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Adsorption of Remazol Blue (Rb) onto The Chıtosan/SEP Biocomposite From Aqueous Solution

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Abstract In this study, chitosan/sepiolite (CS/SEP) biocomposites were prepared. The effects of molar ratios of CS and SEP, initial pH and temperature on the adsorption capacities of the biocomposites have been investigated. In order to determine the adsorption capacities of the sorbents, the sorption data were analyzed by using Langmuir and Freundlich equations. Langmuir equation showed higher conformity than Freundlich equation. The adsorption of Remazol Blue which has an anionic structure on biocomposite of chitosan changes with the amounts of sepiolite on the biosorbent. As the ratio of negatively charged sepiolite increases, as expected, the adsorption capacity decreases. The adsorption capacities of biocomposites were determined as 256, 126 and 23 mg/g at 318 K for SEP1, SEP2 and SEP5, respectively. The removal of RB was reached to 99% at the optimum pH of 5. From kinetic experiments, it was observed that the sorption process followed the pseudo-second-order kinetic model. According to thermodynamic calculations, the adsorption nature is determined by the results of enthalpy and activation energy as physical activation. It was found that chitosan biocomposites can be used as adsorbents at relatively low pH values..

SULU ÇÖZELTİDEKİ REMAZOL MAVİSİ (RB) 'nin KİTOSAN / SEP BİYOKOMPOZİTİ ÜZERİNE ADSORPSİYONU

Anahtar Kelimeler
Adsorpsiyon,
Kitosan,
Sepiyolit,
Biyokomposit

Özet: Bu çalışmada, kitosan/sepiyolit (CS/SEP) biyokompozitleri hazırlanmıştır. SEP mineralinin molar oranlarının farklanmasının, boya çözeltisinin başlangıç pH değerinin ve sıcaklığın Remazol mavisinin (RB) sulu çözeltiden SEP üzerindeki adsorpsiyonu üzerine olan etkileri incelenmiştir. Adsorpsiyon kapasitesini belirlemek için, adsorpsiyon verileri Langmuir ve Freundlich eşitlikleri kullanılarak analiz edilmiştir. Langmuir eşitliği, Freundlich eşitliğinden daha yüksek uygunluk göstermiştir. Anyonik yapıdaki Remazol mavisinin kitosan biyokompoziti üzerindeki tutunması yapıdaki sepiyolit miktarına göre farklanmaktadır. Negatif yüklü sepiyolit minerali oranı arttıkça adsorpsiyon kapasitesi beklendiği gibi azalmaktadır ve adsorpsiyon kapasitesi SEP1, SEP2 ve SEP5 için 318 K de sırasıyla, 256, 126 ve 23 mg/g olarak belirlenmiştir. %99 RB uzaklaştırılmasına optimum değer olan pH 5' te ulaşılmıştır. Kinetik deneylerden, adsorpsiyon sürecinin yalancı-ikinci-mertebe kinetik modeline uygunluk gösterdiği elde edilmiştir. Termodinamik hesaplamalar sonucunda entalpi ve aktivasyon enerjisi sonuçlarına göre fiziksel adsorpsiyon olduğu belirlenmiştir. Kitosan biyokompozitinin düşük pH değerlerinde adsorbent olarak kullanılabilir olduğu bulunmuştur.

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1. INTRODUCTION

Dyes are widely used in industries such as textiles, leather, rubber, paper, plastic, cosmetics, etc. to color their final products. Wastewater containing even a small amount of dyes can severely affect the aquatic life due to the reduction of light penetration and their toxicity. Many dyes and color effluents are toxic and have carcinogenic and mutagenic effects that influence environment and also human. Therefore, colored wastewater cannot be discharged without adequate treatment. As dyes are designed to resist breakdown with time and exposure to sunlight, water, soap and oxidizing agent, they cannot be easily removed by conventional wastewater treatment processes due to their complex structure and their synthetic origins. Thus, dye removal has been an important but challenging area of wastewater treatment [1].

Dye removal from wastewater effluent is a major environment problem because of the difficulty of treating such streams by conventional physical, chemical, physico-chemical and biological treatment methods. Several studies have been carried out for biological, physical and chemical treatment of dye containing effluents [2, 3]. Among these, biodegradation, adsorption, chlorination and ozonation are the most commonly used conventional methods. Chemical treatment using chlorine or ozone has led to more successful results, but since the required high dosages are not found economically feasible [2]. Among these methods, adsorption has been found to be one of the best popular physico-chemical treatment methods for removing dyes with potential applications.. Activated carbon [4] is normally employed for this purpose; however, Due to its high price it has not been used on a wide-scale application. Therefore, other inexpensive and effective adsorbents have been tested. A number of references outline the application of adsorbents such as fly-ash [5], kaolinite, bauxite and fuller's earth [6], sepiolite [7], rice husk [8], eucalyptus bark [9], post-vanillin V [10] and chitin [11]. They tested in terms of the effect of adsorbent particle size, pH effect and process temperature or mixing speed on the process effectiveness. Many authors have reported that dye adsorption onto biological adsorbents occurs through various mechanisms [5,8-11].

Chitosan (CS) is the *N*-deacetylated derivative of chitin and the second most plentiful natural biopolymer. Chitosan has been extensively investigated for several decades for molecular separation, food packaging film, artificial skin, bone substitutes, water engineering and so on, owing to its good mechanical properties, biocompatibility, biodegradability, multiple functional groups as well as solubility in aqueous medium [12]. However, its all properties such as thermal stability, hardness and gas barrier properties are not good enough to provide those wide applications. [13].

This biosorbent composed of two constituents, namely Chitosan and Sepiolite. Chitosan also has exhibited a higher capacity for adsorption of colorant than activated carbon. Chitosan contains amine or amide nitrogen in varying proportions [14, 15]. Adsorption can occur by van der Waals attraction, hydrogen bonding and coulombic attraction. The amino (-NH_2) and hydroxyl (-OH) groups on Chitosan chains can serve as coordination and reaction sites. These groups can lead to the adsorbents having a larger adsorption capacity for acid dyes or anionic dyes. In addition, Chitosan is economically attractive, since it can be obtained from the deacetylation of chitin [16].

On the other hand, Sepiolite (SEP) is a hydrous magnesium silicate whose ideal formula is $[Si_{12}Mg_8O_{30}(OH)_4](H_2O)_4.8H_2O$ according to the model of Brauner-Preisinger [17, 18]. It is used in various applications due its high surface area, porosity, fibrous structure and surface activity. It is also utilized in the production of stable suspensions of high viscosity at low concentrations. These properties provide the basis for a variety of catalytically, sorptive and rheological application [17, 18].

Adsorption of a dye from solution is mainly dependent on the dye's properties, structure and to an equal extent on the surface chemistry of the adsorbent.

Polymer/layered silicate composites frequently exhibit remarkably improved mechanical and physicochemical properties and are attracting considerable interest in polymer science field [19].

In this study it was intended to synthesize and characterize the CS/SEP biocomposites. The adsorption kinetics and isotherms for Remazol Blue (RB) dye from water solution onto biocomposite with CS to SEP molar ratio of %2:1, %2:2 and %2:5 was compared with bare CS. The effects of various experimental conditions, such as different molar ratios of CS to SEP, initial pH and temperature was also investigated.

2. Materials and Methods

2.1. Materials

Chitosan (highly viscous) was obtained from Fluka (degree of deacetylation: 75-85%, average molecular weight: 5.105-7.105 g mol^{-1}) as a flaked material. Acetic acid (HAc) and sodium hydroxide (NaOH) were purchased from Riedel de Haen. Sepiolite (SEP) was obtained from Eskişehir, Turkey. The chemical composition and X-ray diffraction (XRD) data of the SEP was given in previous publication [20].

2.2. Preparation of the Biocomposites

Chitosan /Sepiolite biocomposite was synthesized according to our previous study [7]. Chitosan solution was prepared by dissolving chitosan (CS) in a 2% (v/v) aqueous acetic acid solution at a concentration of 2 wt% followed by filtering to remove the insoluble material. SEP was first swelled by 50 mL distilled water and then added to 50 mL chitosan solution with SEP contents of 1 wt%, 2 wt%, 5wt%, followed by stirring at 60ºC for 6h. After that, CS/SEP solutions were cast on a Petri dish and dried in vacuum oven at 60ºC for 48 h. The dry films still contained a small quantity of the solvent (HAc), which formed chitosonium acetate. After drying, the films were soaked in 1 M aqueous NaOH for 5 h to neutralize the acid followed by rinsing in distilled water to neutral and then dried at vacuum oven at 60ºC for 24 h. They were termed SEP-X in which X is the content of SEP percentage.

2.3. Adsorption from Solution Experiments

Adsorption isotherms were determined by using batch equilibrium method. For batch adsorption experiments, 0.02 g of CS/SEP was added into 25 mL of different initial concentrations of RB solution. Concentrations of RB in aqueous solutions were between 3 and 50 ppm. The solutions were shaken at 100 rpm in a temperature controlled shaking water bath for 24 h. After 24 h, CS/SEP film was taken out and equilibrium concentration of RB was determined spectrophotometrically by using Shimadzu UV-Visible 1601 Model Spectrophotometer at 602.0 nm.

The amount of RB adsorbed on CS/SEP was calculated by difference of initial and the equilibrium concentrations of RB. The same procedures were performed at solution temperatures of 298K, 308K and 318K to find thermodynamic parameters. Experiments were also carried out at various time intervals to determine the kinetic parameters.

The influence of pH on RB removal was studied by adjusting pH of the RB solutions (200 ppm) in the range of 2-12 using a pH meter (Inolab WTW). The solutions were agitated with 25 mL of dye solution and 0.02 g of adsorbent at 25ºC for 24 h.

3. Results

3.1 Adsorption Kinetics

In order to optimize the design of an adsorption system of RB onto SEP1, SEP2 and SEP5, it is important to establish the most appropriate correlations for the equilibrium data for each system. Adsorption kinetics was determined using two different equations which are known as pseudo-first-order (1) and pseudo-second-order equations (2).

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \qquad (1)$$

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

where q_t is the amount of RB adsorbed (mg g^{-1}) on chitosan at various time t, q_e the amount of RB adsorbed at equilibrium (mg g^{-1}) for the pseudo first order adsorption, k_1 the pseudo first order rate constant for the adsorption process (min^{-1}), q_e the maximum adsorption capacity (mg g^{-1}) for the pseudo second order adsorption, k_2 the rate constant of pseudo second order for the adsorption (g mg^{-1} min^{-1}). The results were given in Table 1, 2 and Figure 1. The adsorption of RB on SEP1, SEP2 and SEP5 were better described by the pseudo-first-order model rather than by the pseudo-second-order. As it can be seen in Table 1 and 2, correlation coefficients for pseudo-first-order model were greater than those of pseudo-second-order model. Also the adsorption capacity of biocomposites was increased with decreasing with amount of sepiolite due to the anionic character of RB. On the other hand, these kinetic studies were carried out at 298K and 308K. The difference of the temperature positively influenced adsorption capacity and was increased the capacity of adsorption.

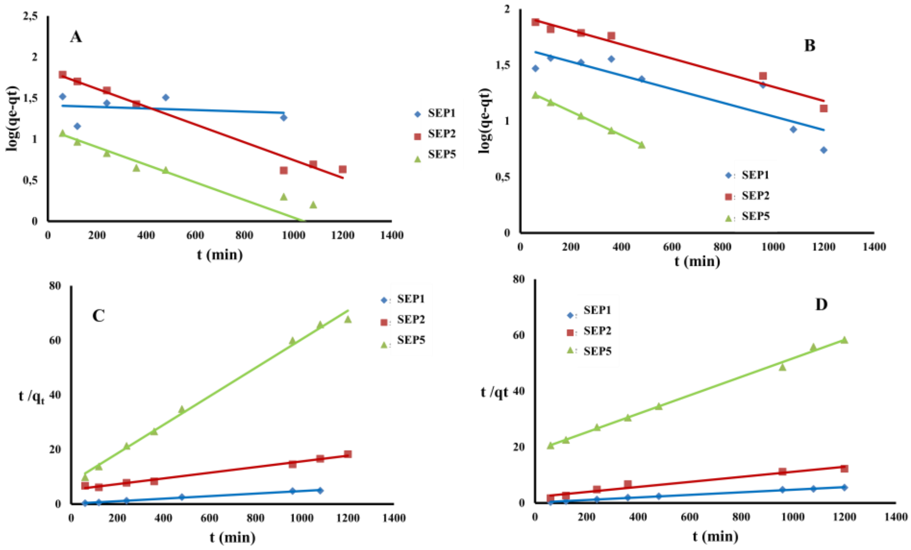

Figure 1. Pseudo-first-order plots for adsorption of RB onto SEP1, SEP2 and SEP5 at 298K (A), 308 K (B); Pseudo-second-order plots for adsorption of RB onto SEP1, SEP2 and SEP5 at 298K (C), 308 K (D).

Table 1. The pseudo-first-order parameters for RB (200 mg g^{-1}) on SEP1, SEP2 and SEP5 at different temperatures

298K	R_1^2	k_1 (min^{-1})×10^{+3}	q_e (mg g^{-1})
SEP1	0.05	0.2	26.0
SEP2	0.98	3.0	67.7
SEP5	0.87	3.0	13.1
308K			
SEP1	0.63	2.3	49.3
SEP2	0.97	1.4	86.4
SEP5	0.85	3.2	22.5

Table 2. The pseudo-second-order parameters for RB (200 mg g^{-1}) on SEP1, SEP2 and SEP5 at different temperatures

298K	R_2^2	k_2 (min^{-1})×10^{+5}	q_e (mg g^{-1})
SEP1	0.99	26.0	212
SEP2	0.99	2.1	96
SEP5	0.99	3.4	19
308K			
SEP1	0.99	12	222
SEP2	0.96	3.8	111
SEP5	0.99	5.9	30

3.2. Adsorption Isotherms

Adsorption studies were carried out to determine the adsorption isotherms in terms of Langmuir and Freundlich isotherms. Langmuir (3) and Freundlich equations (5) are applied to evaluate the adsorption data.

$$C_e / q_e = 1 / (q_m L) + C_e / q_m \quad (3)$$

where q_e is the RB uptake per unit weight of adsorbent per unit weight of adsorbent at equilibrium (mg g^{-1}) and C_e is the equilibrium RB concentration in aqueous phases (mg L^{-1}). The constant q_m is the monolayer adsorption capacity (mg g^{-1}) and L is related with the energy of the adsorption (L mg^{-1}). Plots of C_e/q_e versus C_e yield a straight line with slope $1/q_m$ and intercept $1/q_mL$.

To determine the adsorption process is favorable or unfavorable, for the Langmuir type adsorption process, the isotherm shape can be classified by a term R_L, *a* dimensionless constant separation factor, which is defined as below;

$$R_L=1/(1+ LC_0) \quad (4)$$

Where C_0 is initial RB concentrations (mg L^{-1}). The shapes of the isotherms for $0<R_L<1$, $R_L>1$, $R_L=1$ and $R_L=0$ are favorable, linear and irreversible respectively [21].
The values of R^2, q_m, L and R_L for each biocomposites were given in Table 3. The adsorption capacity of SEP1 for RB was higher than the mean values of those of SEP2 and SEP5. The monolayer sorption capacities were determined for SEP1 as 196, 250 and 256 mg g^{-1} at 298 K, 308K and 318 K, respectively (Table 3). As is also understood from the results, the monolayer sorption capacity was increased with temperature. Also, as it can be clearly seen in Table 3, the monolayer capacity was changed with temperature.

Heterogeneous surface sorption is explained by Freundlich isotherm equation (5);

$$\log q_e = 1/n \log C_e + \log K_f \quad (5)$$

Where q_e is the equilibrium of solid phase amount of RB adsorbed per unit weight of the biocomposite (mg g^{-1}), C_e is the equilibrium RB concentration (mgL^{-1}). The values of n and K_f were calculated from the slope and intercept of the plot of log q_e versus log C_e. The Freundlich constant K_f indicates the capacity of adsorption of the biocomposites (mg g^{-1}) and n is a measure of the deviation of the model from linearity of the adsorption.
Freundlich model for SEP1, SEP2 and SEP5 was given in Figure 2. The R^2, K_f, relative adsorption capacity and n_f, adsorption intensity are given in Table 4. From Table 4, it is seen that the values of n_f are smaller than 1, reflecting a favorable adsorption. That the adsorption is favorable is also deduced from dimensionless separation factors of Langmuir isotherm [21].
As can be seen from Table 3 and 4, Langmuir adsorption isotherm gave a better fit than Freundlich model based on the correlation coefficients (R^2) value.

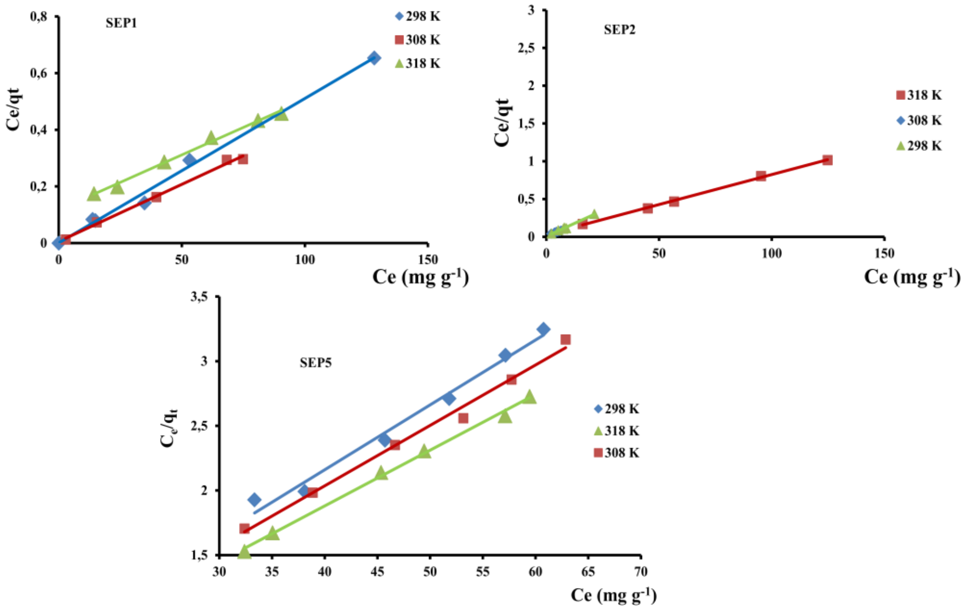

Figure 2. Langmuir isotherms for adsorption of RB onto SEP1, SEP2 and SEP5 at 298K, 308K and 318 K

Table 3. The adsorption of Langmuir equation for RB onto SEP1, SEP2 and SEP5 at different temperatures

298K	**R^2**	**q_m (mg g^{-1})**	**L (L mg^{-1})**	**R_L**
SEP1	0.99	196	12.75	0.0002
SEP2	0.99	74	1.58	0.0080
SEP5	0.98	20	0.30	0.0400
308K				
SEP1	0.99	250	0.69	0.0050
SEP2	0.99	116	0.35	0.0350
SEP5	0.99	21	0.28	0.0420
318K				
SEP1	0.9943	256	0.03	0.009
SEP2	0.9973	126	0.25	0.015
SEP5	0.997	23	0.27	0.044

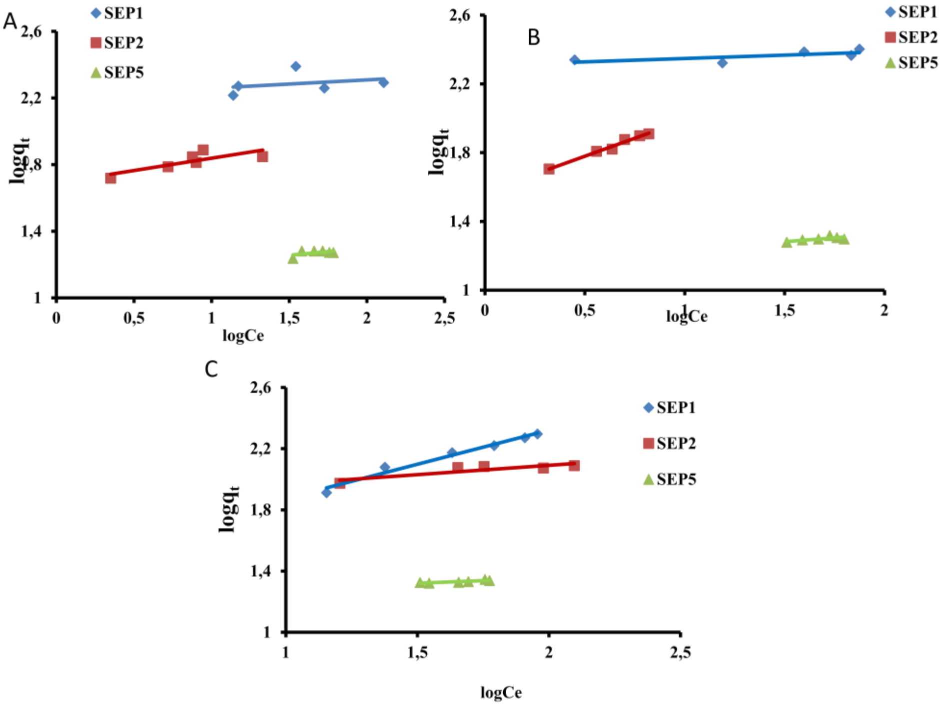

Figure 3. Freundlich isotherms for adsorption of RB onto SEP1, SEP2 and SEP5 at 298K (A), 308 K (B), 318 K (C).

Table 4. The adsorption of Freundlich equation for RB onto SEP1, SEP2 and SEP5 at different temperatures

298K	**R^2**	**K_f (mg g^{-})**	**n_f**
SEP1	0.09	162.3	0.0492
SEP2	0.64	49.07	0.1484
SEP5	0.01	12.65	0.0222
308K			
SEP1	0.50	203.30	0.0394
SEP2	0.98	37.17	0.4192
SEP5	0.55	14.12	0.0883
318K			
SEP1	0.97	26.78	0.4468
SEP2	0.77	70.11	0.1229
SEP5	0.72	16.44	0.0697

3.3. Thermodynamics of Adsorption

Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were estimated for RB adsorption onto SEP1, SEP2 and SEP5. ΔG° values at different temperatures were calculated from the following equation;

$$\Delta G° = -RT\ln(1000K_d) \qquad (6)$$

where Kd is the equilibrium constant at temperature T; R, gas constant (8.314 Jmol-1K-1), and T, absolute temperature (K).

For each temperature, the same t values selected as 1440 min and from this value, firstly qt and then qe and C_e values were calculated by using pseudo-first-order equation. K_d was estimated using the following equation;

$$"K_d = " \ "q_e" /"C_e" \qquad (7)$$

where C_e is the equilibrium concentration (mg L-1), qe the amount of adsorbed (mg g-^{1}).

To determine the values of ΔH° and ΔS°, the van't Hoff equation is used;

$$\ln K_d = (\Delta S°/R) - (\Delta H°/RT) \qquad (8)$$

ΔS° and ΔH° values can be calculated from the plot of K_d versus 1/T as intercept and slope of the line. Thermodynamic parameters calculated with the first-order rate constant are presented in Table 4.

In order to obtain activation energy of sorption process, Arrhenius equation was used in the following form;

$$\ln k2 = \ln A - Ea/RT \qquad (9)$$

where Ea is the activation energy of sorption, k2, pseudo-second-order rate constant, A, Arrhenius constant, R, the gas constant (8.314 $Jmol^{-1}K^{-1}$) and T is the solution temperature (K). The Ea value is obtained from the slope of Arrhenius plot of lnk1 against 1/T. The importance of activation energy (Ea) is that it is used to determine the type of adsorption (physical or chemical). The physisorption usually has energies in the range of 0-40 kJ mol-1, while higher activation energies (40-800 kJ mol-1) suggest chemisorptions [22]. Ea values (higher than 40 kJ mol-1) shows that chemical adsorption occurs in adsorption process. The absolute magnitude of ΔG° may give an idea about the type of adsorption. Chemisorption has an energy range 80–400 kJ per unit mole, physical sorption has a range 0 to −20 kJ per unit mole [23]. Since ΔG° values obtained in this study are in the range 0 to −20 kJ mol−1, sorption of RB onto SEP can be considered as physisorption process.

Table 5. Thermodynamic parameters for adsorption of RB onto SEP1, SEP2 and SEP5 at different temperatures

	E_a ($J\ mol^{-1}$)	**ΔH° ($kJ\ mol^{-1}$)**	**ΔS° ($J\ mol^{-1}K^{-1}$)**	**-ΔG° ($kJ\ mol^{-1}$)**		
				298 K	**308 K**	**318 K**
SEP1	1.8	87.5	359.9	19.7	23.3	26.9
SEP2	1.6	35.1	170.7	15.7	17.4	19.1
SEP5	1.2	9.8	71.2	11.4	12.1	12.8

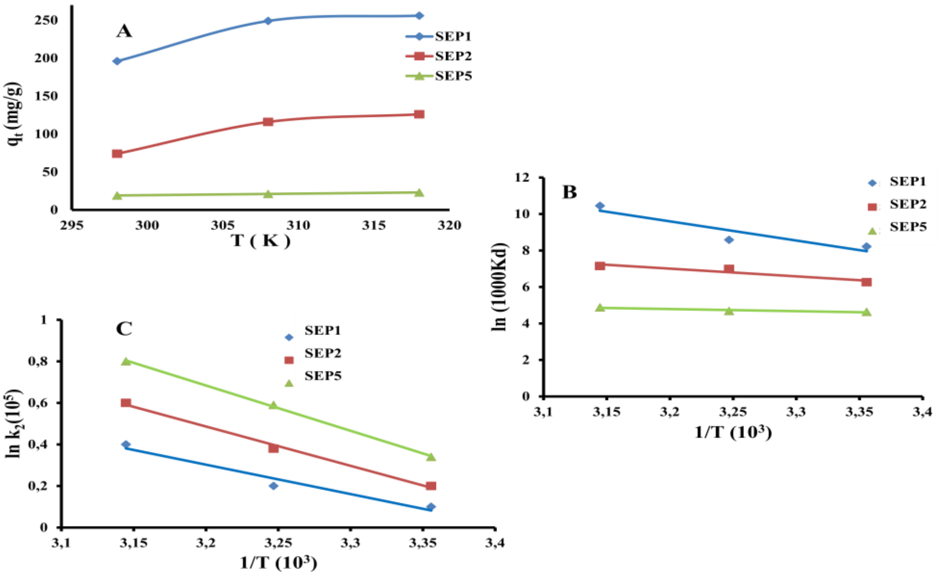

Figure 4. Effect of temperature on RB adsorption (A), Thermodynamic parameters for the adsorption of RB onto biocomposites (B), Thermodynamic parameters calculated from the second-order rate (C).

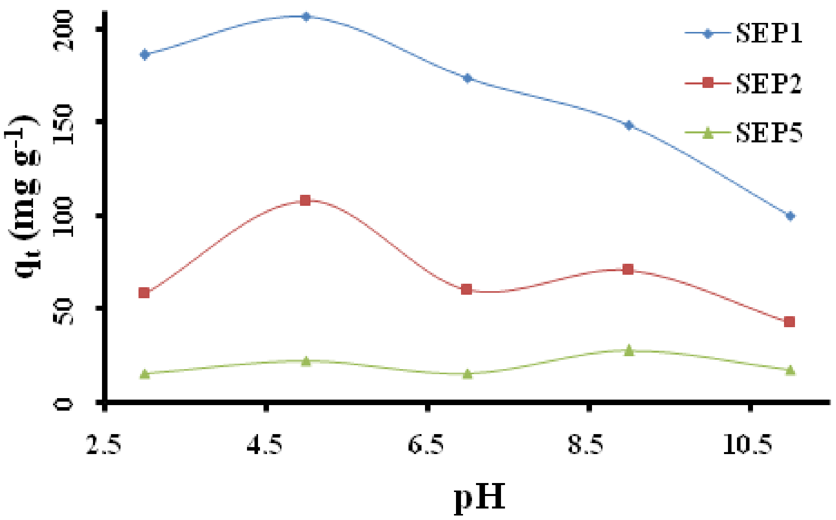

Figure 5. Effects of pH on the adsorption of RB

3.4. Effect of pH on Adsorptıon of RB onto CS/SEP

In order to investigate the effect of pH on adsorption, the studies were performed at different pH values (pH 3, 5, 7, 9 and 11) at a constant temperature of 298K. In the experiments, adsorbent dosage was selected as 0.02 g. Polyethylene vessels were filled with 25 mLs of dye solutions of 200 ppm concentration. The solutions were shaken at 100 rpm in a temperature controlling shaker for 24 hours. Equilibrium dye concentrations were measured spectrophotometrically at 602.0 nm by using UV-Visible spectrophotometer.

The results were presented in Figure 5. It is obvious that maximum adsorption at equilibrium was provided at pH = 5.

4. Conclusion

The adsorption of dye from an aqueous solution onto CS/SEP sepiolite has been investigated under different conditions. The fit of the Langmuir model in the present system shows the formation of a monolayer coverage on the surface of the adsorbent. The Freundlich model was also used to analyze the adsorption data. The adsorption capacities were determined reasonably high at molar ratio CS to SEP 2:1, at 298K and pH=5 for adsorption of RB (reactive dye) respectively. The values of dimensionless equilibrium parameters like the separation factor (R_L) (for different SEP1, SEP2 and SEP5) indicates the favorability of the process described in the present study. The kinetics of adsorption of RB followed the pseudo-second-order rate expression. The Langmuir and Freundlich models can be used to describe the dye sorption onto CS/SEP. However, better fit on Langmuir model was observed in the evaluation of the adsorption and the kinetic data.

As the pH of the system increases, the number of negatively charge sites increased. A negatively charged surface site on the adsorbent favors the adsorption of dye due to the electrostatic repulsion.

As shown in the reported data should be useful for the design and fabrication of an economically viable treatment process using bath (or) stirred tank reactors for dye adsorption and for diluting industrial effluents.

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