METHYL VIOLET DYE ADSORPTION ONTO CLINOPTILOLITE (NATURAL ZEOLITE): ISOTHERM AND KINETIC STUDY

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ABSTRACT

The dyes and pigments have poisonous and mutagenic effect on humans and animals. In this study, the use of Bigadiç clinoptilolite (natural zeolite) as an adsorbent for removal of methyl violet dye from solutions was investigated. The dye adsorption experiments were carried out in batch mode as a function of pH (3-9), temperature (30-50 ºC), ionic strength (0-0.1 M NaCl) , clinoptilolite calcination temperature (0-200 ºC), particle size (0-45;180-425 µm) and solid-to-solution ratio (0.1-1.5g/50 mL). The dye adsorption capacity of the clinoptilolite mineral increased with high solution pH, high temperature, high salt concentration, low particle size and low solid-to-solution ratio. Clinoptilolite mineral provided higher adsorption capacity at calcination temperature of 50 ºC. The equilibrium adsorption data fitted to the Langmuir isotherm rather than Freundlich model. The kinetic data could be explained by the pseudo second order model. Also, the kinetic data fitted to the intra particle diffusion model and this indicated that pore diffusion was rate controlling step in the applied batch process. Maximum adsorption capacity of the clinoptilolite mineral was calculated as 75.25 mg/g at pH 9.

KEYWORDS:
Clinoptilolite; Methyl Violet Dye; Isotherm; Kinetic

1 INTRODUCTION

The dyes and pigments are the main source of the color pollution in the surface waters [1, 2]. Textile industries are the primary dye consumers and produce wastewaters at high volumes. Textile effluents are characterized by strong color, high chemical oxygen demand and changing pH levels [3]. Dyes that are mixed to the surface waters reduce photosynthetic activity in the aqueous mediums by impeding the sun light penetration to the water. Dyes and pigments cause to death of the soil microorganisms [4]. Hence, the dye containing effluents are not appropriate for irrigation. Approximately, 10,000 different types of dyes and pigments are used in industrial processes [2, 5]. Among these dyes and pigments, triphenylmethane type of dyes (for instance methyl violet) have been reported as toxic, carcinogenic, mutagenic water pollutants and thereby dyes may lead to adverse health effect in human and animals [5]. Therefore, dyes must be removed from wastewaters by a suitable method.

The most commonly found zeolites in the nature are clinoptilolite, mordenite, ferrierite, chabazite, erionite, philipsite and analcime [6]. The clinoptilolite mineral is one of the most abundant zeolites. Due to replacement of silica (Si^{4+}) with aluminum (Al^{3+}), clinoptilolite has a negative surface charge. The grinding of clinoptilolite causes to break of bonds at the siloxane groups (Si-O-Si) and this also produces a negative charge on the clinoptilolite surface [7]. This negative charge is balanced by the cations, such as Na^{+}, K^{+}, Ca^{2+} and Mg^{2+}. The use of clinoptilolite for removal of cationic dyes has been investigated by several researchers [8-11]; however, there are limited studies on dye removal by clinoptilolite as a function of pH, particle size, temperature, calcination, ionic strength, and solid-to-solution ratio. Besides investigation of the effects of various parameters, the characteristics of adsorption process such as isotherm and kinetics were determined in this study.

2 MATERIALS AND METHODS

2.1. Characterization and Properties of the Clinoptilolite Sample

The used clinoptilolite sample was collected from a deposit in Bigadiç-Balıkesir in Turkey. Chemical composition of the clinoptilolite sample is given in Table 1. Total exchange capacity of the clinoptilolite was calculated as 2.458 meq/g by taken into consideration the amount of total exchangeable cations. The clinoptilolite sample was classified as calcium clinoptilolite as it had high calcium content. The specific surface area and pore diameter of the clinoptilolite sample were reported as 13.4 m^2/g and 17.0 Å by Çağın et al. [6]. The clinoptilolite sample was

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grinded and sieved to 0-45, 45-90, 90-180, 180-425 µm particle size fractions.

TABLE 1 - Chemical composition of the Bigadiç clinoptilolite.

Constituent	Weight,%
SiO_2	64.99
Fe_2O_3	1.15
CaO	4.03
K_2O	2.83
Al_2O_3	11.66
MgO	1.14
Na_2O	0.15
MnO	0.008
TiO_2	0.093
P_2O_5	0.033
BaO	0.24
Cr_2O_3	0.02
H_2O	13.00

2.2 Equilibrium and Kinetic Experiments

The experiments were carried out in batch mode by means of a temperature controlled incubator shaker (ZHICHENCG, China). In the experiments, the effects of the pH, temperature, ionic strength, solid-to-solution ratio, particle size and calcination temperature on adsorption capacity were investigated. The chemical index no of cationic methyl violet dye was 42535. The molecule weight of the dye was 393.6 g/mol (FLUKA, India). The pH levels of the solutions were adjusted with appropriate droplets of NaOH or HCl solutions. Ionic strength of the solutions was adjusted by diluting appropriate volumes of 1 M NaCl solution. The clinoptilolite samples were calcinated at different temperatures in a furnace during 24 hours. The all studied solution concentrations were prepared from the stock solution having a concentration of 1,969.8 mg/L.

The results of optimum time experiments are given in Figure 1. A time span of 96 hours was determined as efficient for equilibrium. Batch experiments were conducted at equilibrium conditions to determine the best fitting isotherm model. For this purpose, a series of 50 mL dye solutions of which concentrations were ranged from 39.36 and 1,181 mg/L were treated with 0.3 g of clinoptilolite at different pH levels, temperatures and ionic strength conditions. Experiments were carried out at 140 rpm agitating speed. At the end of the adsorption, solutions were centrifuged at 10,000 rpm. After centrifugation, 1 mL solution sample was pipetted for dilution. The diluted solutions were analyzed at 584 nm by means of an UV-Visible spectrometer (UNICAM, England). Calibration curve was prepared in the concentration range of 1-2.5×10^{-5} M. Distilled water was used as reference in the measurement of residual dye absorbance. All chemicals used in the study were of analytical grade. The structure of the dye is given in Figure 2.

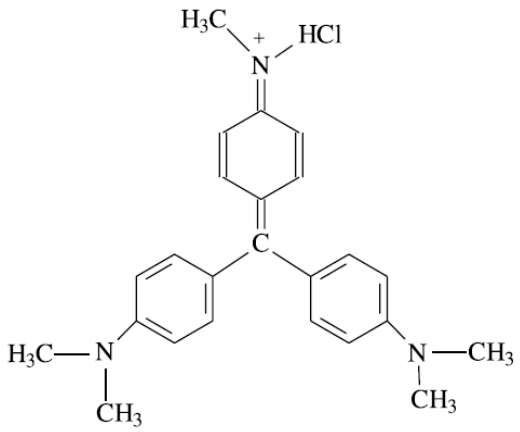

FIGURE 2 - Chemical structure of methyl violete (MV) dye.

The kinetic studies were conducted to determine the dye adsorption mechanism and kinetics. Experiments were carried out at different concentrations and parameters such as pH and temperature were kept constant. Stirring speed was kept constant at 500 rpm during all experiments. A thermostat was used to keep constant the reaction tem-

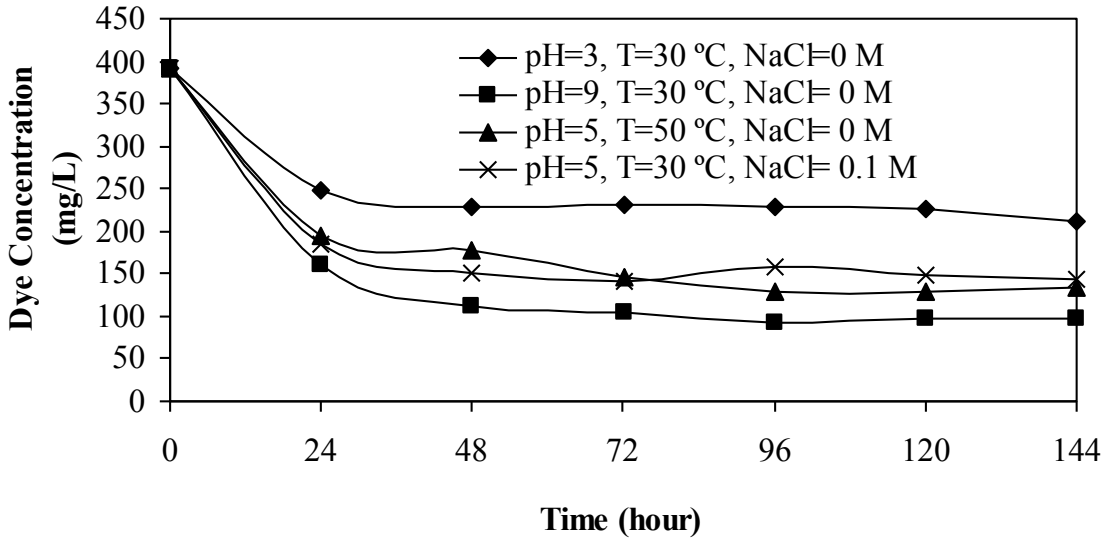

FIGURE 1 - Time effect on dye adsorption onto clinoptilolite.

perature within accuracy of ± 1. Solution pH and temperature were measured using a pH meter (WTW, Germany). Solid-to-solution ratio was 4.5g/500mL. The volume of the jacketed reactor was 1.3 L. Dye concentration values were in the range of 100-400 mg/L. The adsorption capacity of the used clinoptilolite was calculated by a mass equilibrium equation. The mass equilibrium equation can be expressed as follows:

$$\left(qe = (Co - Ce) \times V / m\right) \quad (1)$$

Where, Co and Ce are the initial and equilibrium concentrations in liquid phase, respectively (mg/L). V is the solution volume (L). m is the clinoptilolite mass (g). qe is the adsorption capacity of the used clinoptilolite at equilibrium (mg/g).

3 RESULTS AND DISCUSSION

3.1 Effect of Solution pH

The solution pH is known as one of the important parameters because the zeta potential of the adsorbents varies with solution pH level. Experimental parameters were chosen as follows: temperature 30 ^{o}C, agitation speed 140 rpm, NaCl 0 mol/L, particle Size 90–180 µm, solid-to-solution ratio 0.3g/50 mL, no calcination, concentration 39.36-787.2 mg/L. Experimental results for the solution pH effect are given in Figure 3. When the solution pH was increased from 3 to 9, the equilibrium capacity of the clinoptilolite increased from 36.27 to 75.25 mg/g. At the basic pH levels, clinoptilolite surface was negatively charged and this negative charge caused to the electrostatic binding of the cationic dye molecules to the clinoptilolite surface [12]. Also, basic pH levels decreased the repulsive forces against cationic dye molecules by neutralization of the positively charged sites at the broken edges on the clinoptilolite [7]. At acidic pH levels, the amount of adsorbed dye was found as less because the surface of the clinoptilolite was protonated with H^+ ions and competitive adsorption occurred between H^+ ions and free cationic dye molecules [13]. Similar pH effect on cationic dye removal by clinoptilolite was reported by Han et al. [10].

3.2 Effect of Solution Temperature

Generally, an adsorption process has either endothermic or exothermic nature. Experimental parameters were chosen as follows: agitation speed 140 rpm, pH=5, NaCl 0 mol/L, particle Size 90–180 µm, solid-to-solution ratio 0.3g/50 mL, no calcination, concentration 39.36-984 mg/L. Experimental results for temperature effect are given in Figure 4. When the solution temperature was increased from 30 to 50 ^{o}C, the equilibrium capacity of the clinoptilolite increased from 37.87 to 45.15 mg/g. Increasing temperature caused to sufficient energy gathering by the dye molecules for interaction with active sites on the clinoptilolite surface [14]. Adsorption capacity increase with increasing temperature indicated to the endothermic process. Similar temperature effect on cationic dye adsorption by clinoptilolite was reported by Yener et al. [8].

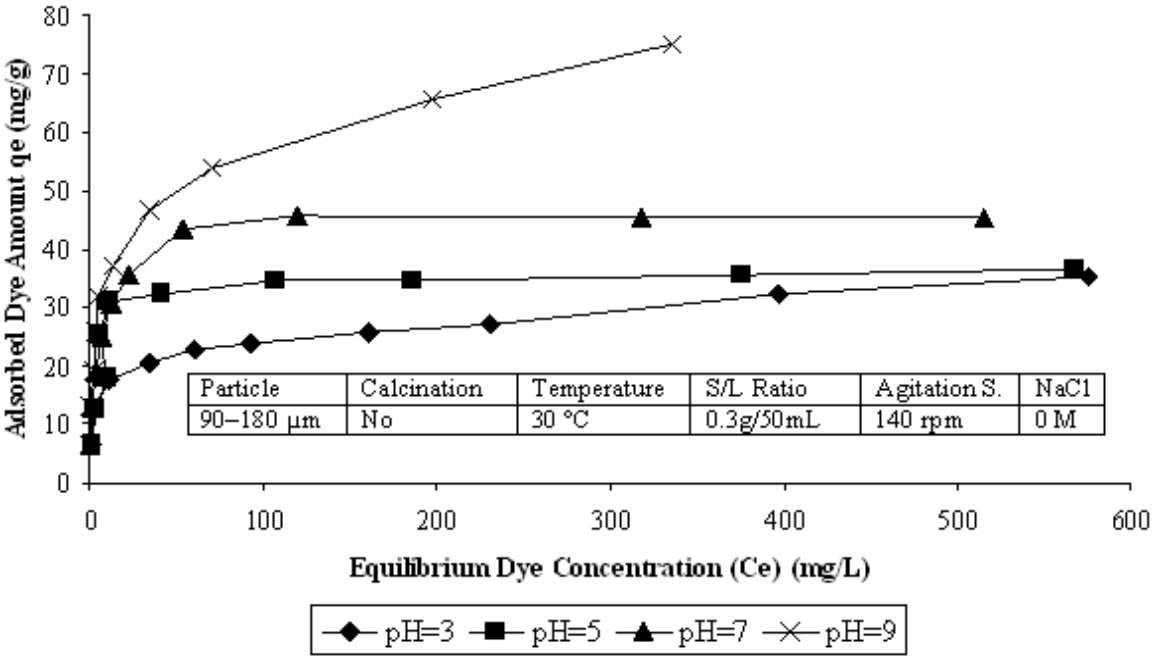

FIGURE 3 - The effect of initial solution pH on dye adsorption

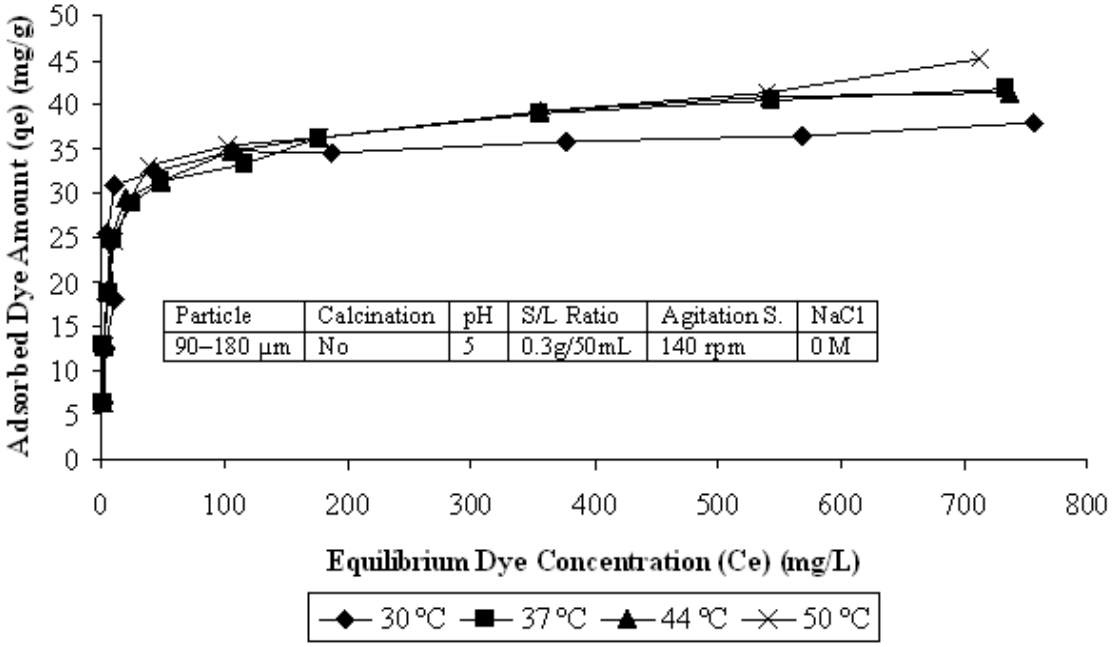

FIGURE 4 - The effect of temperature on dye adsorption

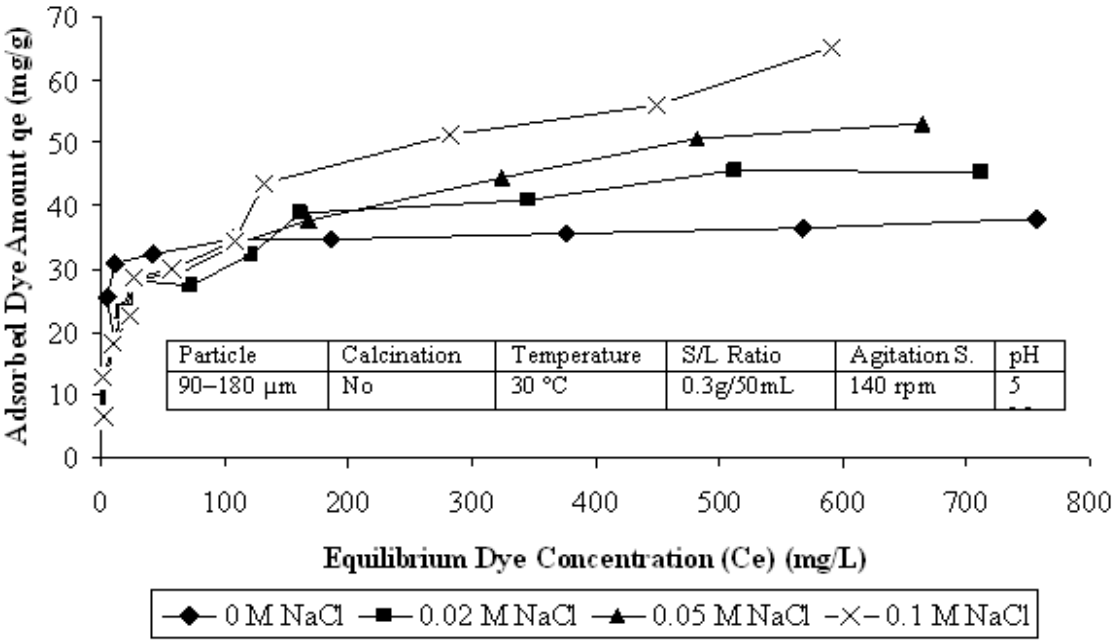

FIGURE 5 - The effect of salt concentration on dye adsorption

3.3 Effect of Ionic Strength

The existence of the salts such as NaCl and $CaCl_2$ in textile effluents is common and causes to change of solution and adsorbent surface chemistry. For instance, salt cations such as Na^+ and Ca^{2+} diminish the surface negativity of the adsorbent. Experimental parameters were chosen as follows: temperature 30 °C, agitation speed 140 rpm, pH 5, particle size 90–180 µm, solid-to-solution ratio 0.3 g/50 mL, no calcination, concentration 39.36-984 mg/L. Experimental results for ionic strength effect are given in Figure 5. When the ionic strength was increased from 0 to 0.1 M NaCl concentration, the capacity of the clinoptilolite increased from 37.87 to 65.36 mg/g. Increasing salt cation in the dye solution caused to decrease of the dye dissolution by aggregating the dye molecules. This aggregation resulted in multilayer adsorption of dye molecules on the clinoptilolite surface. Aggregation of methyl violet dye by salt existence in aqueous solution was reported by Özdemir et al. [14].

3.5 Effect of Solid-to-Solution Ratio

Experimental results for solid-to-solution ratio effect are given in Figure 6. Experimental parameters were chosen as follows: temperature 30 °C, agitation speed 140 rpm, pH 5; particle size 90–180 µm, NaCl 0 mol/L, dye concentration 400 mg/L, no calcination. Results showed that low solid-to-solution ratio had an enhancing effect on adsorption capacity. As can be seen in Figure 6, 0.1g/50 mL solid-to-solution ratio was determined as an optimum value. The increase in the dye adsorption capacity of the clinoptilolite was attributed to the fact that the low solid-to-solution ratio provided high dye concentration on per clinoptilolite granule and hence provided high driving force for more dye adsorption onto clinoptilolite surface [13].

3.6 Effect of Clinoptilolite Calcination Temperature

Clinoptilolite mineral has cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} in its structure and this cations are surrounded with water molecules. Therefore, calcination of the clinoptilolite can provide much more surface area in the case of evaporation of the structural water. Experimental parameters were chosen as follows: temperature 30 °C, agitation speed 140 rpm, pH 5; particle size 90–180 µm; NaCl 0 mol/L, dye concentration 400 mg/L, solid-to-solution ratio 0.3g/50 mL. Experimental results for calcination effect are given in Figure 7. Results showed that increasing calcination temperature had a convex effect on adsorption capacity. As can be seen in Figure 7, calcination of clinoptilolite caused to lose of the structural water that increased effective surface area up to 50 °C, however; above 50 °C, temperature increased the surface deterioration and decreased the adsorption capacity of the clinopti-

lolite. Adsorption capacity decrease with augmenting calcination temperature was also due to shrink of clinoptilolite granules resulting in pore diameter and surface area decrease with lose of the structural water [15].

3.7 Effect of Particle Size

Experimental results for the particle size effect are given in Figure 8. Experimental parameters were chosen as follows: temperature 30 ^{o}C, agitation speed 140 rpm, pH 5, dye concentration 400 mg/L, solid-to-solution ratio 0.3g/ 50 mL, NaCl 0 mol/L, no calcination. Results showed that lower particle size had an enhancing effect on adsorption capacity of clinoptilolite. Decreasing particle size provided higher surface area for more dye adsorption [16].

3.8 Isotherm Analysis

3.8.1 Langmuir Isotherm

According to theory of Langmuir isotherm, when an adsorbate molecule occupies a site, no further adsorption can take place at that site. The Langmuir equation assumes that all sorption sites are identical in related to adsorption affinity. The Langmuir isotherm is characterized by monolayer coverage [17]. Langmuir isotherm has showed good agreement with a wide variety of experimental data and is represented as follows [18].

$$qe = q_m k_a Ce/(1 + k_a Ce) \quad (2)$$

The equation above can be rearranged to the following linear form,

$$Ce/qe = 1/q_m k_a + Ce/q_m \quad (3)$$

Where, Ce is the equilibrium concentration in liquid phase (mg/L). qe is the maximum amount of the dye adsorbed (mg/g). qm is qe for a complete monolayer (mg/g). ka is a sorption equilibrium constant (L/mg).

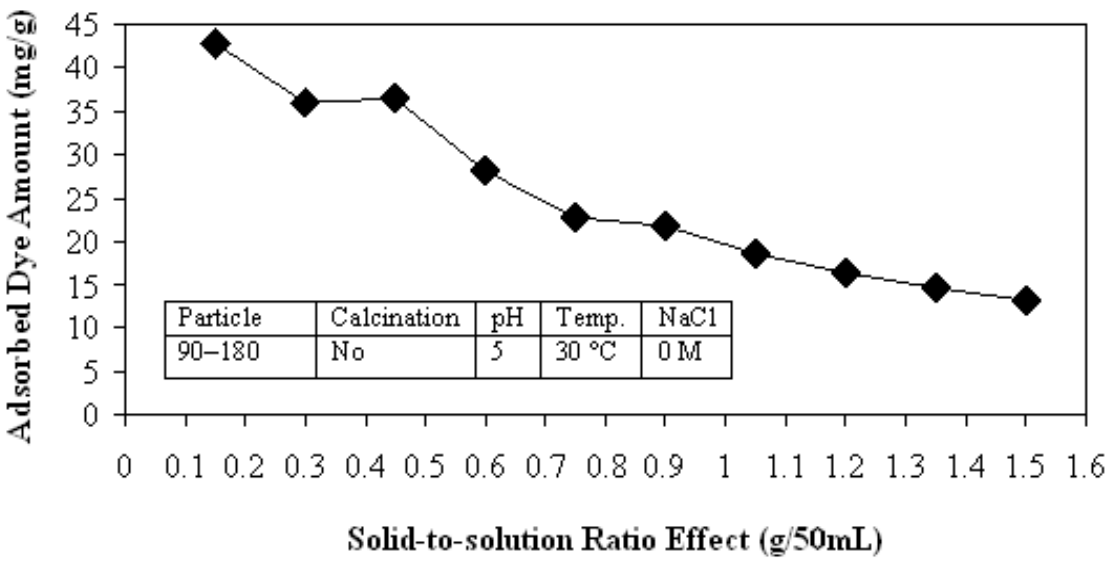

FIGURE 6 - The effect of solid-to-solution ratio on dye adsorption

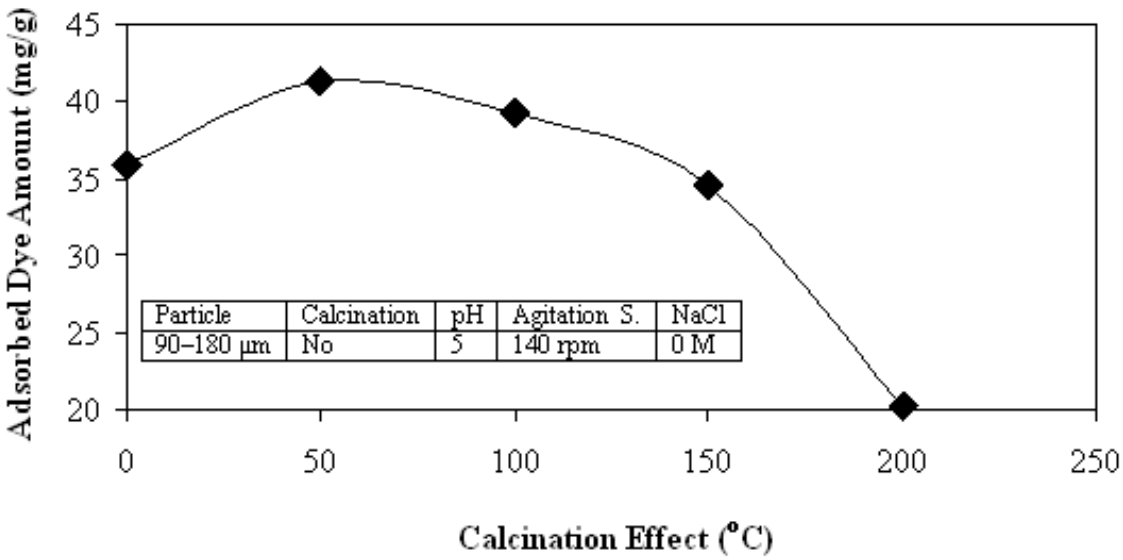

FIGURE 7 - The effect of calcination on dye adsorption

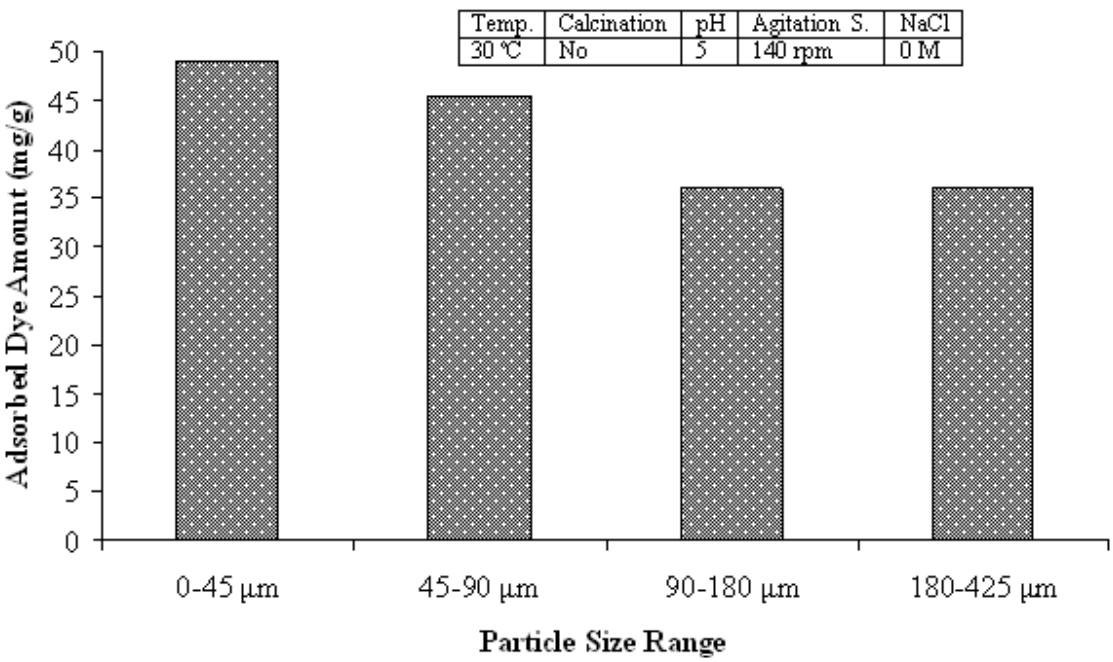

FIGURE 8 - The effect of particle size on dye adsorption

3.8.2 Freundlich Isotherm

According to the theory of Freundlich isotherm, at low concentrations, the amount of adsorbed adsorbate increases with increasing solution concentration and at high concentrations of adsorbate, the amount of adsorbed adsorbate approaches a constant value. Freundlich model describes the adsorption on energetically heterogeneous surface. The Freundlich isotherm explains the multi layer ad-sorption [17]. Freundlich isotherm is given as follow [18]:

$$qe = k_F Ce^{1/n} \quad (4)$$

The equation is frequently used in the linear form by taking the logarithm of the both sides of the above equation.

$$\ln qe = \ln k_F + \ln Ce/n \quad (5)$$

Where, Ce is the equilibrium concentration in liquid phase (mg/L). qe is the maximum amount of dye adsorbed (mg/g). k_F is the Freundlich adsorption capacity. 1/n is sorption equilibrium constant.

Adsorption shape of the methyl violet dye onto clinoptilolite surface was analyzed using Freundlich and Langmuir isotherm models. Adsorption isotherm plots for dye adsorption on the clinoptilolite at various pH level, temperature and ionic strength are given in Figures 3-5. Coefficient of determination values for isotherm models are given in Table 2. Coefficient of determination values given in Table 2 showed that the data fitted to the Langmuir isotherm model. The fitness of the data to the Langmuir iso-therm showed that active sites were of the same affinity and homogeneously distributed throughout the clinoptilolite surface. Also dye adsorption onto clinoptilolite was limited by a monolayer [17,18]. In addition to those, as can be seen in Figure 3, at pH 9 due to high negative zeta potential, dye adsorption capacity of clinoptilolite mineral went away from a constant value for studied concentration range. As can be seen in Figure 1 a time span of 96 hours was enough for equilibrium and high dye concentrations should be applied to reach a constant adsorption capacity value for pH 9. Also, at pH 3 due to competitive adsorption of dye molecules with H^+ ions the adsorption capacity increased with increasing dye concentration and went away from a plateau value. The same trend can be seen in Figure 5 because aggregation of dye molecules increased with salt concentration and this increased the multilayer adsorption on clinoptilolite surface. Together with those opposite results, it can be seen in Table 2, all adsorption data fitted to the Langmuir isotherm. Maximum dye adsorption capacity for clinoptilolite mineral was obtained as 75.25 mg/g at pH 9 and this result was comparable with the capacity of multi-walled carbon nano-tubes of which capacities were reported as 32.87, 46.10, 58.01, and 71.76 mg/g at 0, 25, 45, and 60 °C [19].

3.10 Kinetic Theory and Analysis

Kinetic models are used in order to get information about reaction rate that is important parameter for design of the batch adsorbers [20]. The kinetic models are also applied to kinetic data to understand the reaction mechanism. Generally, (ad)sorption reactions are managed by either chemical reaction or physical binding, and both of them may also occur simultaneously. In practical operation conditions, several parameters such as solution pH, temperature, concentration, surface and pore structure of adsorbents can determine the magnitude of the reaction rate [13]. The widely used kinetic models in order to explain the adsorption kinetic data are the pseudo first and second order models. A series of kinetic experiments were carried to determine the kinetic mechanism of clinoptilolite dye system. Experimental parameters were as follows: temperature 30 °C, pH 9, solid-to-solution ratio 4.5g/500 mL, NaCl 0 mol/L, particle size 90-180 µm, no calcination. The pseudo first order, pseudo second order and intra particle diffusion model were applied to the data. The equations can be given as follows. The pseudo first order equation represented by Lagergren has been generally expressed as follow [21]:

$$\ln(qe - qt) = -k_1 t \tag{9}$$

The pseudo second order equation proposed by Ho is generally expressed as follow [22]:

$$t/qt = \left(1/qe^2 k_2\right) + \left(t/qe\right) \tag{10}$$

The intraparticle diffusion model can be given as follow [23]:

$$qt = k_3 t^{1/2} + C \tag{11}$$

Where, k_1 is the rate constant of the pseudo first order equation. k_2 is the rate constant of the pseudo second order equation. k_3 is the rate constant of the intraparticle diffusion model. qe is the theoretically adsorbed amount at equilibrium. qt is the adsorbed amount at any time t. Fitness of the equations are determined from slope and coefficients of determination values.

The results of the kinetic experiments were given in Figure 9. Results showed that adsorption capacity of the clinoptilolite increased with increasing concentration. Optimum interaction time was determined as 15 min. Pseudo first order and pseudo second order kinetic models were applied to the data. Adsorption rate constants and coefficient of determination values were given in Table 3. As can be seen in Table 3, the obtained data fitted to pseudo second order model with a coefficient of determination value range of 0.999–1. Also, the mechanism of the adsorption process was tested with application of the data to the intraparticle diffusion model. The data fitted to intraparticle diffusion model with a two stage graphical inclination. The fitness of the data to the intraparticle diffusion model is given in Figure 10. It can be seen from Figure 10 that while the left stage of the lines indicates surface coverage, the right stage of the lines indicates intraparticle diffusion of the CMV dye molecules into clinoptilolite pores with

TABLE 2 - Coefficient of determination values and isotherm parameters for isotherm models under various parameters effect

Isotherm	Parameters									
	pH				Temperature, °C			Salt, M		
	3	5	7	9	37	44	50	0.02	0.05 M	0.1 M
Langmuir(R^2)	0,997	0,999	0,999	0,992	0,995	0,995	0,994	0,995	0,988	0,975
qm (mg/g)	30.03	36.49	45.87	74.62	41.84	41.49	43.86	46.51	53.76	64.93

Ka (L/mg)	0.066	0.199	0.251	0.088	0.056	0.0605	0.061	0.041	0.03	0.023
Freundlich(R^2)	0,893	0,661	0,867	0,968	0,850	0,789	0,853	0,915	0,936	0,959
k_F	8.864	16.067	16.12	17.33	11.08	11.21	11.01	9.29	8.78	8.392
1/n	0.2096	0.1488	0.2005	0.2644	0.2205	0.2189	0.235	0.2635	0.2906	0.3222

TABLE 3 - Kinetics parameters for concentration effect

Model		100 mg/L	200 mg/L	300 mg/L	400 mg/L
Pseudo First Order	k_1	0.0648	0.0681	0.1268	0.0662
	R^2	0.965	0.948	0.923	0.803
Pseudo Second Order	k_2	0.0676	0.0368	0.0527	0.0401
	R^2	0.999	0.999	0.999	0.999

k_1 values belong to first 15-20 minute reaction period of kinetic experiments

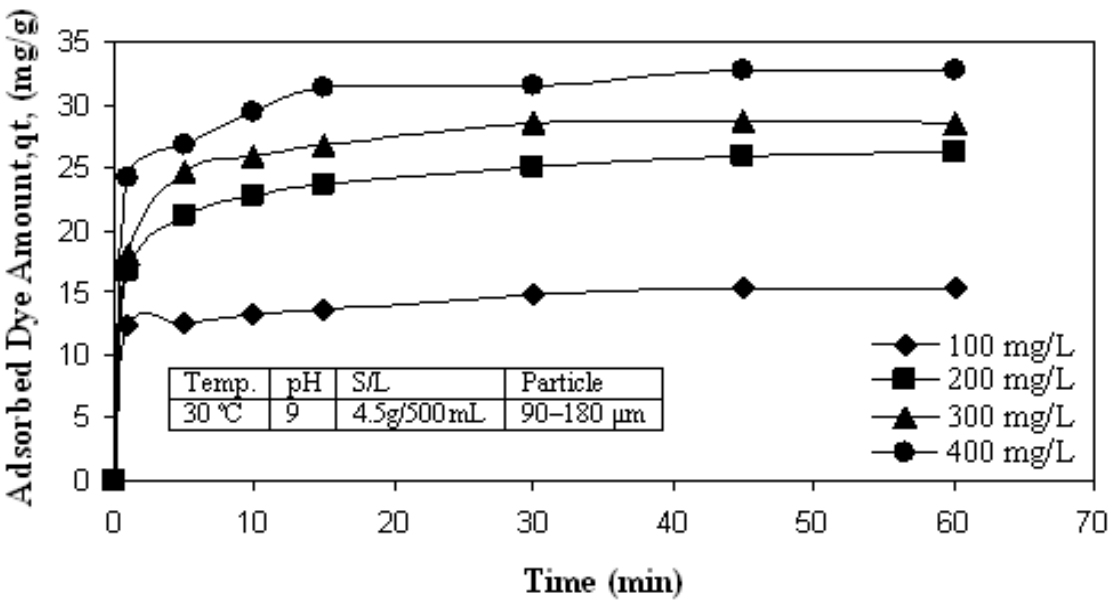

FIGURE 9 - Kinetics plots for different concentrations

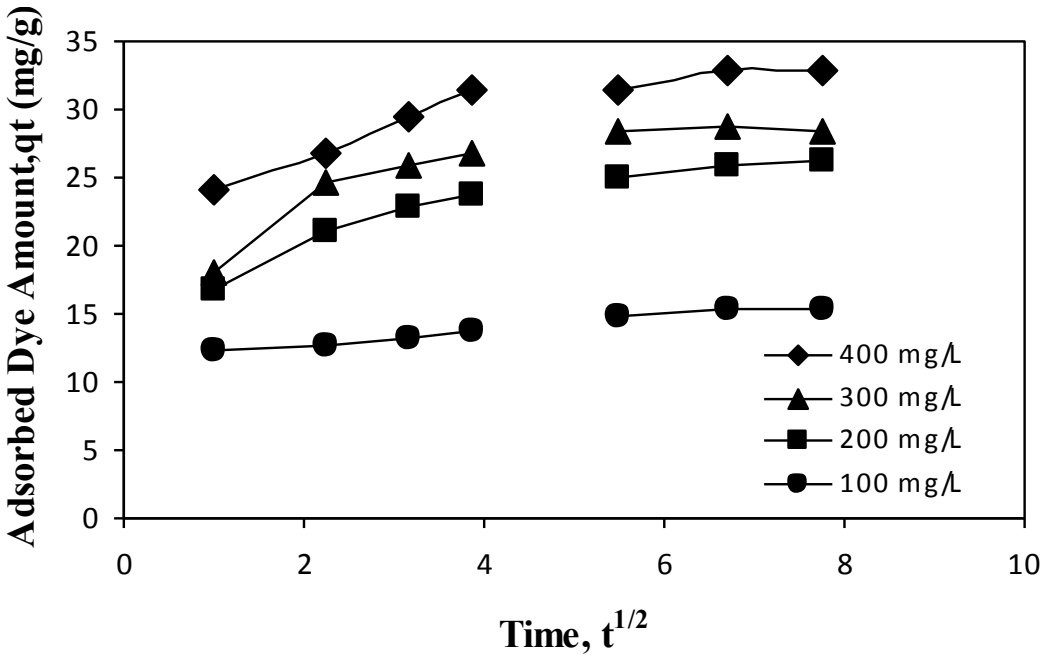

FIGURE 10 - The fitness of kinetics data to the intraparticle diffusion model (Data belong to Figure 9).

gradually adsorption increase. The fitness of the kinetic data to the intra particle diffusion model indicated that the rate controlling step was particle diffusion.

4 CONCLUSION

The main results of this study can be given as follows.

- Dye adsorption increased with high pH level, high temperature, high ionic strength, lower particle size and low solid-to-solution ratio.
- Calcination showed a convex inclination on dye adsorption due to structural deterioration of clinoptilolite with increasing calcination temperature.
- Equilibrium data fitted to the Langmuir isotherm with a correlation range of 0.994-0.999.
- Kinetic data could be explained by the pseudo second order model. Also, it was found that intra particle diffusion of the dye to the clinoptilolite was rate controlling step.
- Under the studied experimental conditions; maximum adsorption capacity of the clinoptilolite sample was calculated as 75.25 mg/g. Due to high adsorption capacity, clinoptilolite can be an alternative adsorbent in place of activated carbon.

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