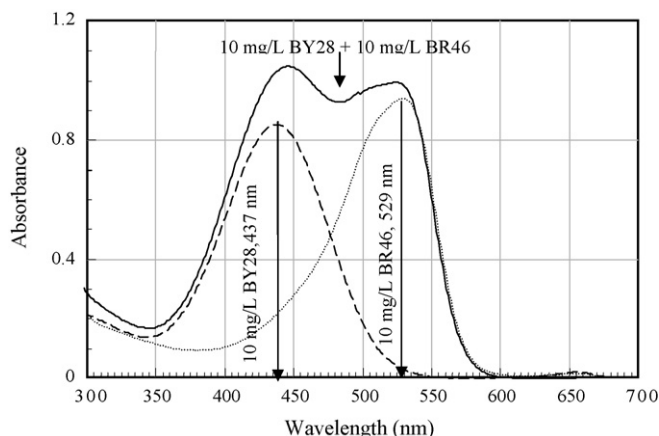


Fig. 3. Zero order absorption spectra of BY28 and BR46 in single and binary solutions.

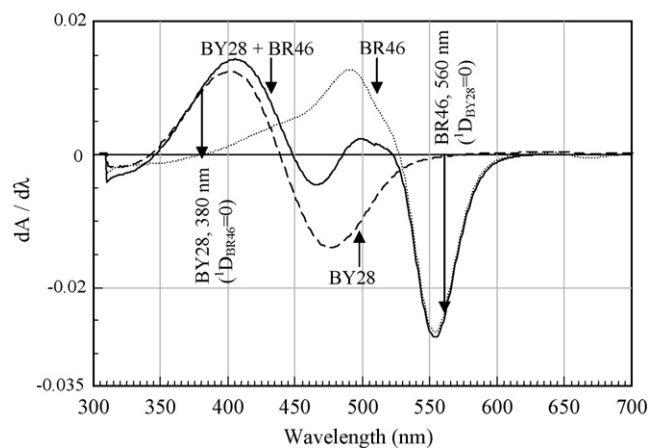


Fig. 4. First order derivative spectra of BY28 and BR46 in single and binary solutions (initial dye concentration of 10 mg/L).

and BR46 dyes in binary mixture overlapped while the maximum absorbances of BY28 and BR46 dyes in their single solutions were obtained at 437 nm and 529 nm, respectively. The overlapping of the BY28 and BR46 dyes spectra show the interference between the zero order spectra of BY28 and BR46 dyes, so their concentrations could not be determined by direct absorbance measurement in their mixture. Hence, it was not possible to determine the amount of BY28 or BR46 dyes in binary mixtures. Therefore, derivative spectrophotometric method was used to simultaneous analysis of BR46 and BY28 dye in binary mixture.

The variations of first order derivative absorption spectra of BY28 and BR46 in single and binary mixture with wavelength were given in Fig. 4. The first order derivative spectra of BY28 and BR46 dyes in single solution and binary mixture showed that BY28 dye can be determined at 380 nm ( $^1D_{380}$ ) in the presence of BR46, where the absorbance of BR46 is zero; and BR46 dye can be determined at 560 nm ( $^1D_{560}$ ) in the presence of BY28, where the absorbance of BY28 dye is zero (Fig. 4). Where  $D$  is the absorbance value of dyes at the first order derivative wavelength. The calibration equations for BY28 and BR46 dyes

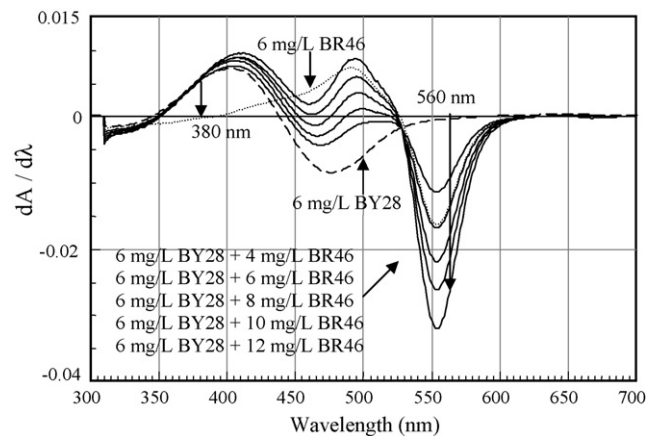


Fig. 5. First order derivative spectra of BY28 and BR46 in binary solutions at 6 mg/L of constant BY28 concentrations and in the range of 4–12 mg/L of BR46 concentrations.

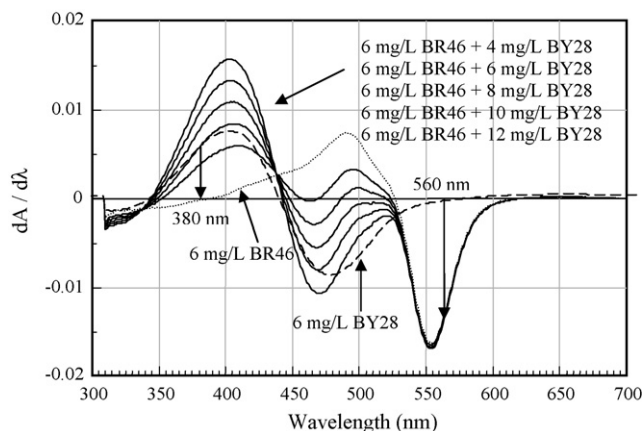


Fig. 6. First order derivative spectra of BY28 and BR46 in binary solutions at 6 mg/L of constant BR46 concentrations and in the range of 4–12 mg/L of BY28 concentrations.

were obtained at 380 nm ( $^1D_{380}$ ) and 560 nm ( $^1D_{560}$ ) for binary dye systems, respectively.

The recovery studies were done to check the accuracy of the first order derivative method used in the determining of the dye concentration in binary solutions. In the recovery studies, the binary dye solutions of BY28 and BR46 containing different concentrations of each dye were prepared and the first order derivative spectra of the binary mixtures were recorded. The recorded spectra of each binary dye solution were given in Figs. 5–7. The BY28 and BR46 contents in binary mixtures were determined from the first order derivative spectra by measuring the absorbance, which was set at the suitable wavelength for the studied dye, the concentration of each dye was calculated from the calibration graphs. The results obtained from resolution of synthetic binary mixtures were sum-

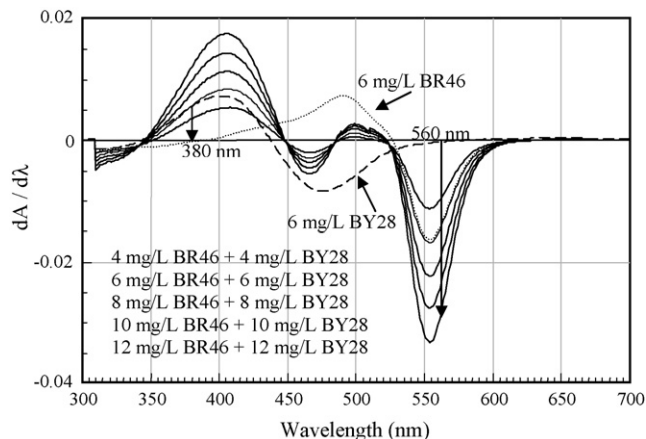


Fig. 7. First order derivative spectra of BY28 and BR46 in the range of 4–12 mg/L of BY28 and BR46 concentrations in binary solutions.

marised in Table 2. The recoveries (%), errors (%) and average percentage errors ( $\epsilon$ , %) between the theoretical ( $C_t$ ) and measured concentrations ( $C_m$ ) were calculated using Eqs. (9)–(11), respectively. In Eq. (11),  $N$  shows the number of measurements.

$$\text{Recovery (\%)} = \frac{C_m \text{ (mg/L)}}{C_t \text{ (mg/L)}} \times 100 \quad (9)$$

$$\text{Error (\%)} = \frac{C_m \text{ (mg/L)} - C_t \text{ (mg/L)}}{C_t \text{ (mg/L)}} \times 100 \quad (10)$$

$$\epsilon \text{ (\%)} = \frac{\sum_{i=1}^N |(C_m - C_t)/C_t|}{N} \times 100 \quad (11)$$

As can be seen from Table 2, the recoveries for the determination of the BY28 and BR46 dyes in binary mixtures by the first order derivative spectrophotometric method were in the

Table 2  
Results of percentage recovery, error and average error values for BR46 and BY28 in binary mixture by first order derivative spectra method

Theoretical (mg/L)		Measurement (mg/L)		Recovery (%)		Error (%)	
$C_{\text{BY28}}$	$C_{\text{BR46}}$	$C_{\text{BY28}}$	$C_{\text{BR46}}$	BY28	BR46	BY28	BR46
6	4	5.7	4.1	95.0	102.5	+5.00	-2.50
6	6	6.0	6.1	100.0	101.7	0.00	-1.66
6	8	6.1	8.1	101.7	101.3	-1.66	-1.25
6	10	5.9	9.8	98.3	98.0	+1.66	+2.00
6	12	6.0	12.0	100.0	100.0	0.00	0.00
6	14	5.9	13.8	98.33	98.6	+1.66	+1.42
4	6	4.0	6.3	100.0	105.0	0.00	-5.00
6	6	6.0	6.1	100.0	101.7	0.00	-1.66
8	6	7.9	6.1	98.8	101.7	+1.25	-1.66
10	6	9.8	6.2	98.0	103.3	+2.00	-3.33
12	6	11.7	6.0	97.5	100.0	+2.50	0.00
14	6	14.5	6.2	103.6	103.3	+3.57	+3.33
4	4	3.8	4.0	95.0	100.0	+5.00	0.00
6	6	6.0	6.1	100.0	101.7	0.00	-1.66
8	8	8.0	8.2	100.0	102.5	0.00	-2.50
10	10	10.1	10.3	101.0	103.0	-1.00	-3.00
12	12	12.4	12.4	103.3	103.3	-3.33	-3.33
14	14	14.5	14.3	103.6	102.1	+3.57	+2.14
$\epsilon$ (%)						1.79	2.03

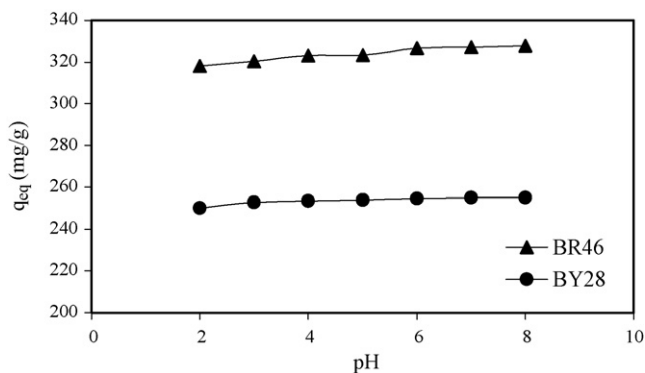


Fig. 8. The effect of initial pH for BY28 and BR46 adsorption onto bentonite (temperature 30 °C, 400 mg/L initial dye concentration).

range of 95–104% for two basic dyes, and average percentage errors ( $\epsilon$ , %) were 1.79 and 2.03% for BY28 and BR46, respectively. According to recovery studies, it can be said that BY28 and BR46 contents in binary mixture can be accurately determined using the derivative spectrophotometric method. Also, this method can be proposed for analysis of other dye mixtures in which their spectra overlapped.

#### 4.3. The effect of the initial pH on the adsorption of BY28 and BR46

The effect of initial pH values for the adsorption of BY28 and BR46 dyes in solution onto bentonite was investigated in the range of pH 2.0–8.0 and given in Fig. 8. As can be seen from Fig. 8, the adsorption of BY28 and BR46 dyes on bentonite is controlled by a pH-independent adsorption mechanism. Similar result were reported for the adsorption of crystal violet, a basic dye, from aqueous solutions onto bentonite by Eren and Afsin [3]. In this situation, the adsorption mechanism occurs partly by ion exchange releasing exchangeable cations in the interlayer and basal plane surfaces and partly via non-coulombic interactions between an adsorbed cation and a neutralized site [3]. For further adsorption studies, the dye solution pH's were adjusted at pH 6.0, which is approximately equal to natural aqueous dye solutions pH.

#### 4.4. The effect of temperature on the adsorption of BY28 and BR46

The adsorption of BY28 and BR46 onto bentonite was investigated as a function of temperature with a constant initial dye concentration of 300 mg/L for both dyes, and given in Fig. 9. The adsorption of BY28 and BR46 onto bentonite slightly increased with increasing temperature. The equilibrium adsorption capacities of bentonite increases from 278.4 to 292.1 mg/g for BR46 and 230.8 to 241.7 mg/g for BY28 when temperature of dye solutions increases from 20 to 60 °C. This increase in the equilibrium adsorption of dyes with temperature indicates that higher temperatures favour the dye removal by adsorption onto bentonite. This may be a result of increasing mobility of the large dye ion with temperature [24,25].

#### 4.5. The effect of the initial dye concentration for the adsorption of BY28 and BR46 in binary mixtures

In this part of the study, the effect of initial dye concentration for the adsorption of BY28 and BR46 dye in binary mixture onto bentonite was investigated in different concentration range of dyes and compared with single dye solution systems. In the first stage, the initial BY28 dye concentration was changed from 100 to 400 mg/L while the initial BR46 dye concentration was held at 0, 100, 200, 300 and 400 mg/L for each run at pH 6.0 and temperature 30 °C. In the second stage, the initial BR46 dye concentration was changed and BY28 concentration was held at the same concentrations range. The individual and total adsorbed dye amounts at equilibrium [ $q_{eq,i}$ , mg/g;  $q_{eq,total} = (q_{eq,BY28} + q_{eq,BR46})$  mg/g], the individual and total adsorption yields (%) were calculated according to Eqs. (6)–(8). The obtained data were given in Table 3 for the adsorption of BY28 dye and in Table 4 for the adsorption of BR46 dye in single solution and binary mixture, respectively.

In the application of adsorption for purification of wastewater, the solution will normally be a mixture of many compounds rather than a single one. The interactions of these compounds may mutually enhance or mutually inhibit adsorption capacity [26]. In general, a mixture of different adsorbates may exhibit three possible types of behaviour: synergism, antagonism and non-interaction [27]. As can be seen from Tables 3 and 4, the individual and total adsorbed dye amounts and adsorption yields at equilibrium change with the initial dye concentration of mixtures containing different concentrations of each dye. For the adsorption of BY28 from single solution, the uptake capacities increased from 98.7 to 253.3 mg/g, respectively, with increasing the initial BY28 concentration from 100 to 400 mg/L. But in the same concentration range and also in the presence of 300 mg/L initial BR46 concentration, the uptake capacity of bentonite obtained as 83.0–177.5 mg/g, respectively. As a results, dye uptake capacity of bentonite reduced in the presence of other dye. The similar trend was also observed for the adsorption of the other BY28 and BR46 combinations onto bentonite.

When the single and binary component systems were compared according to their adsorption yields, it was seen that the individual adsorption yields of dyes in binary component sys-

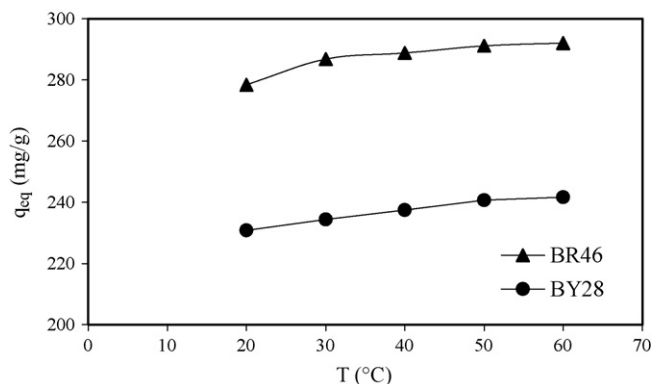


Fig. 9. The effect of initial temperature for BY28 and BR46 adsorption onto bentonite (initial pH 6.0; initial dye concentration 300 mg/L).

Table 3  
Comparison of the individual and total adsorption equilibrium uptake and yields found at increasing initial BY28 concentrations in the absence and presence of increasing initial constant concentrations of BR46 onto bentonite

$C_{0,BY28}$ (mg/L)	$C_{0,BR46}$ (mg/L)	$C_{eq,BY28}$ (mg/L)	$C_{eq,BR46}$ (mg/L)	$C_{eq,total}$ (mg/L)	$q_{eq,BY28}$ (mg/g)	$q_{eq,BR46}$ (mg/g)	$q_{eq,total}$ (mg/g)	$Ad_{BY28}$ (%)	$Ad_{BR46}$ (%)	$Ad_{Tot}$ (%)
99.4	0.0	0.7	0.0	0.7	98.7	0.0	98.7	99.25	0.0	99.25
201.7	0.0	15.0	0.0	15.0	186.7	0.0	186.7	92.56	0.0	92.56
292.7	0.0	58.2	0.0	58.2	234.5	0.0	234.5	80.11	0.0	80.11
401.1	0.0	147.9	0.0	147.9	253.3	0.0	253.3	63.14	0.0	63.14
97.5	102.1	1.5	2.5	4.0	96.0	99.6	195.6	98.46	97.50	98.00
198.0	101.7	22.8	22.9	45.7	175.2	78.8	254.0	88.48	77.48	84.75
304.0	105.8	92.0	42.9	134.9	212.0	62.9	274.9	69.74	59.45	67.08
405.0	110.8	175.0	55.0	230.0	230.0	55.8	285.8	56.79	50.36	55.41
102.5	204.2	13.0	29.6	42.6	89.5	174.6	264.1	87.32	85.50	86.11
206.5	205.2	54.0	82.8	136.8	152.5	122.4	274.9	73.85	59.65	66.77
297.5	201.0	111.0	103.6	214.6	186.5	97.4	283.9	62.69	48.45	56.95
402.5	209.4	205.0	121.3	326.3	197.5	88.1	285.6	49.07	42.07	46.67
106.0	299.3	23.0	106.3	129.3	83.0	193.0	276.0	78.30	64.48	68.10
200.0	302.0	71.0	150.4	221.4	129.0	151.6	280.6	64.50	50.20	55.90
298.0	304.3	138.5	180.3	318.8	159.5	124.0	283.5	53.52	40.75	47.07
395.0	296.8	217.5	187.9	405.4	177.5	108.9	286.4	44.94	36.69	41.40
107.5	394.8	32.5	189.1	221.6	75.0	205.7	280.7	69.77	52.10	55.88
204.5	398.6	84.5	235.7	320.2	120.0	162.9	282.9	58.68	40.87	46.91
305.0	398.5	153.5	264.5	418.0	151.5	134.0	285.5	49.67	33.63	40.58
407.5	400.0	242.0	279.5	521.5	165.5	120.5	286.0	40.61	30.13	35.42

tem were lower than those in single component system. For instance, in the absence of BY28, the adsorption yields for the 200 mg/L of BR46 were found as 98.38%. But in the presence of BY28 dye for 100, 200, 300, 400 mg/L, the individual adsorption yields of BR46 were found as 85.50, 59.65, 48.46, 42.07%, respectively. Also, the total dye adsorption yields of bentonite

in binary mixtures were found lower than expected total adsorption yields that calculated considering the total concentration of each dye in single solutions. When the total adsorption yield was calculated according to Eq. (8), for the 401.0 mg/L initial total dye concentration consisting 201.7 mg/L BY28 and 199.3 mg/L BR46 together, it was expected that total adsorption

Table 4  
Comparison of the individual and total adsorption equilibrium uptake and yields found at increasing initial BR46 concentrations in the absence and presence of increasing initial constant concentrations of BY28 onto bentonite

$C_{0,BR46}$ (mg/L)	$C_{0,BY28}$ (mg/L)	$C_{eq,BR46}$ (mg/L)	$C_{eq,BY28}$ (mg/L)	$C_{eq,total}$ (mg/L)	$q_{eq,BR46}$ (mg/g)	$q_{eq,BY28}$ (mg/g)	$q_{eq,total}$ (mg/g)	$Ad_{BR46}$ (%)	$Ad_{BY28}$ (%)	$Ad_{Tot}$ (%)
100.6	0.0	0.6	0.0	0.6	100.0	0.0	100.0	99.45	0.00	99.45
199.3	0.0	3.2	0.0	3.2	196.1	0.0	196.1	98.38	0.00	98.38
296.9	0.0	10.1	0.0	10.1	286.8	0.0	286.8	96.60	0.00	96.60
402.4	0.0	81.0	0.0	81.0	321.4	0.0	321.4	79.88	0.00	79.88
102.1	97.5	2.5	1.5	4.0	99.6	96.0	195.6	97.50	98.46	98.00
204.2	102.5	29.6	13.0	42.6	174.6	89.5	264.1	85.50	87.32	86.11
299.3	106.0	106.3	23.0	129.3	193.0	83.0	276.0	64.48	78.30	68.10
394.8	107.5	189.1	32.5	221.6	205.7	75.0	280.7	52.10	69.76	55.88
101.7	198.0	22.9	22.8	45.7	78.8	175.2	254.0	77.48	88.48	84.75
205.2	206.5	82.8	54.0	136.8	122.4	152.5	274.9	59.65	73.85	66.77
302.0	200.0	150.4	71.0	221.4	151.6	129.0	280.6	50.20	64.50	55.90
398.6	204.5	235.7	84.5	320.2	162.9	120.0	282.9	40.87	58.68	46.91
105.8	304.0	42.9	92.0	134.9	62.9	212.0	274.9	59.45	69.74	67.08
201.0	297.5	103.6	111.0	214.6	97.4	186.5	283.9	48.46	62.69	56.95
304.3	298.0	180.3	138.5	318.8	124.0	159.5	283.5	40.75	53.52	47.07
398.5	305.0	264.5	153.5	418.0	134.0	151.5	285.5	33.63	49.67	40.58
110.8	405.0	55.0	175.0	230.0	55.8	230.0	285.8	50.36	56.79	55.41
209.4	402.5	121.3	205.0	326.3	88.1	197.5	285.6	42.07	49.06	46.67
296.8	395.0	187.9	217.5	405.4	108.9	177.5	286.4	36.69	44.94	41.40
400.0	407.5	279.5	242.0	521.5	120.5	165.5	286.0	30.13	40.61	35.42

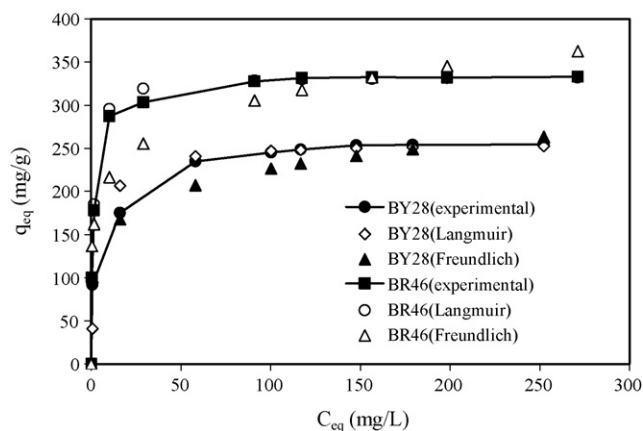


Fig. 10. Comparison of the experimental and modelled isotherms for BY28 and BR46 adsorption on bentonite in single-component solutions.

yields must be equal to 95.46%. But, it is seen that from Tables 3 and 4, total adsorption yield was found as 66.77% for total 411.7 mg/L BY28 and BR46 mixture consisting of 206.5 mg/L BY28 and 205.2 mg/L BR46 together. The binary solution exhibited inhibitory (antagonistic) adsorption for each dye, thereby resulting in a lower adsorption yield. At lower dye concentrations, all dye molecules present in solution could interact with the binding sites and thus the adsorption yields (%) were higher than those at higher initial BY28 and BR46 concentrations. At higher dye concentrations, lower adsorption yield is due to the saturation of adsorption sites. The high uptake values at the high initial dye concentrations are due to a higher initial concentration providing an important driving force to overcome all mass transfer resistances of dye between the aqueous and solid phases [28,29]. The presence of the other dye develops a competition for these adsorption sites on the surface and some sites are occupied by the second component, especially at relatively high concentration of them.

#### 4.6. Equilibrium modelling

##### 4.6.1. Application of mono-component adsorption models to equilibrium data

The adsorption studies of BY28 and BR46 dyes in single and binary mixture onto bentonite were done in a batch reactor by varying the initial concentrations of the studied dyes at initial pH 6.0 and temperature 30 °C. The Langmuir and Freundlich isotherm models were applied to the adsorption data of BY28 and BR46 dye onto bentonite for single component and binary mixture neglecting the possible interference from other dye. The experimental data and isotherms were given in Figs. 10–12 for single component adsorption, for BY28 adsorption in presence of BR46 dye, and for BR46 adsorption in presence of BY28 dye, respectively. The isotherm constants were calculated and presented in Table 5 for BY28 and BR46 adsorption.

The experimental  $q_{eq}$  values were found to be smaller than  $q_{max}$  indicating that the adsorption of BY28 and BR46 dye onto bentonite occurred by a monolayer type adsorption in which the surface of bentonite is not fully covered.  $K_a$ , calculated from the

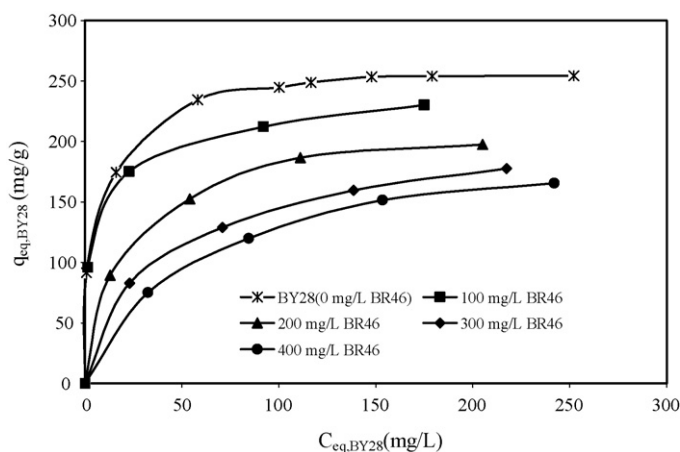


Fig. 11. Non-linear adsorption isotherms of BY28 in the absence and in the presence of increasing BR46 concentrations.

Langmuir isotherm model indicates the affinity for binding of dye. A large value of  $K_a$  also implies strong bonding [30,31]. As can be seen from Table 5, the  $K_a$  value of BR46 was higher than that of BY28 in single solution. But, the  $K_a$  values of BR46 in binary mixture systems decreased with the increasing concentrations of BY28. Also, the  $K_a$  values of BY28 in binary mixture systems decreased with the increasing concentrations of BR46, but these decreasing were lower than those of BR46 (Table 5). This can be explained by the fact that the affinity of the adsorbent toward BR46 dye is greater in single solution than that of binary mixtures. As a result of the presence of both dyes, the decreasing tendency of the calculated  $K_a$  values may indicate competition for adsorption sites. The Freundlich constants,  $K_F$  and  $n$ , were also calculated for the adsorption of BY28 and BR46 dyes in single and binary mixtures and were presented in Table 5. The  $n$  values calculated for the adsorption in binary mixture reduced with the increasing of the other dye concentration, indicating that the adsorption intensity was contrarily affected by presence of other dye. The value of  $n$ , which is significantly higher than unity, indicated that both BY28 and BR46 dyes are favourably adsorbed by bentonite. The magnitude of  $K_F$  showed a relatively easy uptake of BY28 and BR46 dye from single and binary aque-

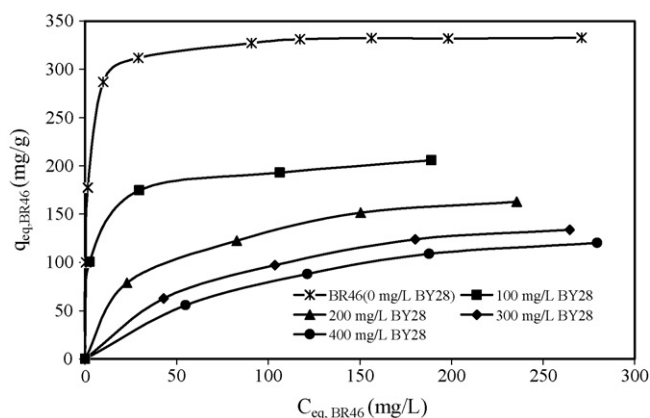


Fig. 12. Non-linear adsorption isotherms of BR46 in the absence and in the presence of increasing BY28 concentrations.



Table 5  
Effect of increasing initial other dye concentration on the Langmuir and Freundlich isotherms constant of BY28 and BR46 adsorption in binary dye systems (initial pH 6.0, temperature 30 °C)

Component	$C_{0, \text{BR46}}$ (mg/L)	Langmuir			Freundlich		
		$q_{\text{max}}$	$K_a$	$R^2$	$K_F$	$n$	$R^2$
BY28	0	256.4	0.257	0.999	105.9	6.071	0.933
	100	232.6	0.174	0.998	91.7	5.388	0.985
	200	217.4	0.050	0.999	43.5	3.353	0.964
	300	208.3	0.025	0.998	28.9	2.916	0.992
	400	204.1	0.018	0.999	19.0	2.474	0.978
Component	$C_{0, \text{BY28}}$ (mg/L)	Langmuir			Freundlich		
		$q_{\text{max}}$	$K_a$	$R^2$	$K_F$	$n$	$R^2$
BR46	0	333.3	0.769	0.999	150.8	6.390	0.820
	100	208.3	0.200	0.999	90.0	6.001	0.957
	200	188.7	0.027	0.997	29.2	3.109	0.991
	300	172.4	0.012	0.998	12.9	2.338	0.984
	400	169.5	0.009	0.998	8.2	2.059	0.980

ous solutions with high adsorption capacity of bentonite. The  $K_F$  values significantly decreased in the presence of other dye in the solution, indicating that the adsorption capacity of bentonite for each component in binary dye systems decreased with the increase of the other dye concentration.

The possible reduction in dye adsorption capacity onto bentonite in binary mixtures was evaluated by comparing the maximum adsorption capacity from single dye solutions to that of binary dye solutions for each particular dye. Such comparisons should only be made if the initial conditions are identical in single and binary dye solution systems. As can be seen from Table 5, bentonite showed a higher maximum monolayer coverage capacity ( $q_{\text{max}}$ ) for BR46 dye than that for BY28 dye in single component. But in binary mixture systems, BY28 uptake onto bentonite was higher than that of BR46. While the presence of other initial dye concentration increased, the maximum adsorption capacities of bentonite decreased and also the percentage reduction of maximum adsorption capacities of bentonite increased for both dye [reduction (%) =  $(q_{\text{max, single}} - q_{\text{max, binary}})/q_{\text{max, single}}$ ]. The decreasing values of BR46 uptake were higher than those of BY28. For example, at the presence of 100 and 400 mg/L of initial BR46 concentration, the maximum monolayer coverage capacities of bentonite and the percentage reduction of maximum adsorption capacities of bentonite for BY28 were 232.6 mg/g and 204.1 mg/g; 9.3% and 20.4%, respectively. But, in the presence of 100 and 400 mg/L of BY28, the maximum monolayer coverage capacity and the percentage reduction of BR46 were 208.3 mg/g and 169.6 mg/g; 37.5% and 49.1%, respectively (Table 5). These data showed that BY28 was much more adsorbed preferentially than BR46 in binary mixtures. The selective adsorption in multi-component systems was also reported by Al-Degs et al. [32], and Allen et al. [33]. Generally, the adsorption capacities of each individual dye are proportionally less with another solute. This can be attributed in the main to the interaction between the dyes on the solid surface, with non-equal competition attributed to the hetero-

geneity of adsorbent surface. Factors that affect the adsorption preference of a sorbent for different kinds of adsorbates may be related to the characteristics of the binding sites (e.g. functional groups, structure, surface properties, etc.), the properties of the adsorbates (e.g. concentration, ionic size, ionic weight, molecular structure, ionic nature or standard reduction potential, etc.) and solution chemistry (e.g. pH, ionic strength, etc.) [21]. It is difficult to determine which factors affect the selective adsorption of bentonite. For that reason, the observed results may result from a combination of all the above factors [21,34].

The analysis of isotherm models for describing adsorption behaviour of dyes in single and binary solutions was made by comparing the experimental equilibrium data and calculated values ( $q_{\text{eq, exp}}$ ;  $q_{\text{eq, calc}}$ ) and according to correlation coefficients ( $R^2$ ) generated by the linear regression of each model. The comparison of the experimental equilibrium data and calculated values ( $q_{\text{eq, exp}}$ ;  $q_{\text{eq, calc}}$ ) from mono-component isotherm models for binary dye systems were showed in Fig. 13 and, given in

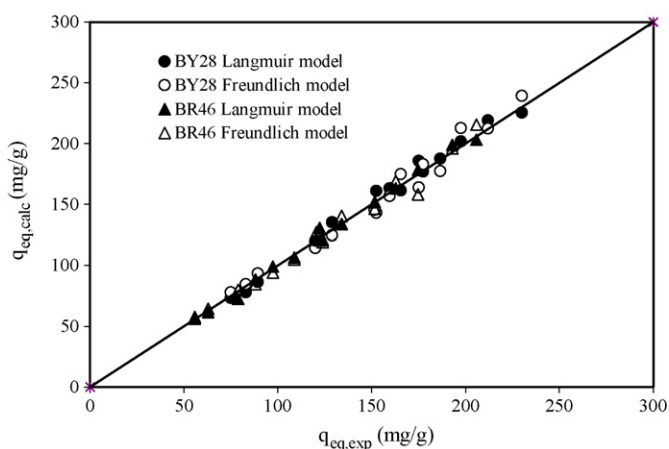


Fig. 13. The comparison of the experimental and calculated  $q_{\text{eq}}$  values from mono-component isotherm models for BY28 and BR46 dyes in binary mixtures.

Table 6

Comparison of the experimental and calculated  $q_{eq}$  values evaluated from Langmuir, Freundlich, modified Langmuir and extended Freundlich isotherm models at increasing initial BY28 concentrations in the absence and presence of increasing initial constant concentrations of BR46 onto bentonite

$C_0, BY28$ (mg/L)	$C_0, BR46$ (mg/L)	$q_{eq, exp, BY28}$ (mg/g)	$q_{eq, exp, BR46}$ (mg/g)	$q_{eq, Lang BY28}$ (mg/g)	$q_{eq, Fr BY28}$ (mg/g)	$q_{eq, calc, BY28}$ (mg/g)		$q_{eq, calc, BR46}$ (mg/g)	
						Mod-Lang	Ext-Fr	Mod-Lang	Ext-Fr
97.5	103.1	96.0	100.6	48.1	98.9	75.7	66.9	100.6	100.6
198.0	101.7	175.2	78.8	185.8	163.8	150.3	122.3	120.4	100.9
304.0	105.8	212.0	62.9	218.9	212.3	196.0	178.3	72.9	76.9
405.0	110.8	230.0	55.8	225.2	239.2	212.9	208.9	53.3	65.2
102.5	204.2	89.5	174.6	86.3	93.5	100.4	89.5	182.3	132.9
206.5	205.2	152.5	122.4	161.0	142.9	129.6	128.9	158.4	125.4
297.5	201.0	186.5	97.4	187.4	177.2	161.2	163.8	119.9	105.6
402.5	209.4	197.5	88.1	201.8	212.8	186.8	197.5	88.1	88.1
106.0	299.3	83.0	193.0	77.9	84.7	65.4	77.3	240.8	177.8
200.0	302.0	129.0	151.6	135.1	124.7	110.2	123.8	186.0	144.9
298.0	304.3	159.5	124.0	163.0	156.8	141.4	158.9	146.8	123.0
395.0	296.8	177.5	108.9	177.0	183.0	166.6	186.9	114.7	104.8
107.5	394.8	75.0	205.7	73.2	77.7	55.4	75.0	256.8	197.7
204.5	398.6	120.0	162.9	119.7	114.3	93.8	117.3	208.5	162.9
305.0	398.5	151.5	134.0	145.7	145.5	123.9	150.4	170.2	139.1
407.5	400.0	165.5	120.5	161.4	174.9	149.4	179.4	137.5	119.7
			€ (%)	3.02	4.15	14.11	8.83	18.44	7.94

Tables 6 and 7 along with their error values for BY28 and BR46, respectively. The average percentage errors between the experimental and predicted values (€, %) were calculated using the following equation, where the subscripts “exp” and “calc” indicate the experimental and calculated values and  $N$  the number of measurements:

$$\epsilon (\%) = \frac{\sum_{i=1}^N |(q_{eq, i, exp} - q_{eq, i, calc}) / q_{eq, i, exp}|}{N} \times 100 \quad (12)$$

As can be seen from Tables 6 and 7, the error values obtained from Langmuir isotherm model are lower than those of Freundlich isotherm model. It can be said that Langmuir isotherm model represents the adsorption of BY28 and BR46 onto bentonite better than Freundlich isotherm model, where the lowest values of  $R^2$  were obtained for single and binary dye systems (Table 5). Previous researchers have also indicated that the modelling of multisolute (binary and ternary) adsorption systems can be successfully described by the Lang-

Table 7

Comparison of the experimental and calculated  $q_{eq}$  values evaluated from Langmuir, Freundlich, modified Langmuir and extended Freundlich isotherm models at increasing initial BR46 concentrations in the absence and presence of increasing initial constant concentrations of BY28 onto bentonite

$C_0, BR46$ (mg/L)	$C_0, BY28$ (mg/L)	$q_{eq, exp, BR46}$ (mg/g)	$q_{eq, exp, BY28}$ (mg/g)	$q_{eq, Lang BR46}$ (mg/g)	$q_{eq, Fr BR46}$ (mg/g)	$q_{eq, calc, BY28}$ (mg/g)		$q_{eq, calc, BR46}$ (mg/g)	
						Mod-Lang	Ext-Fr	Mod-Lang	Ext-Fr
103.1	97.5	100.6	96.0	69.4	104.8	75.7	66.9	100.6	100.6
204.2	102.5	174.6	89.5	178.2	158.2	100.4	89.5	182.3	132.9
299.3	106.0	193.0	83.0	198.8	195.8	65.4	77.3	240.8	177.8
394.8	107.5	205.7	75.0	202.9	215.5	55.4	75.0	256.8	197.6
101.7	198.0	78.8	175.2	72.4	80.0	150.3	122.5	120.4	100.9
205.2	206.5	122.4	152.5	130.7	120.7	129.6	128.9	158.4	125.4
302.0	200.0	151.6	129.0	151.6	146.3	110.2	123.8	186.0	144.9
398.6	204.5	162.9	120.0	163.2	169.0	93.8	117.3	208.5	162.9
105.8	304.0	62.9	212.0	61.7	64.5	196.0	178.3	72.9	76.9
201.0	297.5	97.4	186.5	98.4	94.0	161.2	163.8	119.9	105.6
304.3	298.0	124.0	159.5	120.6	119.1	141.4	158.4	146.8	123.0
398.5	305.0	134.0	151.5	133.6	140.3	123.8	150.4	170.2	139.0
110.8	405.0	55.8	230.0	56.1	57.6	212.9	208.9	53.3	65.2
209.4	402.5	88.1	197.5	88.5	84.6	186.8	197.5	88.1	88.1
296.8	395.0	108.9	177.5	106.5	104.7	166.6	186.9	114.7	104.8
400.0	407.5	120.5	165.5	121.3	126.9	149.4	179.4	137.5	119.7
			€ (%)	2.11	3.78	14.11	8.83	18.44	7.94

Table 8

Comparison of the multi-component isotherm parameters evaluated from the modified Langmuir and extended Freundlich isotherm models for simultaneous adsorption of BY28 and BR46 onto bentonite

Component	Modified Langmuir model	Extended Freundlich model		
	$\eta_i$	$x_i$	$y_i$	$z_i$
BR46	2.567	0.418	0.836	0.592
BY28	0.525	0.729	0.491	0.698

muir isotherm model where apparent dye displacement occurs [32,35].

#### 4.6.2. Application of multi-component adsorption models to equilibrium data

The prediction of multi-component equilibrium data has always been complicated due to the interactive and competitive effects involved. Nevertheless, attempts were carried out to predict and correlate multi-component data from single component data [21]. The simultaneous adsorption of BY28 and BR46 onto bentonite from binary mixtures were investigated at pH 6.0 and 30 °C and expressed by the multi-component modified Langmuir and extended Freundlich isotherm models. The competitive Langmuir and Freundlich isotherm constants evaluated from modified adsorption models for BY28 and BR46 were given in Table 8. The error values between the experimental and calculated  $q_{eq}$  values for entire data set of BY28 and BR46 dyes were also given in Tables 6 and 7, respectively.

The modified Langmuir and extended Freundlich isotherm models fitted reasonably well to the binary adsorption data of BY28 and BR46 dyes onto bentonite. However, the extended Freundlich isotherm model fitted more adequately to the experimental data with the lower error values of 8.83% for BY28; and 7.94% for BR46, respectively. Using the individual and modified multi-component Langmuir and Freundlich isotherm constants,  $q_{eq}$  values were calculated from the modified Langmuir and extended Freundlich models. The comparison curves of the experimental and calculated  $q_{eq}$  values of BY28 and BR46 dyes in binary mixture were presented in Fig. 14. As can be

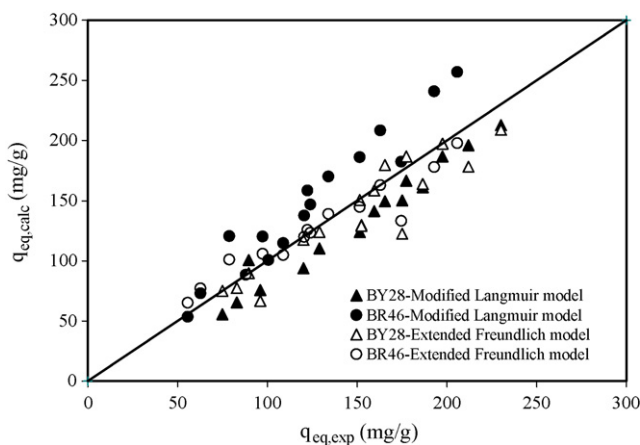


Fig. 14. The comparison of the experimental and calculated  $q_{eq}$  values from multi-component isotherm models for BY28 and BR46 dyes in binary mixtures.

seen from Fig. 14, the correlations between experimental and calculated results in the extended Freundlich model better than modified Langmuir model, however, the correlation deviated at very high mixture concentrations. This could be explained by the lower uptake of BR46 dye than the calculated uptake with respect to the multi-component adsorption models. Also, these results can be attributed to the intensity of both models to competitive and interactive effects existing in multi-component systems and the characteristics of Langmuir model which is not valid for high concentrations assuming limited number of identical sites for adsorption. As a results, the binary adsorption of BR46 and BY28 onto bentonite can be represented satisfactorily and adequately by the extended Freundlich isotherm model.

### 5. Determination of thermodynamic parameters

For the adsorption of BR46 and BY28 dyes onto bentonite in single solutions, thermodynamic parameters such as enthalpy change ( $\Delta H^\circ$ ), free energy change ( $\Delta G^\circ$ ) and entropy change ( $\Delta S^\circ$ ) can be estimated using equilibrium constants changing with temperature. The free energy change of the adsorption reaction is given by the following equation:

$$\Delta G = -RT \ln K_c \quad (13)$$

where  $\Delta G^\circ$  is free energy change (J/mol);  $R$  is the universal gas constant (8.314 J/mol K) and  $T$  is the absolute temperature (K). The Gibbs free energy change,  $\Delta G^\circ$ , is the fundamental criterion of spontaneity. Reaction occurs spontaneously at a given temperature if  $\Delta G^\circ$  is a negative quantity [36]. The equilibrium constant of adsorption is defined as  $K_c = C_{ad,e}/C_{eq}$ . Where  $C_{ad,e}$  is the amount of dye (mg) adsorbed on the adsorbent per L of the solution at equilibrium (mg/L),  $C_{eq}$  is the equilibrium concentration. The equilibrium constant may be expressed in terms of enthalpy change of adsorption ( $\Delta H^\circ$ ) and entropy change of adsorption ( $\Delta S^\circ$ ) as a function of temperature. The relationship between the  $K_c$  and temperature is given by the van't Hoff equation:

$$\ln K_c = \frac{\Delta S}{R} - \left( \frac{\Delta H}{R} \right) \left( \frac{1}{T} \right) \quad (14)$$

Table 9

Thermodynamic parameters for the adsorption of BR46 and BY28 onto bentonite

Dye	$T$ (°C)	$K_c$ (L/mg)	$-\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol K)
BR46	20	23.60	7.70	8.80	0.057
	30	28.40	8.43		
	40	32.86	9.10		
	50	35.51	9.57		
	60	36.10	9.92		
BY28	20	5.51	4.16	8.30	0.0428
	30	6.14	4.57		
	40	7.33	5.19		
	50	7.89	5.55		
	60	8.10	5.79		

where  $\Delta H^\circ$  and  $\Delta S^\circ$  values for dye adsorption can be evaluated from the slope and intercept of the van't Hoff plot of  $\ln K_c$  versus  $1/T$ .  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  values for the adsorption of BR46 and BY28 onto bentonite were presented in Table 9. The negative values of  $\Delta G^\circ$  indicate overall adsorption processes are spontaneous. The positive values of  $\Delta H^\circ$  in the range of 20–60 °C show that the adsorption of BR46 and BY28 onto bentonite is endothermic in nature and an increase in  $T$  causes an increase in  $K_c$ . The positive values of  $\Delta S^\circ$  reflect the affinity of bentonite for BR46 and BY28 and show the increasing of randomness at the solid/liquid interface during the adsorption of dyes onto bentonite.

## 6. Conclusions

In the first part of this study, derivative spectrophotometric method was applied to the simultaneous analysis of Basic Yellow 28 and Basic Red 46 dyes which absorption spectra overlapped, and it was determined that the first order derivative spectrophotometric method can be applied accurately for the simultaneous analysis of dye mixtures. The wavelength values for the determination of BY28 and BR46 dyes in binary mixtures were determined as 380 and 560 nm, respectively, while the analysis of BY28 and BR46 dyes in single solution were done at 437 and 529 nm, respectively.

In the second part of this study, the adsorption of Basic Yellow 28 and Basic Red 46 dyes in single solutions and binary mixtures onto bentonite were investigated in a batch system at pH 6.0 and temperature 30 °C. Since real wastewaters contain many pollutants, adsorption system design must be based on multi-component effluents. For that reason, it is necessary to make multi-component equilibrium data instead of just single ones. The mono- and multi-component Langmuir and Freundlich isotherm models applied to the experimental adsorption data of BY28 and BR46 dyes from single and binary mixture onto bentonite. It was observed that the bentonite had a higher adsorption capacity for BY28 and BR46 in a single dye component system, while the equilibrium uptakes of BY28 and BR46 in the binary mixture decreased because of the presence of other dye due to the antagonistic interaction between these dyes. The individual Langmuir and Freundlich constants obtained from the adsorption of BY28 and BR46 dyes in single solution were used to describe the adsorption equilibrium of BY28 and BR46 dyes in binary mixture. It was concluded that the multi-component Freundlich model agreed reasonably well except for high initial dye concentrations of both components. Thermodynamic parameters were also evaluated using equilibrium constants changing with temperature. The negative values of  $\Delta G^\circ$  indicated that the spontaneity and the positive values of  $\Delta H^\circ$  and  $\Delta S^\circ$  showed the endothermic nature and affinity of bentonite for BR46 and BY28, respectively.

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