Pamukkale Univ Muh Bilim Derg, 26(7), 1335-1342, 2020

Pamukkale Üniversitesi Mühendislik Bilimleri Dergisi

Pamukkale University Journal of Engineering Sciences

Comparison of acid blue 25 adsorption performance on natural and acid-thermal co-modified bentonite: Isotherm, kinetics and thermodynamics studies

Doğal ve asit-termal modifiye bentonit üzerine asit blue 25 adsorpsiyon performansının karşılaştırılması: İzoterm, kinetik ve termodinamik çalışmaları

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Received/Geliş Tarihi: 29.12.2019 Revision/Düzeltme Tarihi: 13.04.2020 doi: 10.5505/pajes.2020.03525
Accepted/Kabul Tarihi: 21.04.2020 Research Article/Araştırma Makalesi

Abstract

In the present study, natural bentonite and acid-thermal co-modified bentonite were utilized for Acid Blue 25 (AB25) removal. The adsorption experiments were executed at the temperature values of 298K, 308K and 318K. According to the results, Freundlich isotherm becomes more convenient model compared with Langmuir and Temkin model. Freundlich model coefficients rise when the temperature increases. Kinetic coefficients were calculated by pseudo first order (PFO) and pseudo second order (PSO) models. Coefficients of R^2 evaluated were higher than 0.99 with experimental and obtained q_e values close to each other explained that this process fits PSO kinetic model. The concentration of AB25 elevates from 30 to 80 mg/L adsorption capacity onto natural, acid-thermal co-modified bentonite increases from 8.36 to 27.00 mg/g and 9.30 to 29.09 mg/g for 298 K, respectively. Absolute values of free energy of AB25 onto natural and acid-thermal co-modified bentonite changes from 4.065 kJ/mol to 8.586 kJ/mol, respectively. Enthalpy values of AB25 onto natural and acid-thermal co-modified bentonite changes from 5.483 kJ/mol to 11.249 kJ/mol and entropy values of AB25 on natural and acid-thermal co-modified bentonite changes from 4.759 J/mol K to 8.940 J/mol K, respectively. It was also found that modified bentonite has higher adsorption capacity than natural bentonite.

Keywords: Acid blue 25, adsorption, Bentonite, Isotherm model, Kinetic coefficient, Thermodynamic parameter.

Öz

Bu çalışmada, Asit Blue 25 (AB25) giderimi için doğal bentonit ve asit-termal modifiye edilmiş bentonit kullanıldı. Adsorpsiyon deneyleri 298K, 308K ve 318K sıcaklık değerlerinde gerçekleştirildi. Sonuçlara göre Freundlich izotermi, Langmuir ve Temkin modeline göre daha uygun bir model haline geldi. Freundlich model katsayıları sıcaklık arttıkça yükseldiği görüldü. Kinetik katsayılar yalancı birinci derece (PFO) ve yalancı ikinci derece (PSO) modelleri ile hesaplandı. Değerlendirilen R^2 katsayıları 0.99'dan yüksekti ve birbirine yakın deneysel ve elde edilen qe değerleri bu sürecin PSO kinetik modeline uyduğu açıklandı. 30 ve 80 mg/L başlangıç konsantrasyonun, doğal, asit-termal modifiye edilmiş bentonit ile adsorpsiyon kapasitesinin 298 K için sırasıyla 8.36'dan 27.00 mg/g'ye ve 9.30'dan 29.09 mg/g'ye yükseldiği gözlendi. AB25'in serbest enerjisinin doğal ve asit-termal modifiye edilmiş bentonite karşı mutlak değerleri, sırasıyla 4.065 kJ/mol'den 8.586 kJ/mol'e değiştiği belirlendi. AB25'in doğal ve asit-termal modifiye edilmiş bentonit üzerindeki entalpi değerleri 5.483 kJ/mol'den 11.249 kJ/mol'e ve AB25'in doğal ve asit-termal modifiye edilmiş bentonit üzerindeki entropi değerleri 4.759 J/mol K'den 8.940 J/mol K.'ye değiştiği görüldü. Modifiye edilmiş bentonitin, doğal bentonitten daha yüksek adsorpsiyon kapasitesine sahip olduğu belirlendi.

Anahtar kelimeler: Acid blue 25, Adsorpsiyon, Bentonit, Izoterm model, Kinetic katsayı, Termodinamik parametre.

1 Introduction

Dyes are colored organic compounds, and their chemical structures are extensively used in several industry such as plastics, rubber, cosmetics, food processing, textile, paper, printing, dye manufacturing and leather tanning [1],[2]. Dye molecules are stable, complex, poorly soluble, toxic to organisms in receiving waters and prejudicial to photosynthetic activities. For that reason, the dyes removals in the industrial effluents are essential. There are several treatment technologies such as processes of ion exchange, oxidation, coagulation-flocculation, reverse osmosis and adsorption [3]. Adsorption processes have relatively economical, flexible, simple design, comfort in operation and efficient removal of dyes with adsorbents [4],[5].

Performance of adsorption process is related with adsorbent materials and several adsorbents have been used for the dyes removal from wastewaters. For example, fly ash, clay minerals, resin, fruit peels, layered double hydroxides, the biological strawhave play a critical role in wastewater purification [6],[7]. A number of clays have several advantages and have high adsorption capacity, which is comparable to activated carbons, towards many groups of dyes [8]. In previous studies, adsorption of dyes using mostly bentonite or some other clay minerals which are demonstrate important dye removal performances while it is required to improve its adsorption capabilities for most effective adsorption process [9],[10].

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Bentonite is one of the low cost and good performed for dye adsorption process clay mineral which is identified clearly in previously published works [11],[12].

Dyes are classified as natural and synthetic dyestuffs. Synthetic dyes are categorized: non-ionic (dispersed), cationic (basic) and anionic (direct, acid and reactive) [13],[14]. Acidic dyes have been commonly utilized for dyeing of leather, silk, polyamide, wool, as well as cosmetics, paper, food, and ink-jet printing. The main categories of acidic dyes are anthraquinone, azo dyes, triphenylmethane, azine, xanthene, nitrozo and nitro. Their removal from wastewater requires more care and attention because of resistant to degradation [15]. Acid Blue 25, an anthraquinone dye, is the most resistant to degradation and perseveres color for the long term in effluents. Because of their toxic effects, dyes have produced concerns relating to its use. In relation with it has been an important detrimental effects, it is essential to eliminate AB25 from aqueous solution [16]. Many adsorbents, for instance, activated carbon, unmodified and modified biosorbent species were investigated for adsorption of AB25, but efficiencies of most adsorbents were not very acceptable [17]. For dye adsorption, AB25 dye was selected because of its commercial importance and its applications availability in dying industry [18],[19].

The interference among the adsorbent and the adsorbate molecules is reported at the adsorption isotherms. A plot of adsorption isotherm associates with the quantity of substance adsorbed by the adsorbent molecules. The adsorbent nature changes with the amount of adsorbate and adsorbent affect the adsorption isotherm profile. Three different isotherm models were used for investigate the result. In this investigation, all mentioned ones are considered. Considering the Langmuir isotherm, the assumption was made that sorption is monolayer and all the active sites on surface of adsorbent are equal in energy. Freundlich isotherm clarifies the multilayer adsorption behavior. To investigate the adsorption mechanism PFO and PSO kinetic equation constants are calculated [20].

The aim of this research is comparison of adsorption performance of the natural bentonite and acid-thermal co-modified bentonite which is low cost and abundant adsorbent for AB25 including isotherm, kinetic, thermodynamic studies.

2 Materials and methods

2.1 Adsorbent (Natural and modified bentonite)

The natural bentonite (Ca-Bentonite) obtained from Kütahya region in Turkey was used. The formula of bentonite is $Al_2H_2O_{12}Si_4$ and molecular weight 360.31 g/mol. The activation process is applied to make changes in the surface area and the physicochemical properties. A reactor made of pyrex glass, with a condenser, was used. 250 mL of 5N HCl solution was slowly added to 50 g of bentonite which had been put into the reactor and allowed to stand for 3 hours under continuous stirring at boiling temperature about 105 °C. The washing 15 times with distilled water was repeated in order to eliminate acid residues after products of reaction were filtered. At the end of each wash, the presence of Cl- ions was checked with the silver acetate solution. Then, the solution was centrifuged at 4500 rpm for 5 minutes. After final wash, the sample was centrifuged and it was incubated at 60 °C for 48 hours. The bentonite sample was milled because of crushing lumps formed during drying and stored in a desiccator after passing through 235 mesh sieves (61.75 μm). After acid activation, bentonite samples were heated at 600 °C for 24 hours and then stored by passing through a 235 mesh sieve (61.75 μm) for thermal activation.

2.2 Adsorbate (Acid Blue 25)

AB25 was used as the adsorbate in the current research. The formula of AB25 is $C_{20}H_{13}N_2NaO_5S$ and molecular weight 416.38 g/mol. This dye was taken from Merck Chemicals.

2.3 Batch adsorption experiments

Different dye concentrations (30-80 mg/L) of AB25 were prepared and 1 g bentonite was treated with 500 mL of dye solution. AB25 concentration in solution was determined for 240 min. The same operations were made for natural, and acid-thermal co-modified bentonite at 298, 308 and 318 K temperatures. To determine the effects of pH values and initial concentrations, batch experiments were carried out in triplicate. Concentration of AB25 in solution at 602 nm absorbance wavelength was evaluated by the UV/VIS spectrophotometer (PG Instruments Ltd, T80 model). The adsorbent capacity towards dye was analyzed as:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

Where V was the solution volume (L), C_0 and C_e were initial and equilibrium concentration of dye (mg/L) and m was adsorbent mass (g).

Dye concentration, temperature and initial pH effects on AB25 adsorption were investigated. Effect of concentration was studied by natural and modified bentonite to a range of 30-80 mg/L AB25. Temperature effects on the equilibrium of AB25 adsorption on the natural and modified bentonite was carried out 298, 308 and 318 K. Effect of pH was determined with adjusting the pH of solution with 0.1 mol/L HCl and 0.1 mol/L NaOH solutions. An investigation of pH on adsorption of AB 25 was carried out at pH range of 2-12 for 2h. pH of the solutions containing adsorbents were determined by adding in two Erlenmeyer flask 1 g of natural and modified bentonite in 50 mL distilled water, stirred for 24 h, filtered, and final pH measured. pH of zero point charge (pH_{ZPC}) was determined as described in [21].

3 Results and discussion

3.1 Characterization of adsorbent

Chemical constituent of bentonite sample was analyzed by X-Ray Fluorescence (XRF). Chemical composition of bentonite was observed as follows: 71.60 wt.% SiO_2, 2.79 wt.% MgO, 13.15 wt.% Al_2O_3, 0.36 wt.% K_2O, 2.23 wt.% CaO, 0.66 wt.% Fe_2O_3, 0.26 wt.%, Na_2O, 0.07 wt.% TiO_2 and 8.45 wt.% loss of ignition. The bentonite samples were characterized with Brunauer Emmett Teller (BET), volumetric analyzer, respectively. Details of the adsorption events based on characterization results are given in [22]. BET analysis of bentonite samples was carried out (Quantachrome NOVA2200 model). The surface areas of bentonite samples are higher than other clays which given in [2].

3.2 Effect of time and initial dye concentration

Time is one of the critical physical parameters used economically for the plan and operating wastewater treatment plants. In Figure 1 and 2, the AB25 removal from the solutions is rapid at the initial period and that the efficiency at the final period that near the reach of the equilibrium state. In the beginning, the surface of the adsorption process is large, so the

adsorption to this surface is fast and the equilibrium time for AB25 adsorption was determined to be 2 h.

Figure 1 and 2 demonstrates that the rise at the initial concentration of AB25 caused the increment in adsorption capacity. As the initial concentration rises from 30 to 80 mg/L adsorption capacity onto natural and acid-thermal co-modified bentonite from 8.36 to 27.00 mg/g and 9.30 to 29.09 mg/g for 298 K, respectively. These data show that AB25 concentration have critical role in the adsorption capacity and that provides a driving force to the interaction between adsorbent and adsorbate. Based on results maximum adsorption capacity was obtained with acid-thermal co-modified bentonite. Previously reported results from various researchers were available for Acid Blue adsorption on different adsorbents and biosorbents such as: cucurbituril, activated carbon, modified silica, olive pomace boiler ash, sawdust, shrimp shell, chitosan [20],[23], [24]. The adsorption capacities obtained in this work were higher than others in previous studies. The results show that bentonite may be an inexpensive material in accordance with other adsorbents for dye removal.

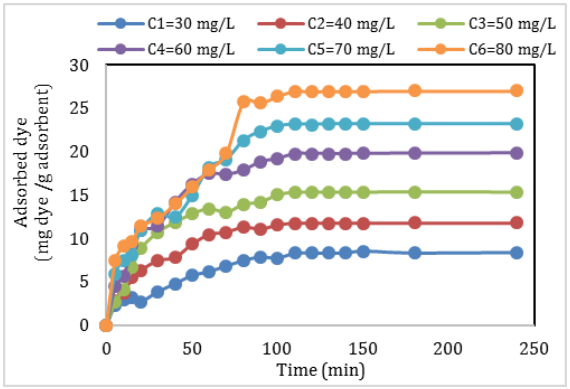

Figure 1. Effect of concentration on dye adsorption with natural bentonite (pH 7.0, 298 K, 1 g adsorbent/L)

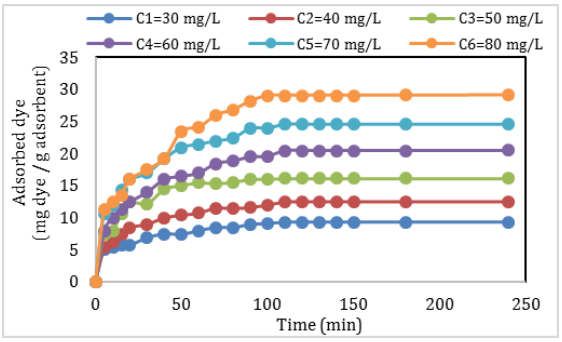

Figure 2. Effect of concentration on dye adsorption with modified bentonite (pH 7.0, 298 K, 1 g adsorbent/L)

3.3 Effect of solution pH

The value of pH can influence the dissociation of sites and the solution chemistry of AB25, particularly degree of ionization. Therefore, AB25 adsorption on the natural and acid-thermal co-modified bentonite was studied at 298 K in the using AB25 concentration of 80 mg/L and bentonite of 1 g/L. The maximum adsorption was observed at an acidic conditions (pH 2) and adsorption decreased slowly with increase in pH values (Figure 3). At a very low pH, concentration of H^+ in bulk solution would be high and carboxyl, hydroxyl, and amino groups would be protonated, thus enhancing electrostatic attraction between adsorbent and adsorbate [5]. A reduction in the number of positively charged adsorbent surfaces would be observed while pH value increased. Similar results were determined for AB25 adsorption by activated carbon and sepiolite [20],[25]. pH_{ZPC} values of natural and modified bentonite were obtained 8.95 and 8.55, respectively (Figure 4). These results support the AB25 adsorption is favoured at $pH < pH_{ZPC}$ because of the surface becomes positively charge.

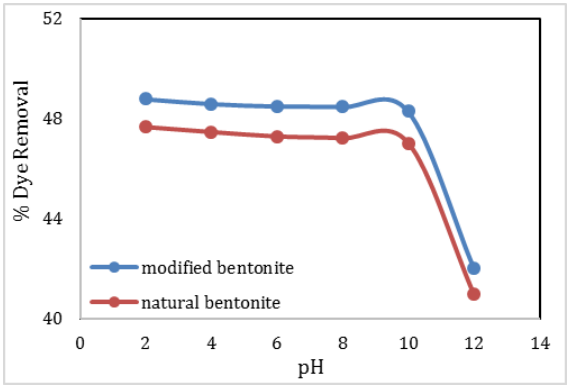

Figure 3. Effect of pH on natural and modified bentonite (80 mg/L dye conc., 298 K, 1 g adsorbent/L)

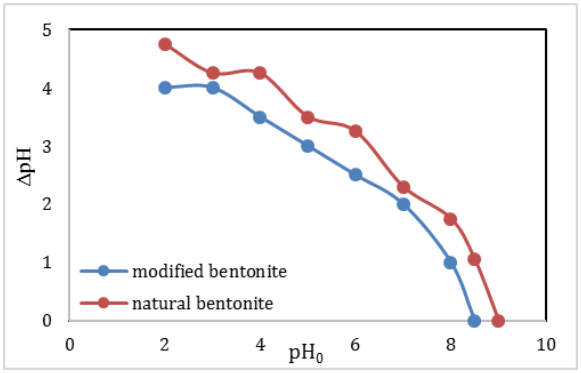

Figure 4. pH_{ZPC} plot of natural and modified bentonite.

3.4 Adsorption isotherm model studies

Many models are used to identify the dyes adsorption on solid surfaces. For the interaction between adsorbate molecules and adsorbent surface investigations, Freundlich, Langmuir and Temkin well-established models were chosen to endeavor to simplify the interactions between dye and adsorbent in the study. Three models were applicable for the descriptions of the experimental results obtained at three different temperatures.

Langmuir isotherm is given in Eq. (2);

$$q_e = (q_m K_L C_e)/(1 + K_L C_e) \quad (2)$$

Where q_m denotes maximum capacity of adsorption (mg/g), C_e represents equilibrium concentration (mg/L), K_L is a Langmuir constant (L/g). A linear form of Eq. 2 was obtained when C_e/q_e versus C_e was plotted. q_m and K_L values can be determined from the plot (Table 1).

Freundlich isotherm equation is mainly reported in Eq. (3);

$$q_e = K_F C e^{1/n} \quad (3)$$

Where K_F is a Freundlich constant (L/g), $1/n$ is an empirical parameter connected to adsorption intensity. A linear form of Eq. 3 was obtained when the natural logarithm of q_e versus Ce was plotted. Slope and intercept of line show n and K_F values, respectively (Table 1).

Table 1. Isotherm model parameters of AB 25 adsorption on bentonite.

Isotherm	Temp	Natural Bentonite			Modified Bentonite		
	K	K_L (L/g)	q_m (mg/g)	R^2	K_L (L/g)	q_m (mg/g)	R^2
	298	0.023	19.608	0.828	0.026	23.231	0.877
Langmuir	308	0.031	16.887	0.851	0.029	21.256	0.894
	318	0.033	12.422	0.857	0.039	18.282	0.899
	K	K_F (L/g)	1/n	R^2	K_F (L/g)	1/n	R^2
	298	0.081	1.789	0.953	0.127	1.725	0.987
Freundlich	308	0.029	2.192	0.974	0.169	1.726	0.992
	318	0.029	2.259	0.978	0.129	1.726	0.996
	K	K_T (L/g)	B	R^2	K_T (L/g)	B	R^2
	298	0.045	28.248	0.857	0.063	28.647	0.859
Temkin	308	0.041	35.678	0.917	0.085	30.559	0.907
	318	0.045	37.353	0.915	0.099	36.427	0.903

Temkin isotherm is expressed with Eq. (4);

$$q_e = Bln(K_T C_e) \quad (4)$$

where K_T represents binding constant corresponding to the maximum binding energy, B illustrates constant related to heat of adsorption, q_e denotes adsorption capacity obtained experimentally (mg/g), C_e stands equilibrium AB25 concentration (mg/L):

$$B = RT/b_T \quad (5)$$

where $1/b_T$ symbolizes adsorption potential; R means gas constant (8.314 J/kmol); and T is temperature in Kelvin (K). B and K_T values for different temperatures are given in Table 1.

Concerning coefficients determined Freundlich model is more fitting than other Langmuir and Temkin models. It is noted that K_F and n values elevate as the temperature rises, as well as, adsorption is approving at higher temperature. R^2 values of three isotherm models are high, but R^2 values of the Freundlich model are higher than other model values for two types of bentonite. Previously reported results from various researchers were available for AB25 adsorption on different adsorbents and biosorbents such as; rubber leaf powder, activated carbon, diatomite, sepiolite, lychee peel, cempedak peel, soya bean waste, tarap peel, water lettuce [26].

3.5 Adsorption thermodynamics

Thermodynamic parameters are significant to detect heat alteration in the adsorption process for dye onto bentonite. These parameters are calculated by the equations given below:

$$K_c = C_{Ads}/C_e \quad (6)$$

$$\Delta G^\circ = -RTlnK_C \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

$$lnK_C = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (9)$$

Where, K_c is equilibrium constant, C_{Ads} represents dye amount adsorbed mg on bentonite per litter of the solution at equilibrium, the adsorbent of adsorbent per unit litter of solution (mg/L). ΔH° (kJ/mol) and ΔS° (J/mol.K) parameters are analyzed from slope and intercept of line ploted logarithm of K_c with respect to $1/T$. These parameters were illustrated in Table 3.

Thermodynamic parameters of AB25 adsorption onto acid-thermal co-modified bentonite are higher than natural bentonite and the parameters which obtained with natural bentonite were found to be the lowest values. The absolute values of free energy of AB25 onto natural and acid-thermal co-modified bentonite changes from 4.0647 kJ/mol to 8.5855 kJ/mol, respectively. Enthalpy values of AB25 onto natural and acid-thermal co-modified bentonite changes from 5.4829 kJ/mol to 11.2496 kJ/mol and entropy values of AB25 on natural and acid-thermal co-modified bentonite changes from 4.7589 J/mol.K to 8.9400 J/mol.K, respectively. ΔG° values alter between 0 and -30 kJ/mol indicates that the adsorption is physisorption and absolute values of ΔG° decrease as temperature rises showing that this separation process is constructive at low temperatures. The positive values of ΔH° and ΔS° shows that process is endothermic and high affinity of bentonite for AB25, respectively [20].

Table 2. Adsorption capacity of AB25 on various adsorbents.

Adsorbent	q_m (mg/g)	References
Baggase pith	17.5	[27]
Shorea dasyphylla sawdust	24.4	[28]
Peat	14.4	[29]
Aspergillus niger	13.8	[30]
Bentonite	8.5	[31]
Modified silica	45.8	[32]
Rubber leaf powder	28.1	[33]
Sawdust walnut	36.9	[34]
Sawdust cherry	31.9	[34]
Sawdust oak	27.8	[34]
Sawdust pitch pine	26.2	[34]
Natural bentonite	27.0	This work
Modified bentonite	29.1	This work

Table 3. Thermodynamic parameters of AB25 adsorption on natural and modified bentonite

Adsorbent	Temp (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.K)	R^2
Natural Bentonite	298	-4.066	5.483	4.759	0.986
	308	-4.017			
	318	-3.969			
Modified Bentonite	298	-8.586	11.249	8.940	0.997
	308	-8.496			
	318	-8.407			

3.6 Adsorption kinetic studies

Kinetic models have been applied for checking experimental results of AB25 adsorption onto bentonite. The adsorption kinetics is important to choose the best test circumstances for adsorption process with the batch technique. The useful kinetic parameters for estimate of adsorption rate, provides vital

knowledge. Kinetics of AB25 adsorption were calculated using PFO and PSO kinetic models. The well-suited model has been chosen depending on the linear regression coefficient of correlation coefficients R^2 values. These models have been investigated according to experimental data at varied temperatures and initial AB25 concentrations.

Lagergren's kinetics equation can be the first for characterization of liquid-solid adsorption systems depending on solid capacity [23]. PFO linear model is given as:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (10)$$

where k_1 (min^{-1}) is constant of PFO model and q_t (mg/g) is adsorption capacity at time t. To achieve constants of this model, plot of $ln(q_e - q_t)$ against t is drawn. PFO kinetic plots for adsorption of AB25 onto natural and acid-thermal co-modified bentonite at various concentrations are given in Figure 5 and Figure 6, respectively.

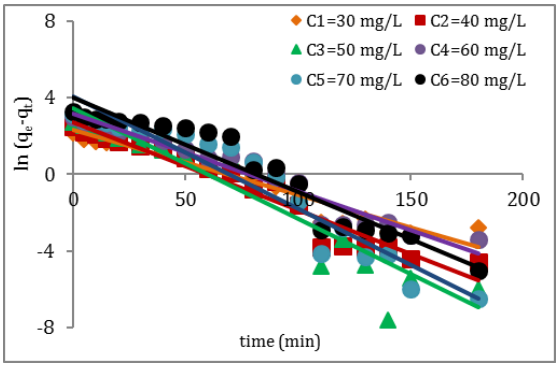

Figure 5. PFO plots for the adsorption of AB25 on natural bentonite at 298K.

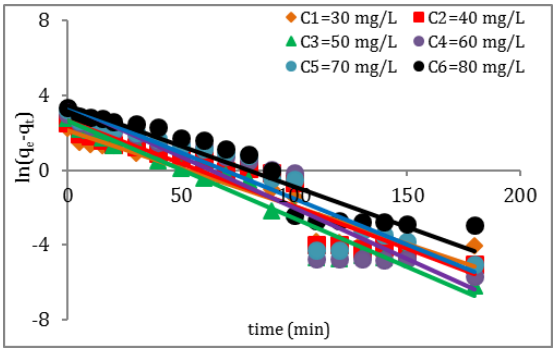

Figure 6. PFO plots for the adsorption of AB25 on modified bentonite at 298K.

Linear form of PSO model based on adsorption capacity is written below:

$$t/q_t = 1/(k_2 q_e^2) + (t/q_e) \quad (11)$$

where k_2 represents rate of adsorption (g/mg.min) and q_t is the amount of dye adsorbed at any time (mg/g). Values of k_2 and q_e were identified from Eq. 11. The plots of PSO kinetic for adsorption of AB25 onto natural and acid-thermal co-modified bentonite at various concentrations are given in Figure 7 and Figure 8, respectively.

PFO and PSO model parameters of AB25 adsorption on natural and acid-thermal co-modified bentonite are given Table 4 and Table 5, respectively. R^2 coefficients are higher than 0.99 with experimental and analyzed q_e values close to each other explained that this process fits the PSO kinetic model. Experimental and analyzed q_e values of acid-thermal co-modified bentonite are higher than natural bentonite values and calculated q_e values of 318 K are higher than 298K and 308K values for two types of bentonite. According to these tables, it is obvious that q_e values increases with increasing concentration of AB25. The kinetic constants are found closer to both temperatures and concentrations for PSO model. This result exhibited that AB25 adsorption kinetics on bentonite results from the PSO and suggested that the step of rate-limiting can be the dye chemisorption [23]. For numerous adsorption systems, adsorption kinetic data are better represented by PSO model with higher values of R^2 than other kinetic models [1].

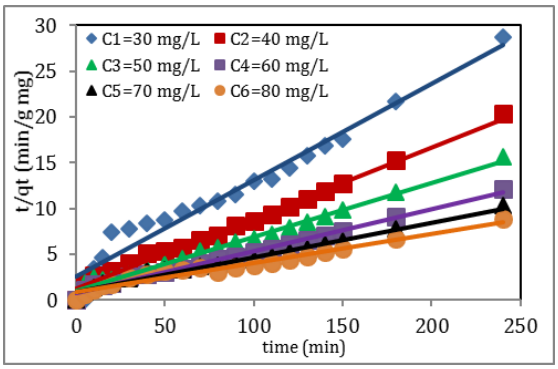

Figure 7. PSO plots for the adsorption of AB25 on natural bentonite at 298K.

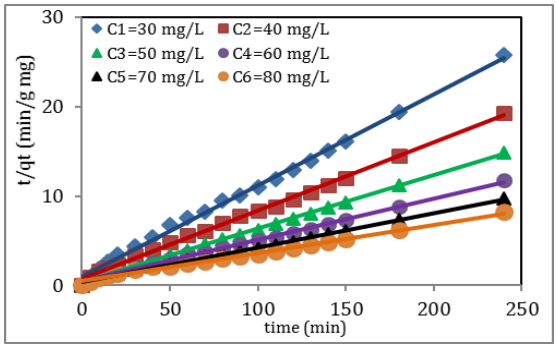

Figure 8. PSO plots for the adsorption of AB25 on modified bentonite at 298K.

4 Conclusion

AB25 adsorption on the natural, thermal modified and acid modified bentonite was examined at various experimental conditions. The current data display that adsorption of AB25 elevates with initial concentration, contact time and temperatures for natural and modified bentonites. As the AB25 concentration elevates from 30 to 80 mg/L dye adsorption capacity onto natural and acid-thermal co-modified bentonite increases from 8.36 to 27.00 mg/g and 9.30 to 29.09 mg/g for 298 K, respectively. The maximum adsorption rate was obtained with modified bentonite and equilibrium time was determined at 120 min for two bentonite types.

Isotherm studies demonstrate that the Freundlich model shows more suitable for AB25 adsorption on bentonite than the Langmuir and Temkin models. It is noted that the values of K_F and n raise as temperature increments, and also indicated that adsorption is approving at higher temperature. R^2 values of two isotherm models are high, but R^2 values of the Freundlich model are higher than other model values for two types of bentonite.

Table 4. PFO kinetic model parameters of AB25 adsorption on bentonite.

	Temp. (K)	PFO kinetic coefficients	30 (mg/L)	40 (mg/L)	50 (mg/L)	60 (mg/L)	70 (mg/L)	80 (mg/L)
		$k_1(min^{-1})$	0.0340	0.0458	0.0576	0.0406	0.0587	0.0491
	298	$q_{e\,exp}$(mg/g)	8.362	11.757	15.311	19.812	23.158	27.000
		$q_{e\,cal}$ (mg/g)	10.172	15.132	20.350	23.441	57.905	53.506
		R^2	0.9251	0.9439	0.8755	0.9444	0.9231	0.9270
		$k_1(min^{-1})$	0.0327	0.0462	0.0474	0.0369	0.0326	0.0414
NB	308	$q_{e\,exp}$(mg/g)	8.594	11.840	15.996	20.472	24.446	28.614
		$q_{e\,cal}$ (mg/g)	7.900	16.420	22.856	16.580	30.753	45.029
		R^2	0.9480	0.9549	0.9437	0.9383	0.9167	0.8953
		$k_1(min^{-1})$	0.0411	0.0523	0.0508	0.0509	0.0415	0.0512
	318	$q_{e\,exp}$(mg/g)	8.740	12.452	16.301	20.599	24.778	29.462
		$q_{e\,cal}$ (mg/g)	8.982	21.257	20.139	34.069	38.432	56.860
		R^2	0.8840	0.9031	0.9428	0.8999	0.9051	0.8520
		$k_1(min^{-1})$	0.0404	0.0457	0.0520	0.0546	0.0492	0.0436
	298	$q_{e\,exp}$(mg/g)	9.302	12.443	16.102	20.442	24.556	29.091
		$q_{e\,cal}$ (mg/g)	9.415	15.194	13.813	32.671	29.9670	32.773
		R^2	0.9123	0.9091	0.9536	0.8810	0.9029	0.9088
		$k_1(min^{-1})$	0.0381	0.0475	0.0454	0.0524	0.0469	0.0488
MB	308	$q_{e\,exp}$(mg/g)	9.893	13.441	17.557	21.314	26.075	30.249
		$q_{e\,cal}$ (mg/g)	9.511	16.675	17.003	28.281	41.846	40.923
		R^2	0.9423	0.8794	0.9374	0.9298	0.9128	0.8937
		$k_1(min^{-1})$	0.0570	0.0467	0.0476	0.0471	0.0538	0.0519
	318	$q_{e\,exp}$(mg/g)	10.359	14.326	18.249	22.806	27.3075	31.862
		$q_{e\,cal}$ (mg/g)	16.589	19.265	19.129	27.777	5.656	58.644
		R^2	0.9112	0.9078	0.9086	0.9348	0.8719	0.8319

Table 5. PSO kinetic model parameters of AB25 adsorption on bentonite.

	Temp. (K)	PSO kinetic coefficients	30 (mg/L)	40 (mg/L)	50 (mg/L)	60 (mg/L)	70 (mg/L)	80 (mg/L)
		k_2(g/mg.min)	0.0038	0.0037	0.0033	0.0026	0.0016	0.0011
		$q_{e\,exp}$ (mg/g)	8.362	11.757	15.311	19.812	23.158	27.000
	298	$q_{e\,cal}$ (mg/g)	9.662	12.953	16.978	21.882	26.455	31.447
		R^2	0.9795	0.9912	0.9899	0.9910	0.9766	0.9796
		k_2(g/mg.min)	0.0083	0.0048	0.0039	0.0026	0.0015	0.0012
NB	308	$q_{e\,exp}$ (mg/g)	8.594	11.840	15.996	20.472	24.446	28.614
		$q_{e\,cal}$ (mg/g)	9.174	12.987	17.391	22.321	29.155	32.679
		R^2	0.9953	0.9908	0.9934	0.9925	0.9822	0.9766
		k_2(g/mg.min)	0.0096	0.0048	0.0051	0.0026	0.0014	0.0015
	318	$q_{e\,exp}$ (mg/g)	8.740	12.452	16.301	20.599	24.778	29.462
		$q_{e\,cal}$ (mg/g)	9.276	13.532	17.212	22.624	28.329	32.679
		R^2	0.9964	0.9910	0.9972	0.9906	0.9974	0.9937
		k_2(g/mg.min)	0.0107	0.0098	0.0096	0.0040	0.0038	0.0021
	298	$q_{e\,exp}$ (mg/g)	9.302	12.443	16.102	20.442	24.556	29.091
		$q_{e\,cal}$ (mg/g)	9.775	13.106	16.722	21.786	25.974	31.645
		R^2	0.9964	0.9972	0.9985	0.9959	0.9968	0.9914
		k_2(g/mg.min)	0.0115	0.0072	0.0066	0.0045	0.0027	0.0025
MB	308	$q_{e\,exp}$ (mg/g)	9.893	13.441	17.557	21.314	26.075	30.249
		$q_{e\,cal}$ (mg/g)	10.309	14.104	18.382	22.522	27.933	32.258
		R^2	0.9976	0.9963	0.9982	0.9966	0.9941	0.9947
		k_2(g/mg.min)	0.0106	0.0072	0.0062	0.0041	0.0023	0.0020
	318	$q_{e\,exp}$ (mg/g)	10.359	14.326	18.249	22.806	27.307	31.862
		$q_{e\,cal}$ (mg/g)	10.834	15.083	18.975	24.038	28.326	33.014
		R^2	0.9966	0.9948	0.9984	0.9967	0.9966	0.9963

Kinetic studies displayed that adsorption of AB25 process follows the PSO model and suggested that the step of rate-limiting could be the dye chemisorption. R^2 coefficients are higher than 0.99 with experimental and evaluated q_e values very close to each other. Kinetic constants are closer to both temperatures and concentrations, and q_e values are increases with increasing concentration of AB25.

Thermodynamic studies demonstrate that this adsorption process is occurred endothermic. Thermodynamic parameters of AB25 adsorption on acid-thermal co-modified bentonite are higher than natural bentonite and the parameters which obtained with natural bentonite were found to be the lowest values. The highest absolute values of free energy of AB25 onto natural and acid-thermal co-modified bentonite changes from 4.0647 kJ/mol to 8.5855 kJ/mol, respectively. The AB25 enthalpy values onto natural and acid-thermal co-modified bentonite changes from 5.483 kJ/mol to 11.249 kJ/mol, and entropy values on natural and acid-thermal co-modified bentonite changes from 4.759 J/mol.K to 8.940 J/mol.K, respectively.

Adsorption amount was observed as maximum at acidic conditions but adsorption reduced slowly with the rise in pH values. pH_{ZPC} values of natural and modified bentonite were obtained 8.95 and 8.55, respectively. It was also found that acid-thermal co-modified bentonite possesses higher adsorption capacity compared to natural bentonite. All of these results reveal that bentonite may be interesting an inexpensive material concerning other adsorbents used for dye removal.

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