

# Surfactant-Modified Feldspar: Isotherm, Kinetic, and Thermodynamic of Binary System Dye Removal

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Received 12 April 2011; accepted 26 January 2012

DOI 10.1002/app.36883

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** In this article, surface modification of feldspar using hexadecyltrimethyl ammonium bromide (HDTMA) and its dye removal ability in single and binary systems was studied. Acid Black 1 (AB1) and Acid Red 14 (AR14) were used as model dyes. The monocomponent Langmuir isotherm model was applied to experimental data and the isotherm constants were calculated for both dyes. The monolayer coverage capacities of surfactant-modified feldspar (HDTMA-feldspar) for AB1 and AR14 dyes in single solution system were found as 6.369 mg/g and 3.984 mg/g, respectively. It was observed that the equilibrium uptake amounts of AB1 and AR14 dye in binary mixture onto sorbent decreased with increasing concentrations of the other dye resulting in their antagonistic effect.

Equilibrium adsorption for binary systems was analyzed by using the Extended Langmuir and Jain and Snoeyink Modified Extended Langmuir models. The rate of kinetic processes of single and binary dye systems onto adsorbent was described by using two kinetics adsorption models. The pseudo-second-order model was the best choice among the kinetic models to describe the adsorption behavior of single and binary dyes onto HDTMA-feldspar. Thermodynamic parameters showed that dye adsorption on HDTMA-feldspar were exothermic and unspontaneous in nature. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** adsorption; dyes/pigments; surfactants; FTIR; X-ray

## INTRODUCTION

Adsorption offers significant advantages over methods of traditional treatment especially environmental point of view. Adsorption as an effective method for contaminant treatment appears for offering the best potential for dye removal. The study of dye adsorption onto a cost-effective adsorbent is significant in the industrial effluent treatment system because it provides valuable insights into the mechanisms and the optimum operating parameters of adsorption processes. In recent years, many alternative technologies and potential adsorbents have been tried for dye-bearing effluent treatment, including clay minerals, peat, and wood.<sup>1–5</sup>

Feldspar is typical constituent in clays. The feldspar surface is composed of negative and positive sites. The positive charges are Na<sup>+</sup> ions in albite and K<sup>+</sup> ions in orthoclase, and the negative sites are non-polar siloxane groups or polar silanol groups. The inorganic cations on the internal and external surfaces of feldspar (e.g., Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>) could be replaced by organic cations, such as quaternary

ammonium salt surfactants, through ion exchange that enhances the adsorption capacity as the feldspar surfaces change from hydrophilic to hydrophobic. So, organophilic feldspar could use as an excellent adsorbent for adsorbing organic pollutants, such as dye molecules.<sup>5–9</sup> The surface properties of feldspar can be greatly modified with a surfactant by simple ion-exchange reactions. This is favored by van der Waals interaction between organic surfactant cations and the reduced solvent shielding of the ions in the interlamellar environment. Large organic cations (cationic surfactants) of the form (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>R, where R is a large (C<sub>12</sub> or greater) alkyl hydrocarbon, occupy the exchange sites of feldspar clay and hence the surface area is increased.<sup>8</sup> As a new adsorbent, surfactant-modified feldspar, could potentially be a good adsorbent for dye removal.

As an important kind of water-soluble anionic dyes, acid dyes are brightly colored and widely applied to dyeing nylon, wool, silk, and so on. Because of the fact which the anionic dyes are negatively charged, the surface of the natural feldspar has to be modified by a cationic surfactant for the dye adsorption experiments. However, only a few studies have been carried out to investigate the adsorption of acid dyes onto activated clays,<sup>4,7</sup> but none of them has investigated adsorption of Acid Red 14 (AR14) and Acid Black 1 (AB1) dyes onto HDTMA-feldspar in single and mixture systems.

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This work was performed to investigate adsorption of single and binary acid dyes aqueous solutions onto HDTMA-feldspar. The constants parameters obtained from single (AR18 and AB1) adsorption equilibrium data were used to predict the binary adsorption behavior of AB1 and AR14. The kinetics and isotherms for dyes adsorption onto HDTMA-feldspar were studied in single and mixture dye systems. The thermodynamic data were also evaluated for both of the dyes.

## MATERIALS AND METHODS

### Materials

Anionic dyes used in this study were Acid Black 1 and Acid Red 14. The dyes were purchased from Ciba Ltd. (Iran) and all of them were used without further purification. The chemical structures of dyes are shown in Figure 1. All other chemicals were purchased from Merck (Germany).

The natural feldspar was provided from Hamedan (Iran). Sample was ground and sieved to 0.08–0.1  $\mu\text{m}$  size fraction. It was washed to remove residuals, and dried at 103°C in an oven for 12 h.

### Material characterization

The chemical analysis of feldspar was determined by X-ray powder diffraction using a Philips Powder Diffractometer PW 1800. FTIR spectra for feldspar and HDTMA-feldspar were obtained on a Perkin-Elmer Spectrophotometer Spectrum One to confirm the surface modification.

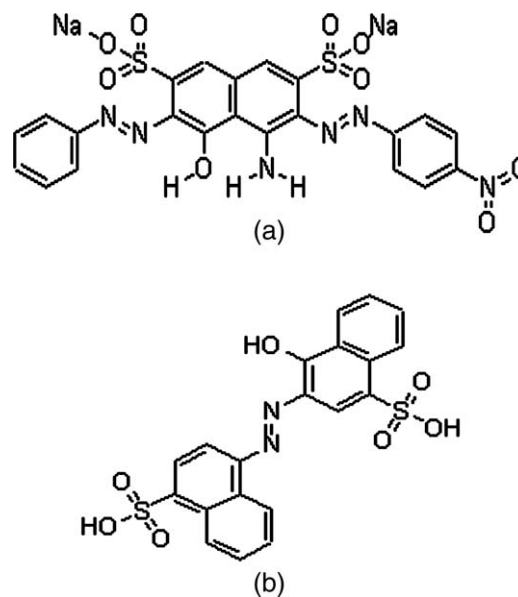
### Preparation of HDTMA-feldspar

The Na-exchanged form of feldspar was prepared by stirring samples for 12 h with 1M NaCl. This was followed by several washings with distilled water and filtrations to remove the excess NaCl and other exchangeable cations from the feldspar. The clay was resuspended and filtered until a negative chloride test was obtained with 0.1M AgNO<sub>3</sub>.

The surface-modified feldspar was prepared as follows. An aqueous Hexadecyltrimethyl ammonium bromide (HDTMA) solution (0.05M) was added to a 7% aqueous clay suspension. The mixture was stirred in a mixer for 3 h at 200 rpm. The organo-modified clay was separated from the mixture by filtration and then was washed with distilled water until free of salts and a negative bromide test had been obtained with AgNO<sub>3</sub> solution (0.1M). It was dried at 100°C for 3 h and used for the adsorption studies.<sup>8,10</sup>

### Single adsorption studies

Stock solutions 400 mg L<sup>-1</sup> of AB1 and AR14 were used in this study. These stock solutions were



**Figure 1** The chemical structure of dyes (a) Direct Red 31 (b) Acid Black 1.

diluted for giving standard solutions from 10 to 250 mg L<sup>-1</sup>. 0.5 g HDTMA-feldspar and 50 mL single-component solution were shaken using a shaker at constant temperature for 90 min for adsorption equilibrium. The liquid and solid phases were separated by centrifuging at 4000 rpm for 10 min. The adsorbate concentration change in each of the solutions was determined spectrophotometrically. All the spectrophotometric measurements were made with a UV-vis spectrophotometer CECIL 2021. The maximum absorbance value of AB1 and AR14 was measured at 618 and 515 nm, respectively. The absorbance calibration graph against concentration obeyed a linear Lambert-Beer relationship.

The color removal efficiency (P%) of the dye was calculated as follows

$$P\% = \frac{(C_i - C_t)}{C_i} \times 100 \quad (1)$$

where  $C_i$  and  $C_t$  are the initial concentration and concentrations of the dye at equilibrium (mg L<sup>-1</sup>), respectively.

The mass of acid dyes adsorbed per unit mass of the adsorbents ( $q$ ) at any time ( $C = C_t$ ) and at equilibrium ( $C = C_e$ ) was calculated from the eq. (2).

$$q = \frac{(C_i - C)V}{m} \quad (2)$$

$q$  is the adsorbed amount of acid dyes in the solid phase at equilibrium ( $q = q_e$ ) and time  $t$  (min) ( $q = q_t$ ), respectively.  $V$  indicates the volume of dye solution (L) and  $m$  is the weight of the adsorbent (g).

### Binary adsorption studies

To investigate the adsorption behavior of dyes in binary system, several initial concentrations of AR14 (10–250 mg L<sup>-1</sup>) were prepared in eight different solutions with the presence of constant initial concentration of 50 mg L<sup>-1</sup> of AB1. Then, the experiment was carried out following the steps as for single system adsorption process. The remaining concentrations of both dyes were also analyzed using UV–vis spectrophotometer. The experiments were repeated for other constant initial concentrations of AB1, which are 100 and 150 mg L<sup>-1</sup>. The experiments were repeated over again in order to study the adsorption behavior of AB1 with the presence of different constant initial concentrations of AR14 (50, 100, and 150 mg L<sup>-1</sup>), as given in Table I.

Dye concentrations were calculated as follows. For a binary system of components A and B measured at  $\lambda_1$  and  $\lambda_2$ , respectively, to give optical densities of  $d_1$  and  $d_2$ :<sup>11</sup>

$$C_A = \frac{k_{B2}d_1 - k_{B1}d_2}{k_{A1}k_{B2} - k_{A2}k_{B1}} \quad (3)$$

$$C_B = \frac{k_{A1}d_2 - k_{A2}d_1}{k_{A1}k_{B2} - k_{A2}k_{B1}} \quad (4)$$

where  $k_{A1}$ ,  $k_{B1}$ ,  $k_{A2}$ , and  $k_{B2}$  are the calibration constants for components A and B at the two wavelengths  $\lambda_1$  and  $\lambda_2$ , respectively.

### Adsorption kinetics studies

Study of adsorption kinetics was carried out in order to investigate the relationship between contact time and dye uptake. The initial concentration influence of the reagent on the adsorption kinetic at constant temperature of 25°C was investigated. In single dye systems, initial dyes concentrations 50, 100, 150 mg L<sup>-1</sup> were used and in mixture dyes systems, initial dyes concentrations 50 + 50, 100 + 100, 150 + 150 mg L<sup>-1</sup> were used. 0.5 g HDTMA-feldspar and 50 mL single and binary component solution were shaken at 25°C while being rinsed with a water bath at a speed of 150 rpm. The samples were subjected to centrifugation at 4000 rpm for 10 min. It was observed that a slower process follows the initial fast process. Although dyes adsorption is very fast up to 15 min, the adsorption equilibrium is established in 90 min. Adsorption data up to 60 min were used for kinetic calculations. Adsorbed dye amount ( $q$ ) at any time was calculated from the concentration changes during adsorption process as follows eq. (2).

### Adsorption thermodynamic studies

The influence of temperature on the dye adsorption was investigated on the single dyes concentrations

**TABLE I**  
Initial System Conditions for Equilibrium Adsorption Isotherms and Kinetics

Adsorption system	HDTMA-feldspar (g) $\pm 0.002$	Dye initial concentration range (in mg L <sup>-1</sup> )
AR14	0.5	AR14: 10-250
AR14 with AB1	0.5	AR14: 50 AB1: 10-250
AR14 with AB1	0.5	AR14: 100 AB1: 10-250
AR14 with AB1	0.5	AR14: 150 AB1: 10-250
AB1	0.5	AB1: 10-250
AB1 with AR14	0.5	AB1: 50 AR14: 10-250
AB1 with AR14	0.5	AB1: 100 AR14: 10-250
AB1 with AR14	0.5	AB1: 150 AR14: 10-250

50, 100, 150 mg L<sup>-1</sup> and binary dyes concentrations 50 + 50, 100 + 100, 150 + 150 mg L<sup>-1</sup> at 298, 313, and 323 K. Totally, 0.5 g HDTMA-feldspar and 50 mL single component solutions were shaken at aforementioned temperatures while being rinsed with a water bath at a speed of 150 rpm. The same experiments were done for binary dyes solutions. After passing 90 min, the samples were subjected to centrifugation at 4000 rpm for 10 min. Adsorbed dye amount ( $q$ ) was calculated from the concentration changes during adsorption process as follows eq. (2).

## RESULTS AND DISCUSSION

### Chemical composition of feldspar

The chemical composition of Na-feldspar is given in Table II. As it can be seen, the major constituents in Na-feldspar are silica and alumina and the impurities are potassium, calcium, iron, magnesium, titanium, and sodium oxides. As a result, it is expected that the adsorbate species will be removed mainly by silica or alumina.

The mineralogical composition of the feldspar was determined from X-ray diffractogram (Fig. 2). The following mineral phases were identified: oligoclase, quartz, illite, and calcite. Figure 2 illustrates the XRD patterns of Na-feldspar and HDTMA-feldspar. In the XRD powder patterns, the reflections of Na-feldspar and HDTMA-feldspar occurred at 8.87 and 8.83°, corresponding to basal spacing of 9.960 and 10.000 Å, respectively. In the range of 5–60°, the diffraction patterns of Na-feldspar and HDTMA-feldspar were similar. This observation suggested that surfactant molecules intercalated into the interlayers of feldspar and the interlayer space was extended.

**TABLE II**  
Chemical Analysis of Feldspar

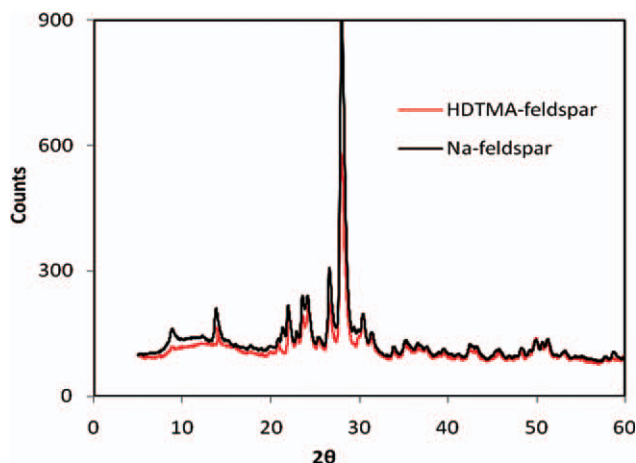
Constituent	Value (wt %)
SiO <sub>2</sub>	64.6
Al <sub>2</sub> O <sub>3</sub>	21.2
Fe <sub>2</sub> O <sub>3</sub>	0.30
TiO <sub>2</sub>	0.86
Na <sub>2</sub> O	5.76
K <sub>2</sub> O	0.85
CaO	4.00
MgO	0.41

### FTIR analysis

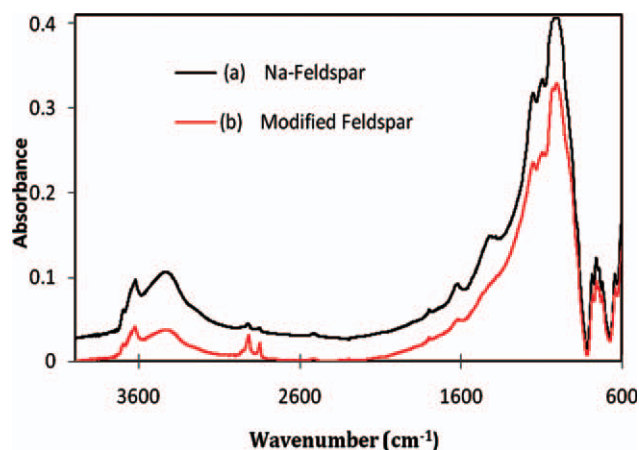
FTIR spectra were recorded in the region 450–4000 cm<sup>-1</sup> (Fig. 3) in order to obtain complementary evidence for the intercalation of quaternary alkylammonium cations into the silicate lattice. A pair of strong bands, 2856 and 2919 cm<sup>-1</sup>, were observed only on surfactant-modified feldspar; they could be assigned to the symmetric and asymmetric stretching vibrations of the methylene group (–CH<sub>2</sub>). The intensity of the absorption band of –OH bending vibration of H<sub>2</sub>O (1623 cm<sup>-1</sup>) decreases, that indicated the H<sub>2</sub>O content reduced with the replacement of the hydrated cations by surfactant cation ions. This observation indicated that the surface properties of feldspar had been changed from hydrophilic to hydrophobic by modifying it with surfactant.<sup>7,12</sup>

### Color removal efficiency in single and mixed dye solutions

The adsorption potential of HDTMA-feldspar was investigated for Acid dyes and the color removal efficiencies were determined in single and mixed dye solutions. As seen in Table III, HDTMA-feldspar exhibited high adsorption efficiency for AB1. Also, comparing with the results in single dye solutions, a



**Figure 2** XRD patterns of feldspar and surfactant-modified feldspar. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3** FTIR spectra of (a) raw feldspar and (b) surfactant-modified feldspar. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

reduction in removal efficiency of the individual dye in the mixed dye solutions was observed, although the amount of reduction was different among the dyes. The AB1 removal efficiency was reduced from 58.393% (in single solution 100 mg L<sup>-1</sup>) to 22.031% (in mixed solution of 100 mg L<sup>-1</sup> AB1 + 100 mg L<sup>-1</sup> AR14) while the AR14 removal efficiency was reduced from 36.842% (in single solution 100 mg L<sup>-1</sup>) to 21.147% (in binary solution of 100 mg L<sup>-1</sup> AR14 + 100 mg L<sup>-1</sup> AB1). The reduction in removal of AB1 was larger than that of AR14, as seen in Table III. Also, when removal efficiency values were compared between single (AR14) and mixed (AR14 + AB1) solution for AR14 and single (AB1) and mixed (AB1 + AR14) solution for AB1, it was observed that these values change in AR14 dye solutions was less than these values change in AB1 dyes solutions. As a result, it was revealed which AB1 was much more removed preferentially than AR14 in mixed dye systems onto modified-feldspar.<sup>13</sup>

**TABLE III**  
Removal Efficiency Values of Single and Binary Reactive Dyes Systems

Component	C <sub>0</sub> (mg L <sup>-1</sup> )	C <sub>e</sub> (mg L <sup>-1</sup> )	Removal efficiency %
AB1	50	3.35	93.31
	100	41.61	58.39
	150	91.12	39.25
AB1 + AR14	50 + 50	22.15 + 39.36	38.49
	100 + 100	64.38 + 91.33	22.14
	150 + 150	115.36 + 137.25	15.80
AR14	50	23.05	53.90
	100	63.58	36.84
	150	112.11	25.26
AR14 + AB1	50 + 50	40.27 + 26.78	32.95
	100 + 100	93.09 + 64.85	21.03
	150 + 150	144.58 + 124.92	10.17

TABLE IV  
Langmuir Constants for the Adsorption of AB1 and AR14

Component	$C_0$ (mg L <sup>-1</sup> )	$q_{\max}$ (mg g <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$R^2$	$R_L$
AB1	10–250	6.37	0.54	0.99	0.01
AB1+50 (mg L <sup>-1</sup> ) AR14	10–250	6.10	0.05	0.99	0.07
AB1+100 (mg L <sup>-1</sup> ) AR14	10–250	4.53	0.04	0.99	0.08
AB1+150 (mg L <sup>-1</sup> ) AR14	10–250	4.37	0.03	0.99	0.13
AR14	10–250	3.98	0.19	0.99	0.02
AR14+50 (mg L <sup>-1</sup> ) AB1	10–250	1.63	0.05	0.99	0.08
AR14+100 (mg L <sup>-1</sup> ) AB1	10–250	1.12	0.03	0.99	0.13
AR14+150 (mg L <sup>-1</sup> ) AB1	10–250	0.87	0.02	0.98	0.15

### Application of mono-component adsorption model to equilibrium data

The equilibrium adsorption data of the single and mixed dye systems were fitted using Langmuir isotherm model. The Langmuir linear form equation is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (5)$$

where  $q_{\max}$  is the maximum capacity of adsorbate to form a complete monolayer on the surface,  $K_L$  is the Langmuir constant related to the adsorption heat. The constant value of  $q_{\max}$  and  $K_L$  are obtained from the slope and intercept of linear plot of  $C_e/q_e$  versus  $C_e$ , respectively.

The essential characteristics by a separation factor  $R_L$ ; which is defined by the following equation:<sup>13,14</sup>

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

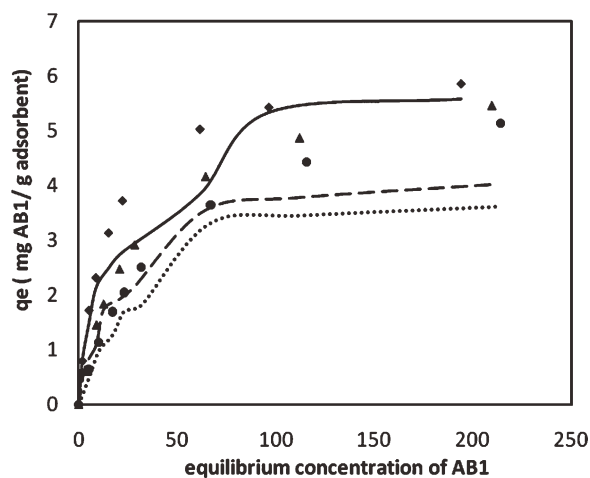
where  $C_0$  is the highest initial solute concentration (mg L<sup>-1</sup>) and  $K_L$  is the Langmuir's adsorption constant (L mg<sup>-1</sup>). The values of  $R_L$  indicate the isotherm type to be either irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), or unfavorable ( $R_L > 1$ ).

The Langmuir constants are given in Table IV. As shown in Table IV, the calculated dimensionless separation factors ( $R_L$ ) values (between 0 and 1) indicates the on-going adsorption process is favorable for the both dyes using HDTMA-feldspar.

The experimental  $q_{\text{eq}}$  values were found to be smaller than  $q_{\max}$  indicating which the adsorption of AB1 and AR14 dye onto HDTMA-feldspar occurred by a monolayer type adsorption in which the surface of adsorbent is not fully covered. As can be seen from Table IV, HDTMA-feldspar showed a higher maximum monolayer coverage capacity ( $q_{\max}$ ) for AB1 dye than that for AR14 dye in single component.  $K_L$ , calculated from the Langmuir isotherm model indicates the affinity for binding of dye. A large value of  $K_L$  also implies strong bonding.<sup>15</sup> As can be observed from Table IV, the  $K_L$  value of AB1 was higher than that of AR14 in single solution. But,

the  $K_L$  values of AB1 in binary mixture systems reduced with the increasing AR14 concentrations. Also, the  $K_L$  values of AR14 in binary systems reduced with the increasing concentrations of AB1, but these decreasing were lower than those of AB1. This can be explained by the fact which the adsorbent affinity toward AB1 dye is greater in single solution than that of binary solutions. As a result of the presence of two dyes, the decreasing tendency of the calculated values of  $K_L$  may indicate competition for adsorption sites.

The possible reduction in capacity of dye adsorption onto HDTMA-feldspar in binary systems 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 observed from Table IV, HDTMA-feldspar indicated a higher maximum monolayer coverage capacity ( $q_{\max}$ ) for AB1 dye than that for AR14 dye in single component. While the presence of other initial dye concentration increased, the maximum adsorption capacities of HDTMA-feldspar reduced and also the percentage reduction of maximum adsorption capacities of HDTMA-feldspar increased for both dyes [reduction (%) =  $(q_{\max, \text{single}} - q_{\max, \text{binary}})/q_{\max, \text{single}}$ ]. The decreasing values of AR14 uptake were greater than those of AB1. For example, at the presence of 100 and 150 mg L<sup>-1</sup> of initial concentration of AR14, the maximum monolayer coverage capacities and the percentage reduction of maximum adsorption capacities of HDTMA-feldspar for AB1 were 4.525 mg g<sup>-1</sup> and 4.368 mg g<sup>-1</sup>; 29.377% and 31.418%, respectively. But, at the presence of 100 and 150 mg L<sup>-1</sup> of initial concentration of AB1, the maximum monolayer coverage capacity and the percentage reduction of AR14 were 1.115 mg g and 0.865 mg g; 72.013% and 78.288%, respectively (Table IV). These data indicated which AB1 was preferentially adsorbed more than AR14 in binary mixtures. The selective adsorption in multi-component systems was also reported by Choy et al.,<sup>11</sup> Sismanoglu et al.,<sup>13</sup> Turabik,<sup>15</sup> Allen et al.,<sup>16</sup> and Al-Degs et al.<sup>17</sup>



**Figure 4** Extended Langmuir Model for AB1 in binary system. (◆) AB1+50 mg L<sup>-1</sup>AR14 experimental, (▲) AB1 + 100 mg L<sup>-1</sup>AR14 experimental, (●) AB1 + 150 mg L<sup>-1</sup>AR14 experimental; (—) AB1+50 mg L<sup>-1</sup>AR14 calculated, (---) AB1 + 100 mg L<sup>-1</sup> AR14 calculated, (- - -) AB1 + 150 mg L<sup>-1</sup>AR14 calculated.

Generally, the adsorption capacities of each individual dye are proportionally less with another solute. This could be attributed in the main to the interaction between the dyes on the surface of solid, with nonequal competition attributed to the adsorbent surface heterogeneity. Factors which affect the adsorption preference of a sorbent for different kinds of adsorbates may be related to the binding sites characteristics such as functional groups, structure and surface properties, the adsorbates properties such as concentration, ionic size, ionic weight, molecular structure, ionic nature or standard reduction potential and solution chemistry such as pH, ionic strength, and etc.<sup>15</sup> It is difficult to determine which factors affect the selective adsorption of HDTMA-feldspar. So, the observed results may result from a combination of all of these factors.

#### Extended Langmuir equation for binary systems

An extended Langmuir equation is used to study the competitive multicomponent adsorption. This model assumes a homogeneous surface with respect to the energy of adsorption, no interaction between adsorbed species, and that all sites are equally available to all adsorbed species:<sup>18</sup>

$$q_{e,i} = \frac{q_{\max} K_{L,i} C_{e,i}}{1 + \sum K_{L,i} C_{e,i}} \quad (7)$$

where  $C_{e,i}$  is the equilibrium concentration of species  $i$ , while  $q_{\max}$  and  $K_{L,i}$  are Langmuir isotherm model parameters obtained from single component studies for particular adsorbent-adsorbate system.<sup>13</sup> For example, for two components 1 and 2:

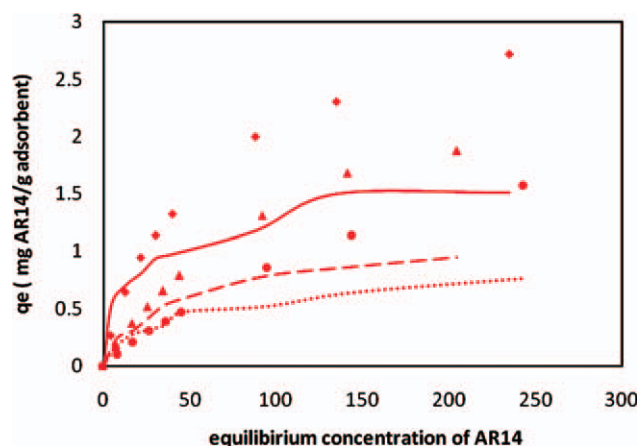
$$q_{e,1} = \frac{K_{L,1} q_{\max,1} C_{e,1}}{1 + K_{L,1} C_{e,1} + K_{L,2} C_{e,2}} \quad (8)$$

$$q_{e,2} = \frac{K_{L,2} q_{\max,2} C_{e,2}}{1 + K_{L,1} C_{e,1} + K_{L,2} C_{e,2}} \quad (9)$$

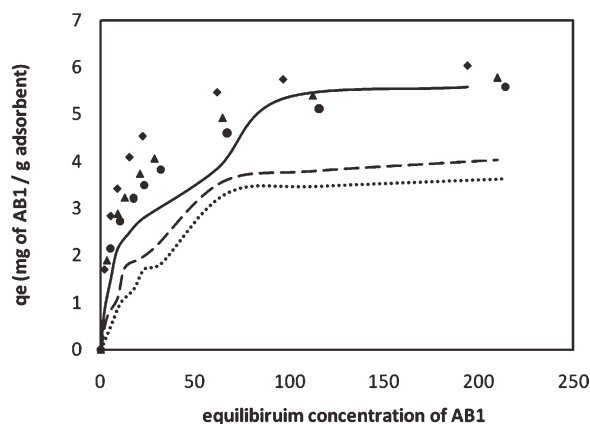
where  $K_L$  and  $q_{\max}$  are the Langmuir isotherm model parameters obtained suitably from eq. (5) in the single solute system. Therefore, the amounts of solute adsorbed were calculated by eqs. (8) and (9) and were presented by Figures 4 and 5 for each different system.

Figure 4 shows the correlation between experimental data and predicted data for the sorption of AB1 in binary solution AB1 with 50, 100, and 150 mg L<sup>-1</sup> of AR14. The single-component isotherms for AB1 and AR14 have monolayer saturation capacities of 6.37 and 3.98 mg g<sup>-1</sup>, respectively. It is obvious which AB1 have a higher absorbed on HDTMA-feldspar than AR14, that it can be caused by differences between molecular structures, molecular size and functional groups of AB1 and AR14, as shown in Figure 1. So, competition and interaction between these two acid dyes would be significant and affect each component to a different extent. The extended Langmuir model gives a very poor fit for AB1 in binary systems. It shows which interaction and competition between these two species are significant.

Similarly, Figure 5 indicates the comparison between experimental data and predicted data for the sorption of AR14 in binary solution AR14 with 50, 100, and 150 mg L<sup>-1</sup> of AB1. The correlation between data in Figure 5 is very poor. It is likely that competitive and interactive processes between the two acid dyes occur in this binary system.



**Figure 5** Extended Langmuir Model for AR14 in binary system (◆) AR14+50 mg L<sup>-1</sup>AB1 experimental, (▲) AR14+100 mg L<sup>-1</sup>AB1 experimental, (●) AR14 + 150 mg L<sup>-1</sup>AB1 experimental; (—) AR14+50 mg L<sup>-1</sup>AB1 calculated, (---) AR14 + 100 mg L<sup>-1</sup>AB1 calculated, (- - -) AR14 + 150 mg L<sup>-1</sup>AB1 calculated. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6** Jain and Snoeyink modified extended Langmuir analysis for AB1 in the binary system: (◆) AB1+50 mg L<sup>-1</sup>AR14 experimental, (■) AB1 + 100 mg L<sup>-1</sup>AR14 experimental, (●) AB1 + 150 mg L<sup>-1</sup>AR14 experimental; (—) AB1+50 mg L<sup>-1</sup>AR14 calculated, (---) AB1 + 100 mg L<sup>-1</sup>AR14 calculated, (- - -) AB1 + 150 mg L<sup>-1</sup>AR14 calculated.

The application of the extended Langmuir isotherm to the prediction of multicomponent acid dyes adsorption on modified feldspar results in poor agreement between the experimental data and the predicted data that it is because of the basic assumptions of the Langmuir equation like as sorption constant energy, no interaction and equal independent competition between species.

### Jain and Snoeyink Modified Extended Langmuir Model

In Jain and Snoeyink model, a portion of adsorption occurs without competition because not all adsorption sites are available to all species. This was attributed to the sites chemical nature and sorbates or the relatively large molecular size of the latter. This model proposed to add an additional term to the extended Langmuir equation.<sup>11</sup> The model is described by

$$q_{e,1} = \frac{(q_{\max,1}^0 - q_{\max,2}^0)K_{L,1}^0 C_{e,1}}{1 + K_{L,1}^0 C_{e,1}} + \frac{q_{m,2}^0 K_{L,1}^0 C_{e,1}}{1 + K_{L,1}^0 C_{e,1} + K_{L,2}^0 C_{e,2}} \quad (10)$$

$$q_{e,2} = \frac{q_{\max,2} K_{L,2} C_{e,2}}{1 + K_{L,1} C_{e,1} + K_{L,2} C_{e,2}} \quad (11)$$

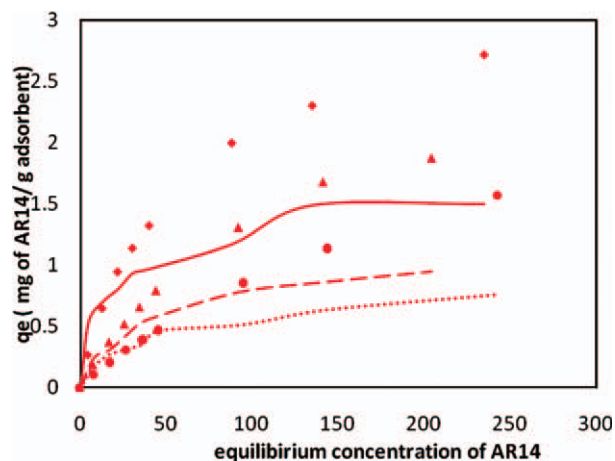
where  $q_{\max}^0$  is the monolayer saturation capacity for the Langmuir model. The first term on the right hand side of eq. (10) relates to the amount of component 1 adsorbed without competition with 2, while the second term refers to the amount of component 1 adsorbed in competition with 2, as described by applying the competition to the Langmuir isotherm. The additional term of eq. (10) is the Langmuir expression for the number of molecules of species 1

that are adsorbed without competition on the surface of adsorbent, and the term is proportional to  $(q_{\max,1} - q_{\max,2})$ , where  $q_{\max,1} > q_{\max,2}$ . The number of molecules of species 2 adsorbed on the surface of adsorbent, proportional to  $q_{\max,2}$  and in competition with species 1, can be computed from the extended Langmuir equation By using eq. (11).

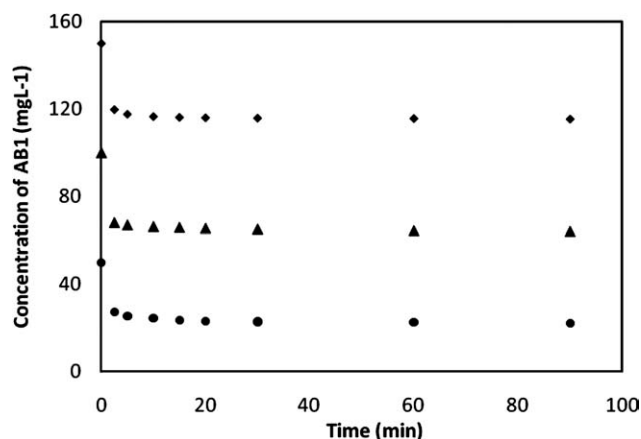
Figures 6 and 7 indicate the comparison between experimental data and predicted data by the Jain and Snoeyink modified extended Langmuir model. Figure 6 indicates the agreement between the model prediction and the experimental data for AB1 in the binary mixture. Comparing with the extended Langmuir equation results, the best fit between the experimental and theoretical data became worse. Figure 7 indicates the predictions for AR14 in the binary solution; similarly, the correlations between the prediction data and experimental data are fairly poor. This model does not provide an improvement over the data predicted by the extended Langmuir model in multicomponent dye systems. Overall, the Jain and Snoeyink modified extended Langmuir model cannot be used to predict multicomponent acid dye adsorption on surfactant modified feldspar.

### Adsorption kinetics model for dyes onto HDTMA-feldspar

Two kinetic models, commonly used in the literature, were applied to experimental kinetic data in order to investigate the behavior of dyes on HDTMA-feldspar. The first one was the pseudo-first-order kinetic model and the integral form of this model was expressed by the following equation<sup>19</sup>



**Figure 7** Jain and Snoeyink modified extended Langmuir analysis for AR14 in the binary system: (◆) AR14+50 mg L<sup>-1</sup>AB1 experimental, (■) AR14+ 100 mg L<sup>-1</sup>AB1 experimental, (●) AR14 + 150 mg L<sup>-1</sup>AB1 experimental; (—) AR14+50 mg L<sup>-1</sup>AB1 calculated, (---) AR14 + 100 mg L<sup>-1</sup>AB1 calculated, (- - -) AR14 + 150 mg L<sup>-1</sup>AB1 calculated. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



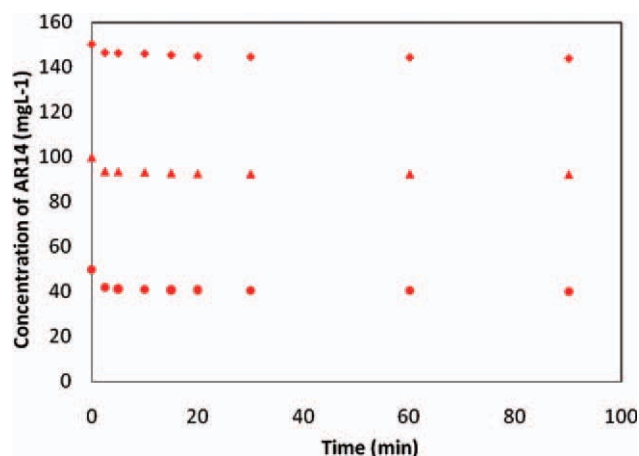
**Figure 8** Plots of concentration of AB1 versus time, using different solution concentrations in binary systems (●) 50+50 mg L<sup>-1</sup>AR14, (▲) 00+100 mg L<sup>-1</sup> AR14, (◆) 150+150 mg L<sup>-1</sup>AR14.

$$\log(q_e - q_t) = \log(q_e) - k_1 t \quad (12)$$

where  $q_e$  and  $q_t$  are the amounts of dye adsorbed on adsorbent at equilibrium and at time  $t$ , respectively (mg g<sup>-1</sup>),  $k_1$  is the rate constant of pseudo-first-order model (1/min); and  $t$  is the contact time (min). In adsorption from binary dye solutions, the total amounts of dyes adsorbed were used in data treatment. As seen in Figures 8 and 9, the values of  $q_e$  were amounts of dyes adsorbed after a contact time of 90 min. Adsorption data up to 60 min were used for kinetic calculations. The integral form of the pseudo-second-order kinetic model is expressed by<sup>20</sup>:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (13)$$

where  $k_2$  (mg g<sup>-1</sup> min) is the equilibrium rate constant of pseudo-second-order adsorption,  $q_e$  (mg g<sup>-1</sup>)



**Figure 9** Plots of concentration of AR14 versus time, using different solution concentrations in binary systems (●) 50+50 mg L<sup>-1</sup>AB1, (▲) 100+100 mg L<sup>-1</sup>AB1, (◆) 150+150 mg L<sup>-1</sup>AB1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

is the equilibrium adsorption capacity. As can be observed in Table V, the values of correlation coefficients of the rate constant of pseudo-first-order are less than  $R^2 < 0.921$ . As a result, the models that provided the best correlation with experimental data were the pseudo-second-order model ( $R^2 = 0.999$ ). When the effect of initial concentration of both single and binary solutions were compared, it was observed which  $k_2$  values decrease with increasing initial dyes concentration.

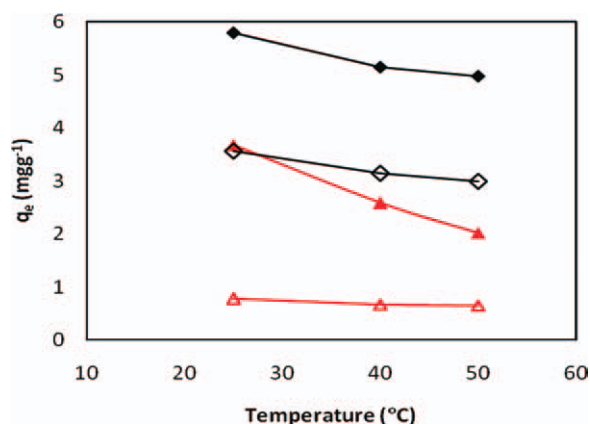
#### The effect of temperature on the adsorption dyes onto HDTMA-feldspar

Figure 10 indicates the effect temperature on the adsorption of AB1 and AR14 onto HDTMA-feldspar in single and mixture systems at initial dyes concentration 100 and 100+100 mg L<sup>-1</sup>, respectively. The adsorption of AB1 and AR14 onto adsorbent slightly

**TABLE V**  
Kinetics Parameters for Adsorption of Dyes from Single and Binary Systems

Dye	Dose (mg L <sup>-1</sup> )	Pseudo-first-order $t = 0-90$ min		Pseudo-second-order $t = 0-90$ min	
		$K_1$ (min <sup>-1</sup> )	$R^2$	$K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
AB1	50	0.11	0.92	0.09	0.99
	100	0.11	0.80	0.09	0.99
	150	0.05	0.89	0.09	0.99
AB1+AR14	50 + 50	0.09	0.87	0.25	0.99
	100 + 100	0.05	0.85	0.17	0.99
	150 + 150	0.15	0.91	0.17	0.99
AR14	50	0.09	0.85	0.58	0.99
	100	0.09	0.82	0.36	0.99
	150	0.10	0.88	0.27	0.99
AB1+AR14	50 + 50	0.07	0.91	0.43	0.99
	100 + 100	0.08	0.83	0.30	0.99
	150 + 150	0.09	0.82	0.20	0.99





**Figure 10** The effect of temperature for AB1 and AR14 adsorption onto HDTMA-feldspar in single and binary solutions (single initial dye concentration 100 mg L<sup>-1</sup> and binary initial dye concentration 100+100 mg L<sup>-1</sup>); (◆) single AB1, (◇) Binary AB1, (▲) single AR14 and (Δ) Binary AR14. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased with increasing temperature in both systems. The equilibrium adsorption capacities of AB1 onto modified feldspar were reduced from 5.786 to 4.965 (in single solution 100 mg L<sup>-1</sup>) and from 3.562 to 2.985 (in mixed solution of 100 mg L<sup>-1</sup> AB1 + 100 mg L<sup>-1</sup> AR14) while the equilibrium adsorption capacities of AR14 onto HDTMA-feldspar were reduced from 3.684 to 2.026 (in single solution 100 mg L<sup>-1</sup>) and from 0.779 to 0.651 (in mixed solution of 100 mg L<sup>-1</sup> AB1 + 100 mg L<sup>-1</sup> AR14) when temperature of dye solutions increases from 25 to 50 °C. This decrease in the equilibrium adsorption of dyes with temperature indicates that the adsorption of acid dyes is controlled by an exothermic reaction.

#### Determination of thermodynamic parameters

Thermodynamic investigates the feasibility and spontaneous the process nature. For the adsorption of AB1 and AR14 dyes onto modified feldspar in

single and binary solutions, thermodynamic parameters such as enthalpy change ( $\Delta H^0$ ), free energy change ( $\Delta G^0$ ), and entropy change ( $\Delta S^0$ ) can be estimated using equilibrium constants changing with temperature.

The  $\Delta G^0$  of the adsorption is given by the following equation:

$$\Delta G^0 = -RT \ln K_s \quad (14)$$

where  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup>K) and  $T$  is the absolute temperature (K). In single solutions, the distribution coefficient is defined as  $K_s = C_{a,e}/C_e$ , where  $C_{a,e}$  is the amount of dye adsorbed on the adsorbent (mg L<sup>-1</sup>) of the solution at equilibrium (mg L<sup>-1</sup>),  $C_e$  is the equilibrium concentration. Also in binary system, the distribution coefficient is defined as  $K_{s,I} = C_{a,e,i}/C_{e,I}$ , where  $C_{a,e,i}$  is the concentration of each ionic species on the adsorbent at equilibrium. The standard enthalpy and entropy change values of adsorption could be determined from the van't Hoff equation given as below:

$$\ln K_s = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (15)$$

As could be seen from eq. (15), if the equilibrium constants for an adsorption reaction at various temperatures are known, the values of standard enthalpy and entropy changes for adsorption could be determined from the slope and intercept of the linear van't Hoff plots of  $\ln K_s$  versus  $1/T$ .  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  values for adsorptions of AB1 and AR14 in single and mixture systems are given in Table VI.

The change of free energy between -20 and 0 kJ/mol is for physisorption, but chemisorption is a range of -80 to -400 kJ/mol. As can be seen from Table VI, the positive values of free energy changes indicate that the adsorption reaction was not a spontaneous one and that the system gained energy from an external source. Although, the negative value of free

**TABLE VI**  
The Thermodynamic Constants of Adsorption Obtained AB1 and AR14 in Single and Binary Systems

Dye	Temperature (K)	$K_s$ (L g <sup>-1</sup> )	$\Delta G^0$ (kJ mol <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )
AB1	298	2.39	-2.16	-39.99	-127.20
	313	0.91	0.24		
	323	0.71	0.92		
AB1+AR14	298	0.17	4.46	-14.93	-65.07
	313	0.12	5.43		
	323	0.10	6.08		
AR14	298	0.15	4.65	-21.53	-87.71
	313	0.11	5.80		
	323	0.08	6.88		
AR14+AB1	298	0.05	7.69	-20.08	-92.71
	313	0.04	8.71		
	323	0.02	10.08		

energy change of AB1 adsorption in the single solution at 25°C ( $-2.16 \text{ kJ mol}^{-1}$ ) indicates that the adsorption reaction for AB1 was a spontaneous one at 25°C. Also it can be seen from Table VI that the positive values of  $\Delta G^0$  increase with increasing temperature in all cases, this indicates the presence of an energy barrier at high temperature in the adsorption, and therefore adsorption was unspontaneous and less favorable at high temperatures. The extent of AB1 and AR14 adsorption in the single and binary systems decreases because it might indicate the operation of weaker attractive forces at higher temperatures. Also an increase in  $T$  causes a decrease in  $K_s$  for both dyes adsorption in the single and binary systems.

The negative values of the standard enthalpy change ( $\Delta H^0$ ), which are  $-39.989$  and  $-13.751 \text{ kJ mol}^{-1}$  for AB1 and  $-21.530$  and  $-20.078 \text{ kJ mol}^{-1}$  for AR14 in the single and mixture systems, respectively, indicate that the interaction of the dye molecule with adsorbent is exothermic in nature. Moreover, the standard enthalpy change is lower than  $40 \text{ kJ mol}^{-1}$ , indicating which the adsorption is physical in nature and involving weak forces of attraction. In addition, adsorption process is exothermic and it would be expected which an increased solution temperature would result in decreased adsorption. Also, the negative values  $\Delta S^0$  revealed the decreased randomness at the solid/solution interface.<sup>21,22</sup> The negative values of  $\Delta H^0$  and  $\Delta S^0$  for both dye adsorptions support the fact that the reaction is spontaneous at low temperature and the negative  $\Delta G^0$  value of AB1 adsorption in single solution at 25°C is also supported by these values.<sup>8</sup>

## CONCLUSIONS

In this study, the adsorption of Acid Black 1 and Acid Red 14 dyes in single and mixture solutions onto surfactant modified feldspar were investigated in a batch system. The mono- and multicomponent Langmuir isotherm models applied to the experimental adsorption data of AB1 and AR14 dyes from single and binary solutions onto HDTMA-feldspar. The adsorption isotherms of AB1 and AR14 onto HDTMA-feldspar were well described by the Langmuir adsorption equation in single system. The single-component isotherms for AB1 and AR14 have monolayer saturation capacities of  $6.369$  and  $3.984 \text{ mg g}^{-1}$ , respectively. It is obvious that AB1 have a higher absorbed on adsorbent than AR14.

The application of the extended Langmuir isotherm to the prediction of multicomponent acid dye adsorption results in poor agreement between the experimental data and the predicted data that it is due to the basic assumptions of the Langmuir equation like as sorption constant energy, no interaction and equal independent competition between species. Also, Jain and Snoeyink modified extended Langmuir model does not provide an improvement over the data predicted by the extended Langmuir model in multicomponent dye systems. The adsorption kinetics of dyes followed the pseudo second-order kinetic equation. The positive values of  $\Delta G^0$  indicated that the adsorption process is unspontaneous and the negative values of  $\Delta H^0$  and  $\Delta S^0$  showed that adsorption process is exothermic in the nature.

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