Journal of Nanopores Systems

Original Research Paper

Kinetic and Thermodynamic studies of Elimination of methylene blue dye by nano clinoptilolite zeolite from aqueous solutions

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Article history
Received: 14 October 2024
Revised: 29 April 2025
Accepted: 2 May 2025

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Abstract: In this study we investigate kinetic and thermodynamic parameters for elimination of methylene blue (MB) dye from aqueous solution by application nano clinoptilolite zeolite (NCZ). The effects of some important parameters such as kinetic and thermodynamic parameters were studied. In order to determine mechanism of adsorption processes such as chemical reaction and removal, the pseudo-first-order adsorption and the pseudo-second-order were used to examine the experimental data. It was found that second-order kinetics model (r^2 = 0.9994) is better than first-order kinetics model (r^2 = 0.1688). The difference between experimental and calculated qe shows no applicability of the pseudo-first order model in predicting the kinetics of the MB adsorption onto the NCZ. The change in Gibb's free energy (ΔG^0), the change in entropy (ΔS^0) and the change in enthalpy (ΔH^0) were also investigated and calculated for this removal. This process had some negative changes in Gibb's free energy (ΔG^0 =-6.627 KJ) and positive in enthalpy (ΔH^0 =+45.061 KJ) and entropy (ΔS^0 =+173.54 KJ). This adsorption was an endothermic and spontaneous process.

Keywords: Nano clinoptilolite, Zeolite, Kinetic, Thermodynamic, Methylene blue

Introduction

Zeolites

Zeolite is a mineral that is mainly composed of porous aluminosilicates with a variety of structures, and its main commercial use in industries is as a surfactant. The name zeolite is a combination of two Greek words (zeo) means boil and (lithos) means stone, by together it means boiling stone. This name was due to the foaming of zeolite due to heat. Zeolites are crystalline solids with fine pores. The bond of water molecules in the network of these minerals is weak and can lose their water due to temperature without leading to collapsing of the network structure, and this process is reversible.

Zeolites are in the form of a crystalline lattice consisting of oxygen and aluminum or silica that form a three-dimensional structure (Fig. 1-2). These materials have a three-dimensional lattice, that have a negative charge, and their general formula is $M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$, where and M is the n-valence cation.

To maintain the charge balance and neutrality of zeolite, the cations are exchanged in the system. Zeolites are widely used in industry to purify water as catalysts and to prepare advanced materials. The most important use of zeolite is in the production of clothes cleaners [1]. Zeolites are usually divided into two categories, natural and synthetic. The difference in use-case of synthetic and natural zeolites originates in their physical and chemical properties, which in turn is a function of the crystal structure and chemical composition of the zeolites.

Natural zeolites were initially identified as a sub-component but extensively in basaltic cavities, and their use in this way on industrial scales has been a difficult and exhausting operation. Clinoptilolite zeolite is one of the examples of natural zeolites, which is also the most abundant natural zeolite.

Fig. 1. Clinoptilolite

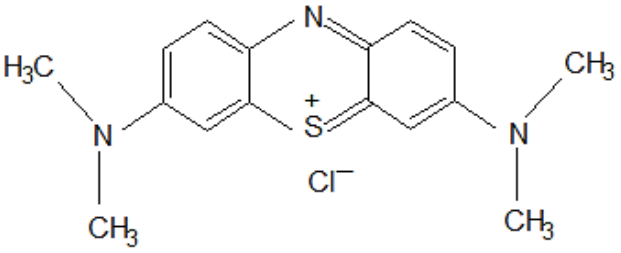

Fig. 2. Molecular structure of methylene blue (MB) dye

Clinoptilolite

Among the zeolites used, Clinoptilolite is one of the most important, most used and cheapest types of extracted natural zeolites. The Greek words (klinein) means to lie asleep and (pitilon) means feather. Clinoptilolite has cavities which its size is less than 2 nm, and a tetrahedral 3D structure in which silicon is found in the form of SiO_4 [2].

If the trivalent aluminum element in this structure replaces the trivalent silicon, three molecules of oxygen in the three corners of the quadruple building will be neutralized, and in one of the corners, an oxygen molecule with a negative charge remains free, this process causes the clinoptilolite molecule to become negatively charged, making it possible to bind to different types of cations. This process enables a feature in the structure of the zeolite called ion convection capacity or ion exchange capacity. This characteristic differs in different zeolites, and for clinoptilolite it is about 1.54 milliequivalent per gram (mEq/g).

There are also channels in the molecular structure of clinoptilolite that are naturally filled with water. If this structure is heated, the molecules dehydrate and their absorption increases. Additionally, the size and diameter of these channels allow passage for ions and small elements, and act as a trap for some large ions and most of the elements, locking them in cage-like lattices. Therefore, Clinoptilolite, has the ability to absorb heavy elements from the environment [3].

The general chemical formula of clinoptilolite is as follows:

$(K_2Na_2, Ca, Mg)_3Al_6Si_{30}O_{72}.24H_2O$

Clinoptilolite has many species, one of which is divided into different classes.

For example:

$(Na,K,Ca)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36}.12H_2O$

They are divided into groups with different structures, an example of which is shown in Figure 1.

Methylene Blue (MB) [4, 5]

Methylene blue is a type of aromatic heterocyclic chemical compound that acts as a redox identifier and demonstrates a different color (blue/colorless) in oxidized or reduced states according to the following semi-reactions:

$MB\ (ox) + 2H^+ + 2e \rightarrow MBH_2\ (red) \quad E^o = +0.1\ V$

$½\ O_2 + 2H+ + 2e \rightarrow H_2O \quad E^o = 0.815\ V$

$MBH_2(red) \rightarrow MB\ (ox) + 2\ H+ + 2e \quad E^o = -0.1\ V$

$½\ O_2 + 2H+ + 2e \rightarrow H_2O \quad E^o = 0.815\ V$

$MBH_2(red) + ½\ O_2 \rightarrow MB\ (ox) + H_2O \quad E^o = +0.715\ V$

Methylene blue takes the form of a dimmer in high concentrations and acidic environments, and its maximum absorption appears at shorter wavelengths. This compound is successfully used in medical science to treat carbon monoxide and potassium cyanide toxicity, as well as an antimalarial drug. In addition, it is also used in the textile industry with the aim of dyeing silk and wool fibers.

In various solutions the dyes create very vivid colors and have absorption in the visible-ultraviolet region. Therefore, spectrophotometry is introduced as the most common method for identifying and quantifying these compounds. The maximum absorption wavelength of methylene blue aqueous solutions is in the 660 nm region.

Surface Adsorption Kinetics

Examining of the mechanism and speed of reactions is one of the critical stages and is always given special attention during the absorption process. The adsorption process consists of four basic steps, which are:

1- Transferring the target soluble compounds to the adsorbent.

2. Penetration of the compounds into the liquid film that surrounds the adsorbent.

3. Intrusion of the compounds into the absorbent's cavities.

4. Absorption of the soluble compounds onto the cavities' surface.

In this process, one of the three (i) Mass Transfer, (ii) Diffusion, and (iii) Chemical Reaction stages will control the overall speed of adsorption. The study of kinetics provides a suitable basis for estimating the time required for the completion of the adsorption process, provides a detailed description of how a reaction is carried out based on the behavior of the particles, facilitates determining the mechanism of adsorption (both chemical and physical), and designing optimal adsorption systems which provides the highest yield in removal of pollutants in the shortest time.

Over the past years, extensive efforts have been made to provide appropriate kinetic equations to justify the mechanism of adsorption of materials on solid surfaces in the solid-liquid systems. Among many different models that have been proposed, we can mention the first-order Lagergren, the second-order Ho Mc Kay, the interparticle diffusion, and Elovitch Kinetics models [6].

It should be noted that if the kinetic equation is dependent on the concentration of the solution and the adsorption capacity, and so, in order to differentiate the equations, instead of the phrase first or second order, the term pseudo first order or pseudo second order is used. Because in the first case, the reaction speed constant depends solely on temperature and is independent of the concentration or other test conditions, while in pseudo first and second order, the speed constant will additionally be affected by the lateral conditions of the reaction. In this project¬, we will study the pseudo-first-order and pseudo-second-order models.

Lagergren's pseudo-first-order kinetic model

In 1898, Lagergren presented the pseudo-first-order equation to explain the adsorption kinetics of oxalic acid and malonic acid on charcoal. This equation was presented as follows:

$$\frac{dx}{dt} = k_1(X - x) \quad (1)$$

X and x (mg/g) represent the adsorbent's adsorption capacity at equilibrium and the t moment (min), respectively. While k1 (1/min) represents the speed constant of the pseudo first-order adsorption. Through integrating equation (1-10) and applying the extreme conditions (t=t, t=0, x=0, x=x, x=X) we'll have:

$$\ln(\frac{X}{X-x}) = k_1 t \qquad x = X(1 - e^{-tk_1}) \quad (2)$$

The linear form of the equation (2-8) will be as follows:

$$\log(X - x) = \log(X) - \frac{k_1}{2.303} t$$

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

The most common form of the Lagergren equation is seen in the form of equation (2-10). In this regard, qe and qt (mg/g) respectively represent the adsorption capacity at the moment of equilibrium and t (time).
By drawing the per t diagram we can achieve k_1 (slope) and Qe (y-intercept).

If the adsorption kinetics follows the pseudo-first-order equation, then it can be claimed that the speed of the adsorption process is controlled by the interparticle diffusion phase [7, 8 and 9].

Pseudo-second-order kinetic model

If the following reactions are single-step, then the second-order speed equation can be written in two ways:

$$2A \rightarrow P \qquad r = k_2[A]^2 \quad (5)$$

$$A + B \rightarrow P \qquad r = k_2[A][B] \quad (6)$$

In this study, we only look at the first type of speed equation, which is mathematically simpler. As mentioned earlier, the adsorption capacity is proportional to the number of sites occupied by the adsorbent surface, therefore, the differential form of the second-order kinetic equation can be represented as following after a rearrangement:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt \quad (8)$$

k_2 is the speed constant of the pseudo-second-order equation (g/mg min), qe is the amount of the compound absorbed at equilibrium (mg/g), and qt is the value of species absorbed at the t moment. By integrating the relationship (8) under extreme conditions (t = 0 to t = t and qt = 0 to qt = qt), the pseudo-second-order equation will be obtained as follows:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_c} + kt \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

By drawing a t/qt diagram in t, the value of k_2 and qe can be obtained. If the adsorption kinetics follow the quadratic equation, then it can be claimed that the adsorption process has been done chemically and the chemical reaction is considered as the slowing down step of the reaction [10, 11].

Thermodynamics of Surface Adsorption

Thermodynamics is a branch of chemistry that studies the changes in energy along with chemical and physical changes. The most important aspect of thermodynamics laws is that it allows appropriate prediction of chemical reactions under certain conditions.

Investigation of thermodynamic parameters during the adsorption process provides an appropriate understanding of the adsorption mechanism and behavior of compounds in equilibrium. In other words, by applying thermodynamic equations, we can understand the absorbate-absorbent interaction, and in turn, design the optimal conditions for maximum efficiency. In the adsorption system, the most important thermodynamic factor to predict the progress of the reaction is the study of standard free energy (ΔG^0). On the other hand, calculating the enthalpy changes of the reaction standard (ΔH^0) provides valuable information about its exothermic or exothermic nature.

In order to establish a logical relationship between these two parameters, we define Gibbs free energy with the following equation:

$$G = H - TS \quad (11)$$

For a chemical equation that takes place at constant temperature and pressure, we have:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

In the (12) equation ΔG^0, ΔH^0 and $\Delta S0$ represent the changes in standard Gibbs free energy (KJ/mol), standard enthalpy changes (KJ/mol), and standard entropy changes (k J/mol), respectively. Where T would be the Absolute Temperature (K).

In a spontaneous change, ΔG^0 is negative, and the free energy of the system decreases. If ΔG^0 is zero, the system is in equilibrium. In the case of non-spontaneous reactions, ΔG^0 is a positive reaction, and so, the reversal reaction will be spontaneous. It should be noted that reactions usually tend to reach the minimum in energy.

Therefore, if the value of ΔH^0 is negative, the reaction is exothermic and the ground for spontaneous reaction will be favorable, the increase in entropy (disorder) of the system is also one of the parameters that leads to a negative value of ΔG^0. Free energy changes can be used to evaluate the equilibrium state of a chemical reaction. Consider the following chemical reaction:

$$aA + bB \leftrightarrow cC + dD$$

The free energy change of the above equation is:

$$\Delta G = \Delta G^0 + RT \ln \frac{(a_D^d)(a_C^c)}{(a_B^b)(a_A^a)} \quad (13)$$

The above fraction contains the activity (a) of the substances participating in the reaction. Since in equilibrium $\Delta G=0$ and the activities related to the equilibrium conditions become applicable, the equation (13) is represented as follows.

$$\Delta G^0 = -RT \ln K_c \quad (14)$$

In equation (18-2), Kc is the thermodynamic equilibrium constant, R is the ideal gas constant equal to 8.314 J/mol k, and T is the absolute temperature (K). By equalizing the equations (12) and (14), the Vant Hoff equation can be obtained:

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad , \quad K_c = \frac{q_e}{c_e} \quad (15)$$

Here, qe represents the adsorption capacity at the moment of equilibrium (mg/g) and Ce is the equilibrium concentration of the absorbed species (mg/L) in the solution. By drawing the ln Kc diagram with respect to 1/T, the values of enthalpy and entropy variations can be obtained from the slope and width from the source [12] respectively.

Experimental Methods

All chemicals used were analytical reagents grade and prepared in distilled water. Nano clinoptilolite zeolite is a mineral material that obtained from mine in khorasan province. In order to obtain nano size of zeolite, ball mill should be used.
Absorbance measurements were carried out on a single beam Perkin-Elmer UV–Vis spectrophotometer with a 1 cm cell was used for measuring all of absorption data.

Preparation of Nano-Clinoptylonite

100 g clinoptillonite with 10 balls with a diameter of 10 mm is placed in a container or cup with a capacity of 500 ml, in this case, the ratio of balls to powder is 0.1. Then, the circumference of the ball mill is set to 400 rpm and the time is set to 40 minutes.

The material of the cup-shaped containers used in the stainless-steel wing is zirconium oxide coating and the material of the orbs is also zirconium oxide.

Effect of contact time and study of adsorption kinetics

To study the effect of contact time, 0.5 g of the adsorbent was placed in pH=2 for 2-20 minutes in contact with 25 mL and 10 mg/L of the dye. After straining the solution and measuring the residual concentration of the dye, the optimal time to reach equilibrium can be estimated.
For kinetic studies, Lagergren's pseudo-first-order and Ho McVey's pseudo-second-order equations were used. The results are based on Charts (Figures 3 and 4) and Table 1.

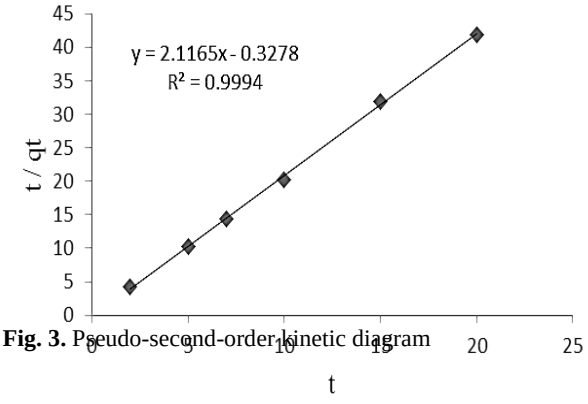

Fig. 3. Pseudo-second-order kinetic diagram

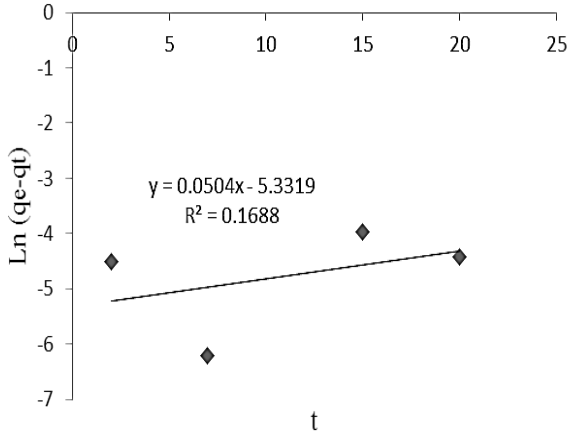

Fig. 4. Pseudo-first-order kinetics diagram

Table 1. Methylene Blue Adsorption Kinetics Parameters

T(K)	Pseudo-First Order				Pseudo-Second Order			
	q_e[a]	K_1	q_e[b]	r_1^2	q_e[a]	K_2	q_e[b]	r_2^2
298	0.0048	-0.0504	0.478	0.1688	0.472	-13.69	0.478	0.9994

[a] Calculated [b] Experimental

Effect of temperature and thermodynamic study of methylene blue adsorption

Temperature is one of the valuable criteria that is analyzed in order to understand the thermodynamics and processes of chemical reactions and provides useful information about the Gibbs standard free energy changes (ΔG^0), standard enthalpy changes (H0 ΔH^0) and standard entropy changes (ΔS^0) of the system. In order to investigate the effect of temperature on the adsorption capacity and calculate the above variables, the adsorbent value of 0.5 g with 25 mL and a constant concentration of each dye (10 mg/L was called at different temperatures (298 K, 308 K, 318 K). After 10 minutes, the amount of dye in the solution and the absorption efficiency and capacity were calculated, and the results were placed in the relevant thermodynamic equations. The results are shown in Table 2 and Figure 5.

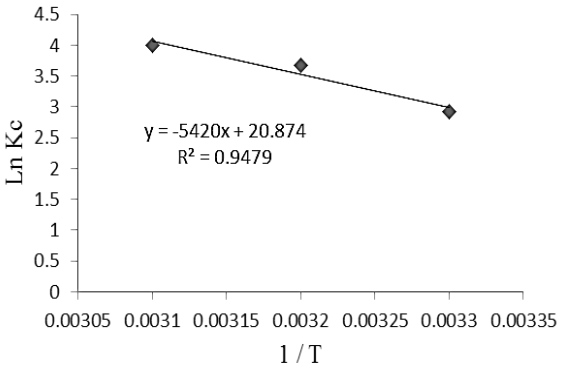

Fig. 5. Vantt hoff equation for removal of MB by NCZ

Table 2. Thermodynamic parameters for adsorption of MB onto NCZ

T (K)	ΔG^0 (KJ)	ΔH^0 (KJ)	ΔS^0 (J)
298	-6.627		
308	-8.361	45.061	173.54
318	-10.096		

Results and Discussion:

Effect of contact time on methylene blue uptake

The contact time of the analyte and the adsorbent is one of the basic parameters in the study of the adsorption process and evaluation of the adsorbent capability and their comparison with each other. Certainly, achieving the desired adsorption capacity in the shortest time and establishing balance is one of the prominent features of a valuable adsorbent. The results show that we have the highest absorption percentage in in 10 minutes with pH=2. According to the results, Absorption is fast in the first 10 minutes and slows down over time. The results are shown in Table 3 and Figure 6.

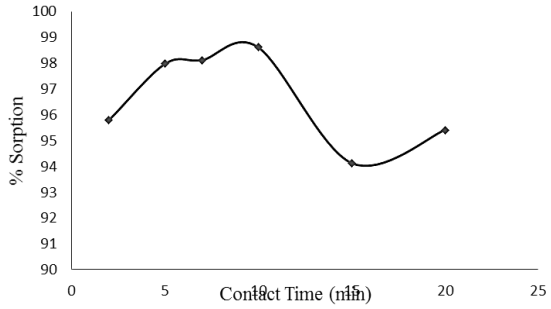

Fig. 6. Effect of Contact Time on MB Adsorption by NCZ

Table 3. Effect of Contact Time on Methylene Blue Adsorption with NCZ

Contact Time (Minutes)	2	5	7	10	15	20
Absorption Percentage	95.79	97.97	97.48	98.61	94.13	95.41
qt (mg/g)	0.478	0.489	0.487	0.493	0.470	0.477

The effects of temperature and thermodynamic study on methylene blue adsorption

Temperature is one of the valuable metrics that is analyzed in order to understand the thermodynamics and processes of chemical reactions and provides useful information about the free energy changes of the Gibbs standard ΔG^0, the enthalpy changes of the standard ΔH^0, and the entropy changes of the ΔS^0 standard of the system. The results illustrated in Table 2 show that the adsorption process is spontaneous because the values of ΔG^0 are negative. This is clearly visible during the experiments. On the other hand, the adsorption process is exothermic because the ΔH^0 is positive. As an undesirable factor, it overshadows the process of spontaneity of the reaction. Adsorption is also associated with the increased entropy and irregularity because the ΔS^0 is positive. This is due to the congestion of colored molecules on the adsorbent surface.

Table 2 shows that the adsorption process is spontaneous because the values of ΔG^0 are negative.

The Effect of Contact Time and Kinetic Study on Absorption

The time required to reach equilibrium plays an important role in adsorption processes and provides valuable kinetic information. By obtaining this information, it is possible to understand the speed and mechanism of chemical reactions and after determining the controlling stage of the process, the corresponding kinetic pattern can be estimated and appropriate modifications can be applied to improve the speed of adsorption.

Adsorption kinetics is one of the critical factors in the selection of the appropriate adsorbent and provides valuable information about the mechanism and factors affecting the speed of the adsorption process. The adsorption process of methylene blue showed that it follows pseudo-second-order kinetics. This can be seen from the computational and experimental qe values in two pseudo-first-order and second-order states.

The results of kinetic calculations show that the process of methylene blue adsorption by clinoptilolite nano-zeolite follows the pseudo-second-order kinetics. This can be seen from the computational and

experimental qe values in the first and second pseudo-order cases, and their correspondence is very close in the second pseudo-order while they are significantly different in the first-pseudo-order. This is easily seen in the r^2 values of the figures.

Conclusions

The difference between experimental and calculated qe shows no applicability of the pseudo-first order model in predicting the kinetics of the MB adsorption onto the NCZ. Because of that, removal the pseudo-second order model is better than the pseudo-first order model. Thermodynamic calculation carried out the sorption of MB by NCZ was an endothermic process and this process had negative changes in Gibb's free energy and spontaneously.

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