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Single and binary adsorption of reactive dyes from aqueous solutions onto clinoptilolite

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ABSTRACT

The adsorption of Reactive Blue 21 (RB21) and Reactive Red 195 (RR195) onto clinoptilolite type natural zeolite (ZEC) has been investigated at 298.15 K. The uptake of single and binary reactive dyes from aqueous solutions has been determined by UV–vis spectroscopy. Two mono-component (RB21 and RR195) and binary component (RB21 with RR195, and RR195 with RB21), isotherms were determined. The mono-component Langmuir isotherm model was applied to experimental data and the isotherm constants were calculated for RB21 and RR195 dyes. The monolayer coverage capacities of clinoptilolite for RB21 and RR195 dyes in single solution system were found as 9.652 and 3.186 mg/g, respectively. Equilibrium adsorption for binary systems was analyzed by using the extended Langmuir models. The rate of kinetic processes of single and binary dye systems onto clinoptilolite 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 behaviour of single and binary dyes onto clinoptilolite.

1. Introduction

Synthetic dyes and pigments released into the environment mainly in the form of wastewater effluents by textile, leather and printing industries cause severe ecological problems. Wastewater from the textile industry is a complex mixture of many polluting substances ranging from organochlorine-based pesticides to heavy metals associated with dyes or the dyeing process. The reactive dyes, which represent the largest class of dyes used in textile processing industries, are almost azo compounds, i.e. molecules with one or several azo bridges (N=N) linking substituted aromatic structures. These dyes are designed to be chemically and photolytically stable, they exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic and/or mutagenic for life.

Various physicochemical and biological techniques can be employed to remove dyes from wastewaters. They include the membrane coagulation/flocculation [1], ion exchange [2], advanced oxidation (chlorination, ozonation) [3], decolourisation and metabolism of the commercially used Remazol dye by a strain of P. Chrysosporium [4], and biological treatment (bacterial and fungal biosorption), biodegradation in aerobic or anaerobic conditions [5].

In comparation with other techniques adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances. Adsorption is one of the most effective physical processes for colour removal. This technique uses a large number of suitable sorbents as activated carbon [6,7].

Activated carbon is normally employed for this purpose, however, due to its high price it has not enjoyed wide-scale application. Therefore, other inexpensive and effective adsorbents have been tested for example; biopolymer [8,9] and various low-cost adsorbents as clays and zeolites material, etc. [10]. Natural zeolite adsorption is used in the chemical process industries and is playing important role in cleaning up plant effluent and municipal wastewater. Especially, clinoptilolite is probably the most abundant zeolite in nature because of its wide geographic distribution and large size of deposits. The presence of 4.5 million tons of natural zeolites of high quality, mainly those of clinoptilolite in Turkey, created an impetus for the utilization of clinoptilolite in wastewater treatment.

This study was performed to investigate adsorption of single and binary reactive dyes aqueous solutions on clinoptilolite. The constants parameters obtained from single (RB21 and RR195) adsorption equilibrium data were used to predict the binary adsorption behaviour of reactive blue21 and reactive red195 [11].

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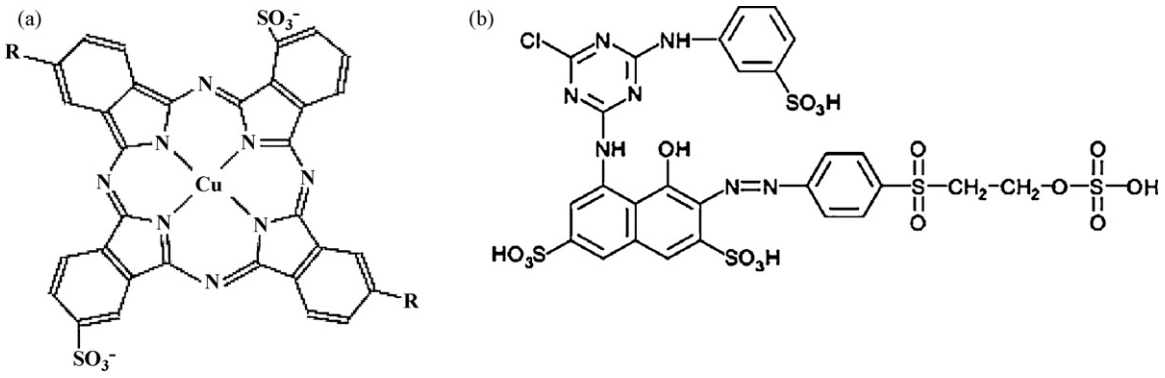

Scheme 1. (a) Possible structure of the reactive blue21. R – reactive linker arms, (b) reactive red195.

The kinetics and isotherms for dyes adsorption onto clinoptilolite (ZEC) were studied in single and binary dye solutions.

2. Materials and methods

2.1. Chemicals and materials

The clinoptilolite was obtained from the rhyolitic tuff level of the Neogene volcano sedimentary sequence in Gördes, West Anatolia, Turkey. Clinoptilolite (ZEC) was used as adsorbents for removal of RB21 and RR195 from aqueous solutions in this study. This adsorbent was used directly for adsorption experiments without any treatments. Clinoptilolite is a species of zeolite group minerals. The typical unit cell formula of natural zeolite mineral, clinoptilolite, is (Ca, Na, K)$_6$[(AlO$_2$)$_6$(SiO$_2$)$_{30}$]·24H$_2$O. It contained about 91% clinoptilolite with the chemical composition of 67.83–66.70% SiO_2, 11.63–12.04% Al_2O_3, 2.35–2.10% CaO, 1.59–0.48% MgO, 0.95% Fe_2O_3, 0.28–0.29% Na_2O, 1.59–4.97% K_2O, % 0.05 SO_3, loss on ignition 11.81% as reported by Esenli [12]. The clinoptilolite (ZEC) was sieved to obtain a particle size smaller than 125 μm. The dyes reactive blue21 (RB21) and reactive red195 (RR195) were purchased from a textile industry in the company (Turkey) region. Colour index name of Türkisblau G133 is reactive blue21 (RB21). This dye is vinyl sulfone dyes and it has chemical class copper-phtalocyanin ($C_{32}H_{16}CuN_8$ molecular weight 576.10 g mol^{-1}) and reactive linker arms of the following structure R: $SO_2NHC_6H_4SO_2CH_2CH_2OSO_3H$ (molecular weight of single R = 550 g mol^{-1}) [13–16]. Colour index name of Synozol Red HF-6BN 150% is reactive red195 and this dye has a chemical class monoazo and molecular weight 1136.30 g mol^{-1}. Stock solutions of 300 mg L^{-1} were prepared with double-distilled water. The values pH of RB21 and RR195 were measured 7.60 and 6.60, respectively. The molecular structures of the two dyes are illustrated in Scheme 1.

2.2. Single adsorption studies

Stock solutions 300 mg L^{-1} of RB21 and RR195 were used in this study. These stock solutions were diluted to give standard solutions from 10 to 250 mg L^{-1}. 0.1 g ZEC and 10 mL single-component solution were shaken using a shaker with a water bath to control temperature at 25.0 °C. The liquid and solid phases were separated by centrifuging at 3950 rpm for 5 min. The change of adsorbate concentration in each of the solutions was determined spectrophotometrically. All the spectrophotometric measurements were made with a CHE-BIOS Optimum UV–vis spectrophotometer. The maximum absorbance value of RB21 and RR195 was measured at 660 and 540 nm, respectively as shown in Fig. 1. The calibration graph of absorbance versus concentration obeyed a linear Lambert–Beer relationship [16].

The color removal efficiency of the dye was calculated as follows

$$\text{Removal efficiency } (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

where C_o and C_e are the initial concentration and concentrations of the dye at equilibrium (mg L^{-1}), respectively.

The mass of reactive 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).

$$q = (C_o - C)\frac{V}{W} \quad (2)$$

q is the adsorbed amount of reactive 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 W is the weight of the adsorbent (g).

2.3. Binary adsorption studies

For binary adsorption system, several initial concentrations of RR195 (10–250 mg L^{-1}) were prepared in 8 different glass-stoppered conical flasks with the presence of constant initial concentration of 50 mg L^{-1} of RB21 in each flask. Then, the experiment was carried out following the steps as for single system adsorption process. The remaining concentrations of both solutions were also analyzed using UV–vis spectrophotometer through the multi-component determination option. The experiments were repeated for other constant initial concentrations of RB21, which are 100 and 150 mg L^{-1}. The tests were repeated over again in

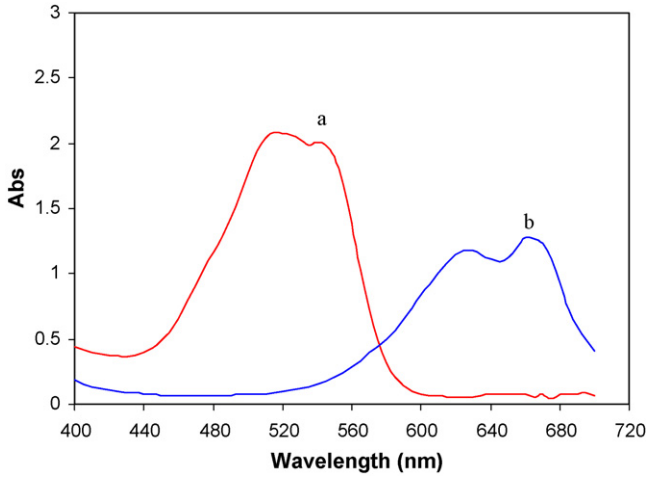

Fig. 1. Typical spectrum of the single dye (a) RR195 (b) RB21.

Table 1
Initial system conditions for equilibrium adsorption isotherms and kinetics.

Adsorption system	ZEC (g) ±0.002	Dye initial concentration range (in mg L^{-1})
RB21	0.10	RB21: 10–250
RB21 with RR195	0.10	RB21: 50 RR195: 10–250
RB21 with RR195	0.10	RB21: 100 RR195: 10–250
RB21 with RR195	0.10	RB21: 150 RR195: 10–250
RR195	0.10	RR195: 10–250
RR195 with RB21	0.10	RR195: 50 RB21: 10–250
RR195 with RB21	0.10	RR195: 100 RB21: 10–250
RR195 with RB21	0.10	RR195: 150 RB21: 10–250

order to study the adsorption behaviour of RB21 with the presence of different constant initial concentrations of RR195 (50, 100 and 150 mg L^{-1}), as given in Table 1 .

2.4. Adsorption kinetics studies

Adsorption kinetics study was carried out in order to test the relationship between contact time and dye uptake. The influence of the initial concentration of the reagent on the adsorption kinetic at constant temperature of 25 °C was studied. The following initial concentrations of dyes were used: single dyes concentrations 50, 100, 150 mg L^{-1}, binary dyes concentrations 50 + 50, 100 + 100, 150 + 150 mg L^{-1}. 0.1 g ZEC and 10 mL single and binary component solution were shaken at 25.0 °C while being rinsed with a water bath at a speed of 140 rpm. The samples were subjected to centrifugation at 3950 rpm for 5 min. A slower process follows the initial fast process. Although adsorption is very fast up to 25 min, the adsorption equilibrium is established in 90 min. Adsorption data up to 45 min were used for kinetic calculations. Amount of dye adsorbed at any time was calculated from the concentration changes during adsorption process as follows Eq. (2).

3. Results and discussion

3.1. Color removal efficiency in single and mixed dye solutions

The adsorption potential of ZEC was assessed for reactive dyes and the color removal efficiencies were measured in single and mixed dye solutions. As shown in Table 2, ZEC exhibited high adsorption efficiency for RB21. Also, comparing with the results in single dye solutions, a reduction in removal efficiency of the individual dye in the mixed dye systems was observed, although the extent of reduction was different among the dyes.

Table 2
Removal efficiency values of single and binary reactive dyes systems.

Component	C_o (mg L^{-1})	C_e (mg L^{-1})	Removal efficiency %
RB21	50	21.36	57
	100	51.33	49
	150	71.46	52
RB21 with RR195	50 + 50	27.3 + 42	31
	100 + 100	73.0 + 100	14
	150 + 150	117+ 150	11
RR195	50	45	10
	100	96	4.0
	150	145	3.3
RR195 with RB21	50 + 50	40+ 50	10
	100 + 100	95+ 98	3.5
	150 + 150	140+ 150	3.3

The removal efficiency of RB21 was reduced from 49% (in single solution 100 mg L^{-1}) to 14% (in binary solution of 100 mg L^{-1} RB21 + 100 mg L^{-1} RR195). But the removal of RR195 was reduced from 4.0% (in single solution 100 mg L^{-1}) to 3.5% (in binary solution of 100 mg L^{-1} RR195 + 100 mg L^{-1} RB21). The reduction in removal of RB21 was larger than that of RR195, as shown in Table 2. When removal efficiency values compared between single RR195 and RR195 + RB21, it was observed that these values did not change for each systems of RR195. As a result, it was revealed that RB21 was preferentially removed in mixed dye systems onto ZEC.

3.2. Single solute equilibrium studies

The equilibrium adsorption data of the single and binary systems were fitted using Langmuir isotherm models. The linearized equation of Langmuir model is as in shown by Eq. (3).

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \tag{3}$$

where q_e is the adsorbed dye amount per unit weight of adsorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of adsorbate (mg L^{-1}), q_m (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. The constant value of q_m is obtained from the slope of linear plot of $1/q_e$ versus $1/C_e$ as shown in Fig. 2. The essential characteristics by a separation factor R_L; which is defined by the following equation [17],

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

where C_o is the highest initial solute concentration and b is the Langmuir's adsorption constant (L mg^{-1}). The value of separation factor R_L, indicates the nature of the adsorption process as given below:

R_L value	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The Langmuir constants are given in Table 3. The calculated dimensionless separation factors, R_L are 0.721 and 0.123 for RR195 and RB21, respectively. The values are less than 1 and greater than 0. The R_L values show that favorable adsorptions of RB21 and RR195 take place on ZEC. Zeolite nanocrystals can act as hosts for supramolecular organization of molecules. Dyes have the tendency to form aggregates even at low concentration. Such aggregates are known to cause fast thermal relaxation of electronic excitation energy. The role of the zeolite is to prevent this aggregation and to superimpose a specific organization. Dye molecules of appropriate size are arranged with their long molecular axis along the one-dimensional channels and they cannot glide past each other. This allows the filling of specific parts of the nanocrystals with a desired type of dye because of the long molecular length of RB21 and RR195. RB21 can be considered to has affinity for ZEC, because the long molecular length of RB21 is longer than that of RR195. Therefore, the maximum adsorption capacity value of RB21 onto ZEC is higher than that of RR195, as seen in Table 3.

3.3. Extended Langmuir equation for binary systems

It is the most generally used model in multi-component system, which permitted derived from the basis of single-component Langmuir model (Eq. (3)). The extended Langmuir is presented by the

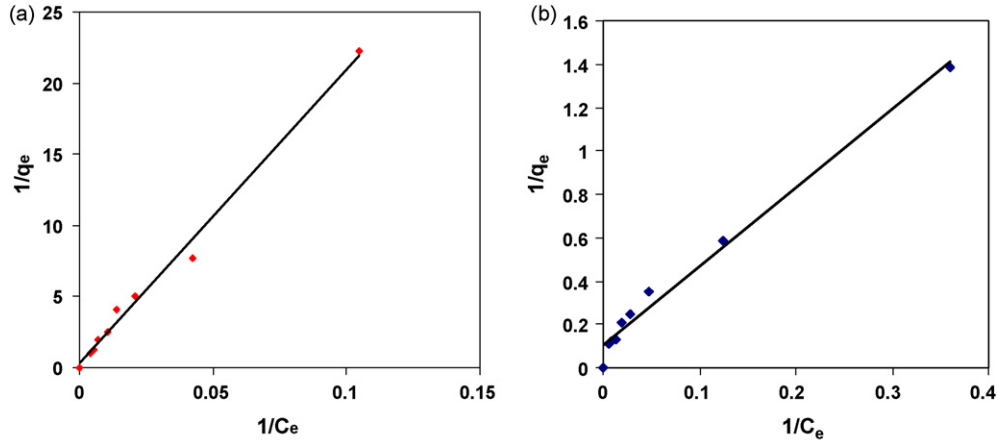

Fig. 2. Langmuir adsorption isotherm of reactive dyes on ZEC at 25 °C (a) RR195 (b) RB21.

Table 3
Langmuir constants for the adsorption of RB21 and RR195.

Component	C_o (mg L^{-1})	q_m (mg g^{-1})	b (L mg^{-1})	R^2	R_L
RB21	10–250	9.652	0.0291	0.99	0.123
RR195	10–250	3.186	0.0015	0.99	0.721

following equation [18].

$$q_{ej} = \frac{q_j^o b_j C_j}{1 + \sum_{k=1}^{1} b_i C_i} \quad (5)$$

where C_j is the equilibrium concentration of species j and C_i is the equilibrium concentration of all other adsorbing species in solution [18], while q_j^o, b_j and b_i are constants obtained from single-component studies for particular adsorbent–adsorbate system [11]. For two components, the model can be expressed as:

$$q_{e,1} = \frac{q_1^o b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \quad (6a)$$

$$q_{e,2} = \frac{q_2^o b_2 C_{e,2}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \quad (6b)$$

where b and q are the Langmuir isotherm model parameters obtained suitably from Eq. (3) in the single solute system. Therefore, the amount of solute adsorbed were calculated Eqs. (6a) and (6b) and presented by Figs. 3 and 4 for each different system. The single-component isotherms for RB21 and RR195 have monolayer saturation capacities of 9.652 and 3.186 mg/g, respectively. It is obvious that RB21 have a higher absorbed on ZEC than RR195, because RB21 has a large size and heavy molecules, as shown in Scheme 1. Competition and interaction between these two reactive dyes would be significant and affect each component to a different extent. By comparing the experimental data for RR195 in binary solution 50, 100 and 150 mg L^{-1} of RB21, it could be observed that the energy of adsorption between the specific absorbing species and the surface site is constant and equal for each site, there is no interaction between components and there is equal competition between species for adsorption sites, as seen in Fig. 4. This is clarified the basic assumption of Langmuir model, where no interaction and equal competition were occurred in the binary solution [19]. On the other hands, the extended Langmuir model could described the adsorption behaviour of RB21 in binary systems. The adsorption of RB21 was independent on the interaction of

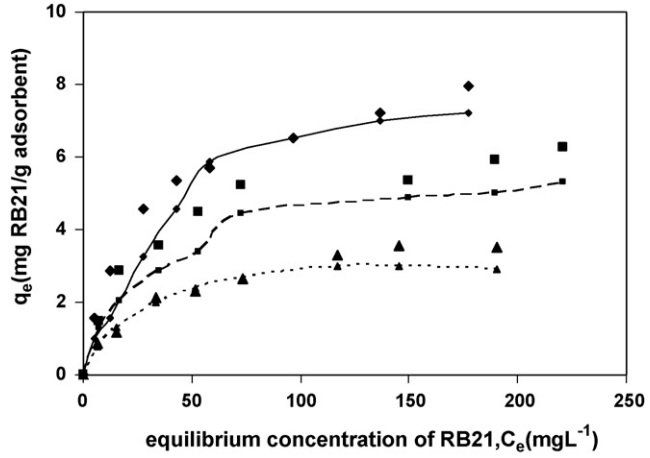

Fig. 3. Extended Langmuir Model for RB21 in binary system. (♦) RB21 + 50 mg L^{-1} RR195 experimental, (■) RB21 + 100 mg L^{-1} RR195 experimental, (▲) RB21 + 150 mg L^{-1} RR195 experimental; (—) RB21 + 50 mg L^{-1} RR195 calculated, (– – –) RB21 + 100 mg L^{-1} RR195 calculated, (- - -) RB21 + 150 mg L^{-1} RR195 calculated.

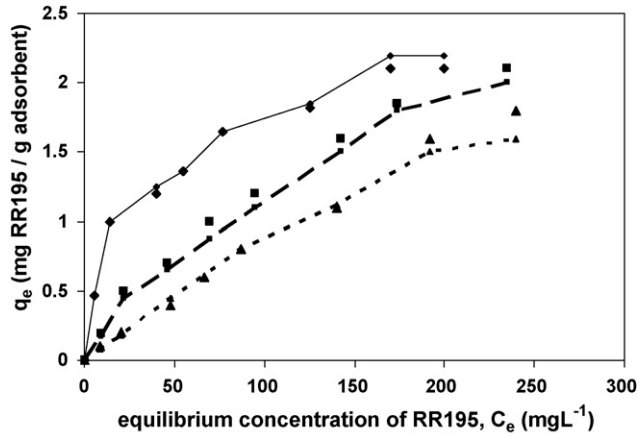

Fig. 4. Extended Langmuir Model for RR195 in binary system. (♦) RR195 + 50 mg L^{-1} RB21 experimental, (■) RR195 + 100 mg L^{-1} RB21 experimental, (▲) RR195 + 150 mg L^{-1} RB21 experimental; (—) RR195 + 50 mg L^{-1} RB21 calculated, (– – –) RR195 + 100 mg L^{-1} RB21 calculated, (- - -) RR195 + 150 mg L^{-1} RB21 calculated.

Table 4
Kinetics parameters for adsorption dyes from single and binary systems.

Dye	Dose (mg L^{-1})	Pseudo-first-order t = 0–45 min		Pseudo-second-order t = 0–45 min	
		k_1 (min^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	R^2
RB21	50	0.120	0.9635	0.304	0.9999
	100	0.105	0.9573	0.039	0.9867
	150	0.060	0.9476	0.025	0.9876
RB21 + RR195	50 + 50	0.108	0.9854	0.052	0.9906
	100 + 100	0.068	0.9724	0.010	0.9866
	150 + 150	0.059	0.9257	0.003	0.9806
RR195	50	0.060	0.9546	0.196	0.9801
	100	0.049	0.9383	0.163	0.9941
	150	0.035	0.7379	0.077	0.9860
RR195 + RR21	50 + 50	0.059	0.9116	0.025	0.9801
	100 + 100	0.058	0.9705	0.017	0.9800
	150 + 150	0.042	0.9578	0.013	0.9892

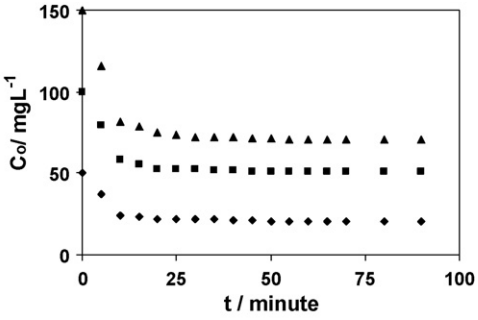

Fig. 5. Plots of concentration of RB21 versus time, using different solution concentrations on ZEC (♦) 50 mg L^{-1}, (■) 100 mg L^{-1}, (▲) 150 mg L^{-1}.

RR195 in binary solution 50, 100 and 150 mg L^{-1} of RR195, as shown in Fig. 3.

3.4. Adsorption kinetics model for dyes onto ZEC

In this work, two kinetic models were employed to fit the experimental data. The first one was the pseudo-first-order kinetic model and the integral form of this model was expressed by the following equation

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where q_e and q_t are the amounts of dye adsorbed on adsorbent at equilibrium and at any time t, respectively (mg g^{-1}), k_1 is the rate constant of pseudo-first-order model (min^{-1}); and t is the contact time (min). The correlations of $\ln(q_e - q_t)$ versus t in adsorption from single and mixed dye solutions. In adsorption from mixed dye solutions, the total amounts of dyes adsorbed were used in data treatment [20]. The values of q_e were amounts of dyes adsorbed after a contact time of 90 min, as seen in Figs. 5 and 6. Adsorption data up to 45 min were used for kinetic calculations because the value of $\ln(q_e - q_t)$ was sensitive to the error in q_t in the case of $q_t \approx q_e$.

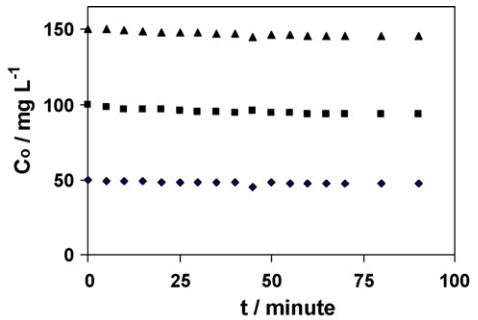

Fig. 6. Plots of concentration of RR195 versus time, using different solution concentration on ZEC (♦) 50 mg L^{-1}, (■) 100 mg L^{-1}, (▲) 150 mg L^{-1}.

The pseudo-second-order kinetic model is analyzed by Ho and McKay [21] based on the adsorption capacity and is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption, mg g^{-1} min^{-1} and q_e is the equilibrium adsorption capacity, mg g^{-1}. When the effect of initial concentration of both single (RB21, RR195) and binary solution (RB21with RR195, RR195 with RB21) were compared, it was observed that k_1 and k_2 values decrease with increasing initial concentrations. As shown in Table 4, the values of correlation coefficients of the rate constant of pseudo-first-order are less than $R^2 < 0.980$. As a result, the models which provided the best correlation with experimental data were the pseudo-second-order model.

4. Conclusions

In the present study the adsorption of reactive dyes, RB21 and RR195 on ZEC has been investigated in batch model. The equilibrium time of adsorption was found to be 90 min for ZEC. In the adsorption in single dye solutions, the adsorption isotherms of RB21 and RR195 onto ZEC were well described by the Langmuir adsorption equation. The single-component isotherms for RB21 and RR195 have monolayer saturation capacities of 9.652 and 3.186 mg/g, respectively. It is obvious that RB21 have a higher absorbed on ZEC than RR195. For single and binary solution of RR195, the basic assumption of Langmuir model could be accepted. The extended Langmuir model could described the adsorption behaviour of RB21 in binary systems. The adsorption kinetics for the two dyes from single dye systems, and the total amounts of dyes adsorbed from mixed dye systems, followed the pseudo-second-order kinetic equation. The adsorption rate constants were observed to decrease with increasing dosage of the reactive dyes.

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