



Güzide Meltem Lüle Senöz

Atatürk University, meltem.lule@atauni.edu.tr, Erzurum-Turkey

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**REMOVAL OF BASIC DYES FROM WASTEWATER BY USING NATURAL ZEOLITE:
KINETIC AND EQUILIBRIUM STUDIES**

ABSTRACT

Due to their availability and low cost, zeolites have found an important role in adsorption applications. In this study, a natural zeolite, clinoptilolite, was investigated as an adsorbent to remove basic dyes (methylene blue and rhodamine B) from aqueous solution by using batch experiment system. The natural zeolite used in this experiment is mainly composed of clinoptilolite, quartz and heulandite and has cation-exchange capacity of 2.76meq.g^{-1} . Parameters affecting adsorption mechanism such as initial concentration of dyes (50-300mg/l) and contact time (10-325 minutes) on the dye adsorption was examined. From the obtained data it was observed that the natural zeolite presented higher adsorption capacity for methylene blue than rhodamine B with the maximal adsorption capacity of 10.776mg.g^{-1} and 7.348mg.g^{-1} at 25°C for methylene blue and rhodamine B respectively. The adsorption rate data were analyzed according to pseudo-first-order and pseudo-second-order kinetic models. Kinetic evaluation indicated that the basic dye adsorption on natural clinoptilolite followed the pseudo-second-order model.

Keywords: Clinoptilolite, Wastewater Treatment, Removal of Dye, Adsorption Isotherm, Adsorption Kinetics

**DOĞAL ZEOLİT KULLANARAK ATIKSULARDAN BAZİK BOYALARIN UZAKLAŞTIRILMASI:
KİNETİK VE DENGE ÇALIŞMALARI**

ÖZ

Zeolitler, kolay elde edilebilirlikleri ve düşük maliyetleri nedeniyle adsorpsiyon uygulamalarında önemli bir rol oynamaktadır. Bu çalışmada, doğal bir zeolit olan klinoptilolit, bazik boyarmaddeleri (metilen mavisi ve rodamin B) sulu solüsyondan uzaklaştırmak için adsorban olarak kullanılabilirliği araştırılmıştır. Bu deneylerde kullanılan doğal zeolit esas olarak klinoptilolit, kuvars ve heulanditten oluşmuştur ve 2.76meq.g^{-1} kation değiştirme kapasitesine sahiptir. Boya başlangıç konsantrasyonları (50-300mg/l) ve temas süresi (10-322 dakika) gibi adsorpsiyon mekanizmasını etkileyen parametreler incelendi. Elde edilen verilerden, 25°C 'de rodamine B ve metilen mavisi için maksimum adsorpsiyon kapasiteleri sırasıyla 7.348mg.g^{-1} ve 10.776mg.g^{-1} olarak bulunmuş, doğal zeolitin rodamine B'ye göre metilen mavisi için daha yüksek adsorpsiyon kapasitesi sunduğu gözlenmiştir. Adsorpsiyon hızı verileri, birinci ve ikinci dereceden kinetik modellere göre analiz edildi. Kinetik değerlendirme, doğal klinoptilolit üzerine bazik boya adsorpsiyonunun ikinci dereceden kinetik modele uyum sağladığını göstermiştir.

Anahtar Kelimeler: Klinoptilolit, Atıksu Arıtımı, Boya Giderme, Adsorpsiyon İzotermi, Adsorpsiyon Kinetiği

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1. INTRODUCTION

Industrialization and urbanization have caused rapid deterioration of water quality. The scientific evidences prove that the effluents released from different industries e.g. textile, leather, paint etc. comprise of different hazardous and toxic compounds, some of which are known carcinogens and others probable carcinogens [1]. Dye effluents, discharged from the dyestuff manufacturing, may contain chemicals that exhibit toxic effects toward microbial populations and can be toxic and carcinogenic to mammals [2 and 3]. Dyes are recalcitrant organic molecules and the treatment of wastewater containing dyes is very difficult because of their resistance to aerobic digestion, stability to heat, light and oxidizing agent and [4 and 5]. Conventional methods for the removal of dyes in effluents include physical, chemical, and biological processes have been reported [6]. Physical adsorption is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes, and activated carbon is the most widely used adsorbent for dye removal [7]. US Environmental Protection Agency cited activated carbon adsorption as one of the best available control technologies [8]. However, activated carbon is expensive, thus making regeneration economically desirable. Therefore, other adsorbents with higher surface areas such as zeolite and clays have become popular as alternative natural materials that can be used instead of activated carbon.

Adsorption of dyes from aqueous solution by different adsorbents have been studied to develop cheaper and more effective adsorbent than activated carbon. Many of them were clay materials (bentonite, kaolinite, montmorillonite, sepiolite) and they were studied by many researchers [9 and 33]. The obtained results from adsorption experiments on clay minerals showed that the adsorption mechanism on clay was mainly dominated by ion-exchange processes. This means that the sorption capacity can vary strongly with Ph. The other materials were zeolites. Zeolites are highly porous aluminosilicates with different cavity structures. Their structures consist of a three dimensional framework, having a negatively charged lattice. The negative charge is balanced by cations which are exchangeable with certain cations in solutions. Zeolites consist of a wide variety of species, more than 40 natural species. However, the most abundant and frequently studied zeolite is clinoptilolite, a mineral of the heulandite group. Due to their unique characteristics, zeolites are commercially used as adsorbents, ion exchangers, molecular sieves, membranes, and catalysts. Several studies have been handled on the sorbent behavior of natural zeolites [16, 31, and 38]. However, raw clinoptilolite has been reported as unsuitable for the removal of reactive azo dyes due to extremely low sorption capacities [34 and 39]. They suggested chemical modification by quaternary amines to modify the solid surfaces and make them amenable to the adsorption of dyes. The main purpose of this study is to investigate the adsorption mechanism of three basic dyes from aqueous solution by natural clinoptilolite. Parameters affecting of adsorption mechanism and adsorption isotherms were investigated to understand adsorption mechanism. Adsorption rate and thermodynamic parameters were also calculated.

1.1. Adsorption Isotherms

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its concentration. In order to clarify the adsorption isotherms, Langmuir and Freundlich equations were used.



1.1.1. Langmuir Isotherm

The Langmuir equation is valid for the monolayer sorption onto surfaces with a finite number of identical sites and it can be expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot K_L} + \frac{C_e}{q_m}$$

where q_e was the equilibrium concentration of dye on clinoptilolite (mg.g^{-1}), q_m the monolayer capacity of clinoptilolite (mg.g^{-1}), K_L the adsorption constant (l.mg^{-1}), and C_e was the equilibrium concentration of dye in solution (mg.l^{-1}) [40].

1.1.2. Freundlich Isotherm

The Freundlich equation is employed to describe heterogeneous systems, and the equation in logarithmic form can be given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where K_F and n were the empirical Freundlich constant and indicative of adsorption capacity and adsorption intensity, respectively, q_e and C_e were as described above the Langmuir equation [41]. The value of $1/n$ is generally between 0 and 1. When $1/n$ value closes to zero, the surface has become more heterogenic. A value for $1/n$ below one depicts a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [42].

1.2. Adsorption Kinetics

The kinetics of basic dye adsorption on natural zeolite were investigated by two common models: Lagergren pseudo-first-order model and pseudo-second-order model.

1.2.1. Lagergren Pseudo-First-Order Model

The Lagergren pseudo-first-order kinetic model used for describing sorption kinetics is expressed by:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$$

where, q_e and q_t are the amounts of surfactant adsorbed at equilibrium (mol/g), and at time t (min), respectively. The equilibrium adsorption capacity (q_e), and the first order rate constant (k_1) were calculated from the slope and y-intercept of the linear plot of $\log (q_e - q_t)$ versus time [43].

1.2.2. Lagergren Pseudo-Second-Order Model

Pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where, q_e and q_t are the amounts of surfactant adsorbed at equilibrium (mol/g), and at time t (min), respectively. The equilibrium adsorption capacity (q_e), and the second order rate constant (k_2) were calculated from the slope and y-intercept of the linear plot of t/q_t versus time.

2. RESEARCH SIGNIFICANCE

Adsorption is a common process frequently used to remove organic and inorganic effluents from water. The use of natural zeolites as adsorbent have increased significantly because of their availability and low cost. Clinoptilolite is one of the most abundant zeolites in nature, and Turkey has very large clinoptilolite reserves. In this study, the adsorption properties of natural clinoptilolite have been investigated for removal of basic dye from wastewater using batch

equilibrium experiment. The influence of initial dye concentration and adsorption time has been analyzed in detail for the purpose of understanding the adsorption mechanism of dyes on zeolite.

3. EXPERIMENTAL METHOD

3.1. Adsorbent and Dyes

The zeolite used in this study was clinoptilolite ((Na, K, Ca)₂₋₃ Al₃ (Al, Si)₂ Si₁₃ O₃₆ .12 H₂O). It was supplied by Rota Mining Corporation from the Manisa Gördes Region in Turkey. In the experiments the zeolite was ground and passed through 80 µm sieve, washed with deionized water, dried in an oven at 100 ± 10 °C for 24 h and kept in a desiccator until use. Three basic dyes, methylene blue (MB), crystal violet (CV), and rhodamine B (RB), were selected for adsorption tests. They were obtained from AJAX Chemical. Their chemical structures are presented in Fig. 1. The stock solutions of dyes were prepared in distilled water (1 g.l⁻¹). All working solutions were prepared by diluting the stock solution with distilled water to the desired concentration. The values of solution pH were near 7.

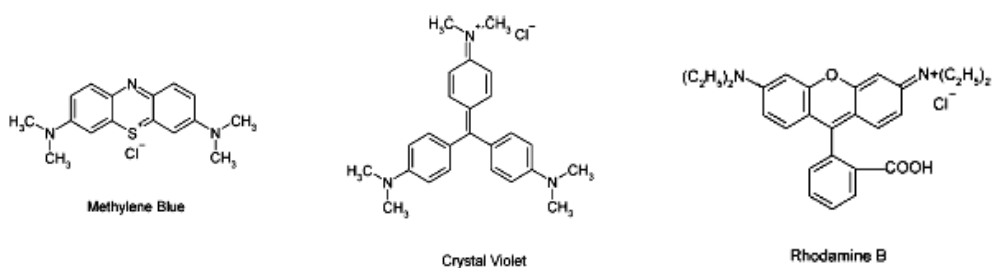


Figure 1. Chemical structure of basic dyes

3.2. Adsorption Experiments

Routine adsorption experiments were carried out as batch technique. Batch technique is a simple phase contacting technique. Here adsorbent (clinoptilolite) is made in contact with solution of any kind of substance. Adsorption experiments were performed by shaking 1 g of solids in a 50 ml dye solution with varying concentrations at 100 rpm at different temperatures. The sample was collected by separation of solid from solution using a centrifuge. The determination of dye concentration was done spectrophotometrically on a Spectra Spectrophotometer by measuring absorbance at λ_{max} of 664, 590, and 556 nm for MB, CV, and RB, respectively. The dye amount in the adsorbent phase was calculated by the following formula:

$$q = \frac{(C_i - C_e)V}{W}$$

where C_i (mg/l) is the initial metal ion concentration and C_e (mg/l) is unadsorbed metal ion concentration in solution at time t, V (l) is the volume of the solution and W (g) the weight of the adsorbent used. The adsorption percentage of metal ions was calculated as follows:

$$\text{Adsorption(\%)} = \frac{C_i - C_e}{C_i} \times 100$$

4. FINDING AND DISCUSSION

4.1. Characterization of Clinoptilolite

X-ray diffraction was used to characterize and identify the phase compositions and crystallinity of the zeolite sample. The XRD patterns were recorded with RIGAKUD/MAX diffractometer using CuKα radiation (40 kV and 40 mA) in General Directorate of Mineral Research and Exploration. X-ray traces were obtained for 2θ values from 5°-50°. In the XRD traces characteristic peaks of clinoptilolite of 9.1681 Å,

3,9750 Å, 3.4338 Å, 2.9852 Å, and 2.8087 Å were observed (Fig 2). Beside these, quartz and heulandite peaks were also seen. X-Ray Fluorescence analyses were performed to determine the elemental composition of zeolite sample by using SPECTRO IQ X-Ray Fluorescence in METU Mining Engineering Department. Sample was prepared by using the pressed powder technique with binder (a certain wax). XRF analysis showed that natural zeolite samples (clinoptilolite) have 75.68% SiO₂, 14.23% Al₂O₃, 0.68% Na₂O, 2.19% K₂O, 3.55% CaO, 1.60% MgO, 1.70% Fe₂O₃ and remaining 0.351% for other elements such as Ti, P, S. Si/Al mole ratio of zeolite was calculated from the result of XRF analyses as 4.52, which is within typical limits (4-5.25) for clinoptilolite [44]. According to results, theoretical cation exchange capacity of (TCEC) the clinoptilolite is 2.76meq/g, which was calculated as the sum of Na⁺, K⁺, Ca²⁺, and Mg²⁺ content of clinoptilolite. The contribution of each exchangeable ion to the exchange capacity are 0.22 meq Na⁺/g (7.96%), 0.468meq K⁺/g (16.94%), 1.27meq Ca²⁺/g (46.01%), 0.8meq Mg²⁺/g (29%). The BET specific surface area and pore size distribution analysis of zeolite was done via an automated gas sorption system (QUANTACHROME Autosorb Automated Gas Sorption System) using N₂ gas as adsorbate in METU Central Laboratory. Average pore diameter, density, and surface area of zeolite were calculated as 0.041µm, 2.10g/cm³, and 40.79m²/g respectively.

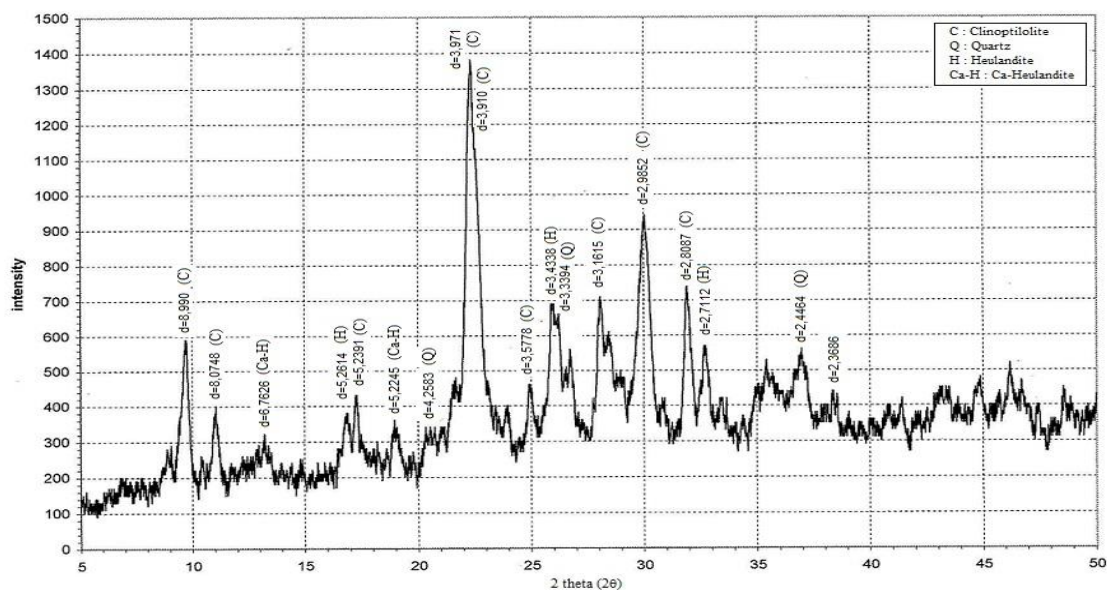


Figure 2. The XRD Pattern of Clinoptilolite

4.2. Effect of contact time and initial dye concentration

The effect of contact time and initial dye concentration on natural zeolite were investigated in the range of 50-300mg/l of initial dye concentration at 30°C for each dye. It can be seen from Figure 3 that the amount of adsorbed Rhodamine B increase within the 60 minutes and then it approaches equilibrium after 80 min. Figure 4 shows that the amount of adsorbed methylene blue increase within 100 minutes and it reaches equilibrium after 150 minutes.

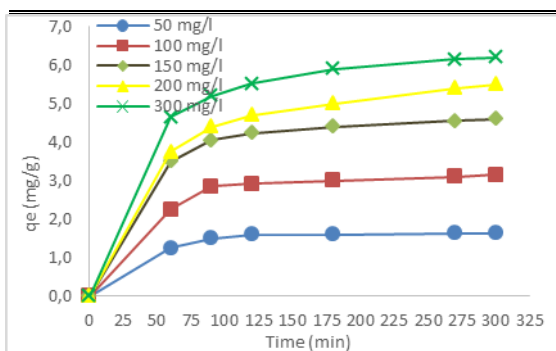


Figure 3. Effect of contact time and initial concentration of Rhodamine B on natural zeolite.

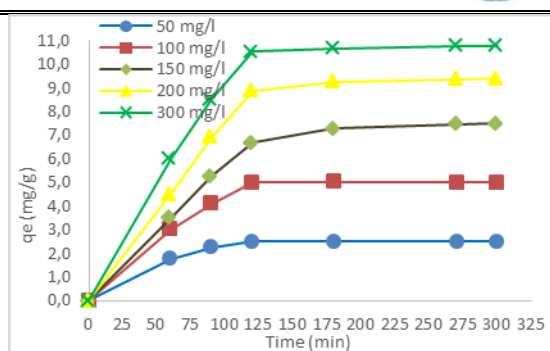


Figure 4. Effect of contact time and initial concentration of Methylene Blue on natural zeolite.

4.3. Adsorption Isotherms

The analysis requires equilibrium to better understand the adsorption process. In this paper, the Langmuir and Freundlich models were applied. An adsorption isotherm is characterized by certain constants which values express the surface properties and affinity of the adsorbent. It can also be used to find the adsorption capacity of adsorbent. The relative parameters were obtained according to the intercept and slope from the plots between $1/q_e$ versus $1/c_e$ and $\log q_e$ versus $\log c_e$ respectively. Figure 5 shows the adsorption isotherms of Rhodamine and Methylene Blue. The parameters obtained from isotherms are given in Table 1.

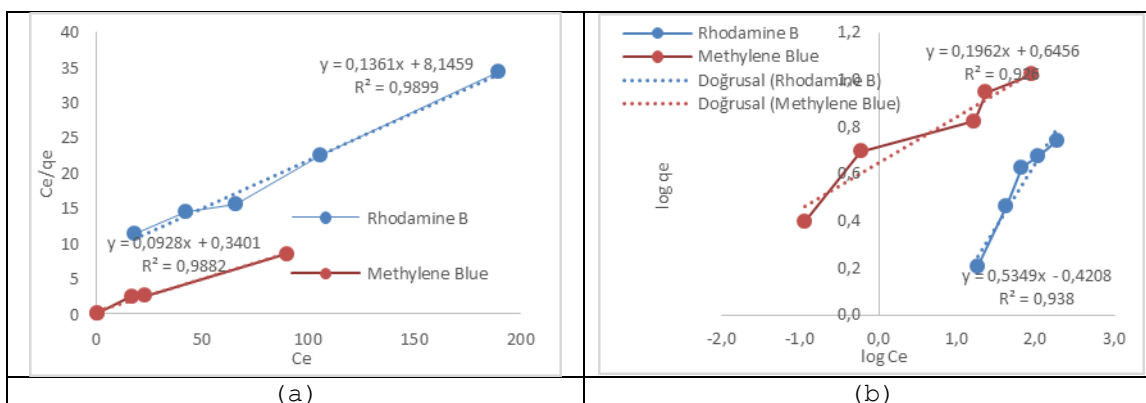


Figure 5. Adsorption isotherm models of Rhodamine B and Methylene Blue
 (a) Langmuir model (b) Freundlich model

Table 1. Langmuir and Freundlich adsorption constants of Rhodamine B and Methylene Blue

Dye	Langmuir Isotherm			Freundlich Isotherm		
	q_{max} (mg.g ⁻¹)	K_L (l.mg ⁻¹)	R^2	n	K_F (l.mg ⁻¹)	R^2
Rhodamine B	7.348	0.017	0.9899	1.87	0.379	0.938
Methylene Blue	10.776	0.273	0.9882	5.97	4.422	0.926

All values of R^2 in Table 1 were bigger than 0.9. So the two isotherms were all used to fit the experimental data. This showed that the adsorption process might be a heterogeneous adsorption. Langmuir constant, q_{max} , represents the monolayer saturation at equilibrium. The other mono-component Langmuir constant K_L indicates the affinity for the binding of basic dye. A high K_L value indicates a high affinity. The values of q_{max} for rhodamine B and methylene blue were obtained as 7.348 and 10.776 mg.g⁻¹ respectively. Freundlich model does not



describe the saturation behavior of the adsorbent as well as Langmuir model. Freundlich constant, n , is related to intensity of adsorption. If the value of n is in the range $1 < n < 10$, the adsorption is favorable. As seen from Table 1, the value of n for rhodamine B was 1.87 and for methylene blue was 5.097. Another Freundlich constant, K_F , has been used as a relative measure of adsorption capacity. K_F values for rhodamine B and methylene blue obtained from experiments were 0.379 and 4.422 mg.l^{-1} respectively.

4.4. Adsorption Kinetics

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption. The modeling of the kinetics of adsorption of basic dyes on natural zeolite was investigated by two common models, namely, Lagergren pseudo-first-order and pseudo-second-order model. The constants of pseudo-first-order kinetic model (k_1 and q_e) and pseudo-second-order kinetic model (k_2 and q_e) are presented in Table 2 along with the corresponding correlation coefficients.

Table 2. Pseudo first order and second order kinetic models for Rhodamine B and Methylene Blue

Dye	Pseudo First Order Kinetic Model			Second Order Kinetic Model		
	k_1	$q_{e,cal}$	R^2	k_2	$q_{e,cal}$	R^2
Rhodamine B	0.00069	4.93	0.9503	0.0042	6.16	0.9995
Methylene Blue	0.0052	5.73	0.7185	0.0012	11.83	0.9581

As seen from the Table 2, the correlation coefficients of first order kinetic model are lower than that of second order. The calculated q_e deviates much from the experimental value, which indicates the inapplicability to the first order kinetics. On the contrary, the second order kinetic model shows much better correlation coefficients. Also the calculated q_e is higher from the experimental value. Thus, it is derived that the adsorption of basic dyes on natural zeolite follows the pseudo second-order kinetics.

5. CONCLUSION AND RECOMMENDATIONS

A natural zeolite has been tested for adsorption of basic dyes, rhodamine B and methylene blue. It is found that zeolite exhibits higher MB adsorption than RB due to the difference in molecular size. The adsorption capacities of rhodamine B and methylene blue were obtained as 7.348 and 10.776 mg.g^{-1} respectively. The Langmuir and Freundlich models can also describe well the adsorption isotherm. Kinetic calculations indicate that the adsorption of basic dyes on natural zeolite follows the pseudo second-order kinetics.

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