

Adsorption Kinetic of Direct Dyes from Aqueous Solution on Zeolite LTA

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ABSTRACT

The analysis of adsorption relies on the equilibrium state of the mass. It is the relationship between the concentration of the adsorbate in the liquid phase and the concentration of the adsorbate in the solid phase. The relationship is written as an isotherm of the adsorption graph. Zeolite LTA was used as adsorbent to remove dye from solution in a batch adsorption system. The adsorption isotherm showed that the Langmuir model was better than the Freundlich model. Adsorption of adsorbate consists of a diffusion process through the fluid layer around the adsorbent material and the diffusion in the cavity. This research found that a pseudo-second order model was a better fit to measured adsorption data.

Keywords: Adsorption; Kinetic; Direct dye; Zeolite LTA

1. Introduction

At present, the environmental problems, especially water pollution, caused by various industrial growth have become more severe. The textile industry, a relatively high growth industry, has developed both in the production step and with higher competition to increase the amount and

numbers of products. Water is an important factor that must be used in conjunction with raw materials in every production process. In addition to the textile industry, there are other industries that use dyes in production, including dyeing, printing, photography, plastics and others [1]. As a result, the use of dyes has increased and these dyes may cause

water environmental problems [2]. The dyeing industry helps change the raw materials of textiles, such as raw yarn and cloth, into finished materials using large amounts of water. The production process uses chemicals and dyes that improve the properties of the fibers, by using water to clean the fabric in various steps. Wastewater from dyeing is mostly released into ponds. The dye cannot be removed from the waste water, because the pigment particles are very small and in forms that cannot be precipitated naturally in water [3]. If the wastewater is not treated to meet the standards for release into natural water sources, the quality of the water source will deteriorate and block the sunlight passing through the water. Blocking photosynthesis of aquatic plants reduces the amount of dissolved oxygen (DO) and affects the ecology in water sources [4]. The wastewater from dyeing must be considered. The effluent is colored and the pH is quite high. If released into public water sources, it may kill aquatic organisms. Colored particles may block the transmission of light into the water and photosynthesis in aquatic plants and algae will be reduced. Water sources that lack oxygen affect the livelihoods of aquatic organisms. Also, the color of the released effluent released generally causes the water source to be unpleasant to viewers. There are many methods for removing color from wastewater emitted by dyeing plants, such as coagulation [5], chemical oxidation [6], ozone [7] and biological treatment [8], membrane-based processes [9] and adsorption [10]. Determining which method to choose depends on various aspects, for example, the properties of raw wastewater, the quality of water required, area available in the treatment plant, treatment costs and the possibility of reusing the waste.

Adsorption is effective in wastewater treatment and it provides some flexibility in designing and controlling the system. The procedure is not complicated and the control system is easier than chemical sedimentation systems and can also be reused after

desorption. Separation of adsorbed substances from the adsorbent makes it easier to get rid of pollutants in the next step [11-13]. Zeolites are crystalline aluminosilicates consisting of molecular-sized pores and channels. These micropore structures have a three-dimensional framework of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra, connected by oxygen atoms. The size of pores in the zeolite material and its adsorption characteristics are influenced by the silicon to aluminum ratio and the number of units within a ring [14-16]. Zeolites have negative charges resulting from the isomorphous substitution of Al^{3+} for Si^{4+} and these negative charges are neutralized by adsorption of cations. Zeolite cation exchange properties have been used in several environmental applications, for example, removal of ammonium and heavy metals [17-21].

Zeolite NaA, with an LTA (Linde Type A) framework, has a silicon to aluminum ratio of ~ 1.0 , which is considerably lower than clinoptilolite. An LTA ideal chemical composition is $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$ [16]. Zeolite LTA can be synthesized using different starting materials as the source of Al and Si [22]. Bukhari et al. showed that zeolite LTA could effectively remove heavy metals from contaminated wastewater [23]. Here, we studied the kinetics of direct dye adsorption with Zeolite LTA by determining the isotherms and the reaction order.

Two commonly used dyes were used to test the efficiency of zeolite removal. Both were water soluble 'direct' dyes, which can be applied to a wide variety of materials. Direct dyes are generally anionic salts containing two azo groups which can effectively bond to cellulose or protein fibers.

2. Materials and Methods

2.1 Materials

Dyes were purchased from Sivasumpan Company, Bangkok. Zeolite

LTA was obtained from Thai Silicate Chemical Co., Ltd. All other chemicals were of analytical grade. Stock solutions were prepared in deionized water and the solutions for adsorption tests were prepared by dilution. Morphology and elemental composition of Zeolite LTA were examined by scanning electron microscope (SEM); model LEO 1455 VP, Germany, coupled with energy-dispersive X-ray (EDX Oxford, ISIS 300, England) analyzer, Oxford Instruments. Powder X-ray diffraction (XRD) data for phase identification were collected by Bruker AXS D8 Advance, Germany automatic powder diffractometer, with Cu-K α filtered radiation used to record the diffraction spectra. Step-scan data were recorded in the angle interval 5 $^{\circ}$ -80 $^{\circ}$ (2θ) with a step of 0.02 $^{\circ}$ (2θ) and accounting time of 1 s per step.

2.2 Adsorption studies

Adsorption was tested in a batch procedure. Kinetic experiments were carried out by shaking 2.5 g of adsorbent with 100 mL of dye solutions with initial concentration of 100-500 mg/L in a conical flask at room temperature (25 \pm 2 $^{\circ}$ C) in a shaker, operated at 160 rpm for 90 min. The concentration of dye after adsorption was analyzed using a UV spectrophotometer (GENESYS 20) by measuring at the wavelength of maximum absorption at 510 nm for red direct dye and 600 nm for blue direct dye. The concentration (mg/g) of adsorbent was calculated from [24]:

$$q_e = \left(\frac{C_o - C_e}{w} \right) \times V, \quad (1)$$

where C_o and C_e (mg/L) are the liquid-phase concentration of direct dye initially and at equilibrium, respectively, V (L) is the volume of direct dye solution and w (g) is the mass of dry zeolite LTA used. Note that, in this and all following equations and plots, SI units were used. Batch kinetic studies by procedures of kinetic experiments were

basically identical to those of the equilibrium tests.

2.2.1 Adsorption isotherms

Experimental isotherm data collected for the adsorption of zeolite LTA were fitted with the Langmuir and Freundlich adsorption isotherm models.

Langmuir model

The Langmuir isotherm assumes monolayer adsorption onto a surface of the adsorbent, and carries equal numbers of molecules with no interaction between adsorbate molecules [25]. If dye adsorption follows the Langmuir model, it can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{K_L q_o} \frac{1}{C_e}, \quad (2)$$

where q_o is the maximum amount of dye per unit weight of zeolite LTA to form a complete monolayer on the surface (mg/g), C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g) and K_L is the Langmuir isotherm constant (L/mg).

Freundlich model

This phase of the study tested the Freundlich equation or Freundlich adsorption isotherm, assuming that it describes equilibrium on heterogeneous surfaces and hence does not assume monolayer capacity and is used to describe the adsorption [26]. It is modeled by this equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (3)$$

where K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity of adsorbents, respectively, and $1/n > 1$, the change in adsorbed dye concentration is greater than

the change in the dye concentration in solution was calculated [24].

2.2.2 Adsorption kinetics

The solute uptake rate, which determines the equilibrium time, required for completion of adsorption, may be determined from kinetic analysis. To determine the mechanism of dye adsorption by zeolite LTA, two well-known kinetic models, pseudo-first order and pseudo-second order kinetic models were considered.

Pseudo-first order kinetic model

A pseudo-first order model is the simplest model describing the kinetics of a liquid-solid phase, based on the adsorption capacity. The pseudo-first-order model is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (4)$$

where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time t (min), and k_1 is the pseudo-first-order rate constant. The values of q_e and k_1 , governing the sorption of dye from aqueous solution onto zeolite LTA, were determined from the intercept and slope of the plot of $\log(q_e - q_t)$ versus t [27].

Pseudo-second order kinetic model

The main assumptions for the pseudo-second-order rate equation, were that the rate limiting step is chemisorption, i.e. the removal from a solution is due to physicochemical interactions between the two phases [28], and that the adsorption follows the Langmuir equation [27]. Therefore, the pseudo-second-order equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (5)$$

where, k_2 is the pseudo-second-order rate constant [27], determined from a plot of t/q_t versus t .

3. Results and Discussion

3.1 Morphology of zeolite LTA

The catalyst was observed using a Scanning Electron Microscope. The SEM image showed the presence of crystals which have crystalline angles that corresponded with sharp peaks in the XRD spectrum having the crystalline attributes of standard zeolite LTA-see Fig. 1.

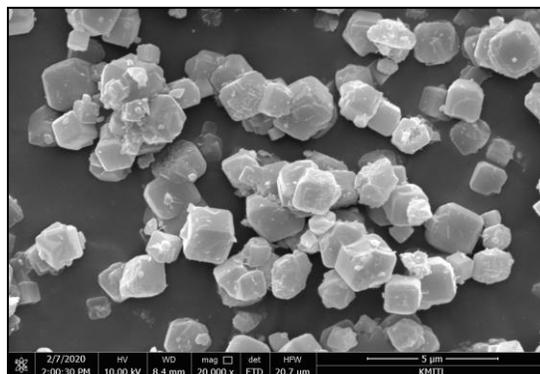


Fig. 1. SEM images of zeolite LTA.

3.2 Composition of zeolite LTA

The chemical composition of zeolite LTA is shown in Table 1. The main component was oxides of silicon, but they contain aluminium, carbon, sodium and rubidium impurities.

Table 1. Chemical composition of zeolite LTA.

Component	%weight
Si	44.11
Al	12.36
C	14.05
Na	12.03
Rb	17.44

3.3 Diffraction of zeolite LTA

X-ray diffraction (XRD) spectra of a sample was recorded and is shown in Fig. 2. The identifications of different crystalline phases were realized by using diffraction pattern files provided by Specimen. It was clearly seen that diffraction peaks exhibit some degree of crystallinity. They are shown and compared to the pattern of standard zeolite LTA in Fig. 2.

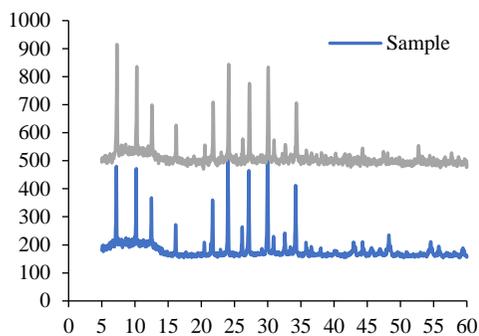


Fig. 2. XRD patterns of zeolite LTA.

3.4 Adsorption isotherms

Isotherms of dye adsorption using zeolite LTA as an adsorbent assuming Langmuir (Fig. 3) and Freundlich equations (Fig. 4) are shown below. Parameters obtained from both models are shown in Table 2. The Langmuir model ($R^2 = 0.8787$ for red dye, 0.9856 for blue dye) clearly fits better than the Freundlich model. Thus, we concluded that the adsorption is a monolayer and that available sites on the zeolite LTA adsorbent were not fully occupied [29].

3.5 Adsorption kinetics

The pseudo-first-order kinetic model for the dye adsorption was plotted as $\ln(q_e - q_t)$ vs. t , in Fig. 5. The kinetics using a pseudo-second-order model are shown in the Fig. 6 plot of t/q_t vs. t . The k_2 and q_e values from the regression are shown in Table 3. Fitting the data to the second-order model leads to $R^2 = 0.9977$ and 0.9975, showing that the pseudo-second-order kinetics led to better correlation coefficients, meaning that chemisorption takes part in the adsorption process. Once the sorption is exhausted, the uptake rate is controlled by the rate of intra particle diffusion [30].

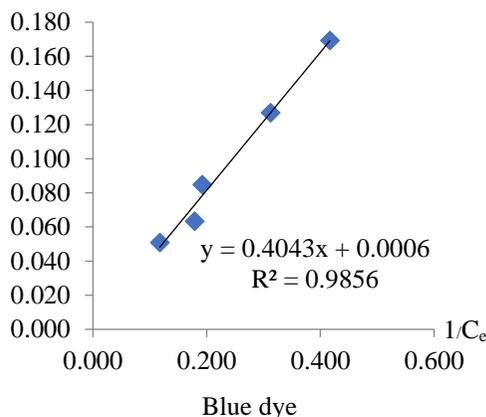
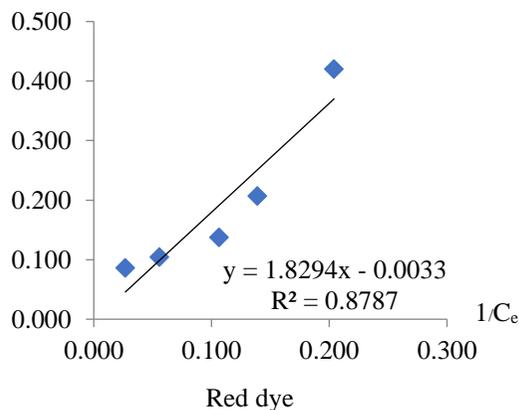


Fig. 3. Langmuir isotherms for dye adsorption on zeolite LTA.

Table 2. Parameters for Langmuir and Freundlich models.

Direct dye	Langmuir model			Freundlich model		
	q_0	K_L	R^2	K_F	$1/n$	R^2
Red dye	303	0.0018	0.8787	1.07	0.7126	0.8232
Blue dye	1667	0.0015	0.9856	2.54	0.9784	0.9708

Table 3. Kinetic parameters for the adsorption of dyes by zeolite LTA.

Direct dye	Pseudo-first order			Pseudo-second order		
	q_e	k_1	R^2	q_e	k_2	R^2
Red dye	0.6445	-0.0072	0.3572	27.1003	0.0625	0.9977
Blue dye	0.2820	-0.0170	0.1409	26.0417	0.0309	0.9975

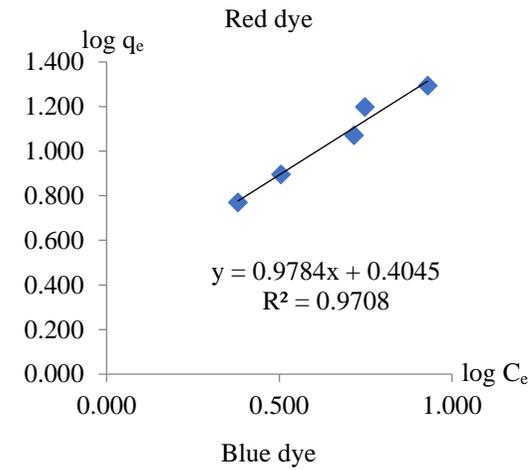
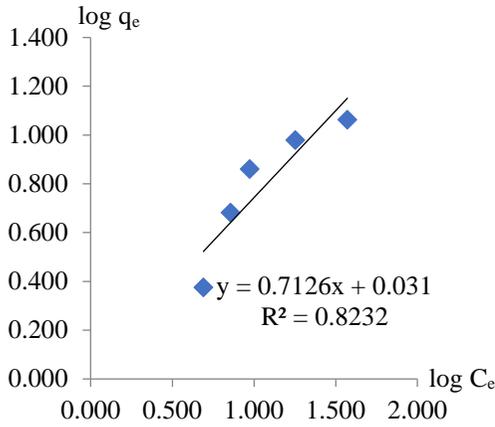
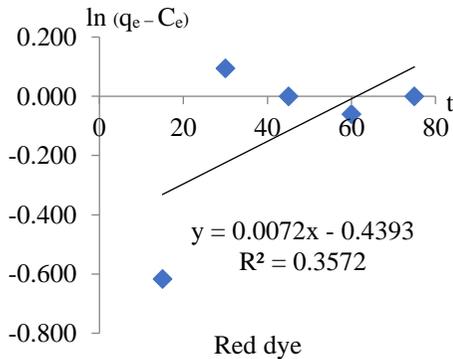


Fig. 4. Freundlich isotherm for dye adsorption on zeolite LTA.



4. Conclusion

Adsorption of both dyes with zeolite LTA was found consistent with Langmuir model and adsorption kinetics follow a pseudo-second-order equation. Our data showed that zeolite LTA provided sufficient

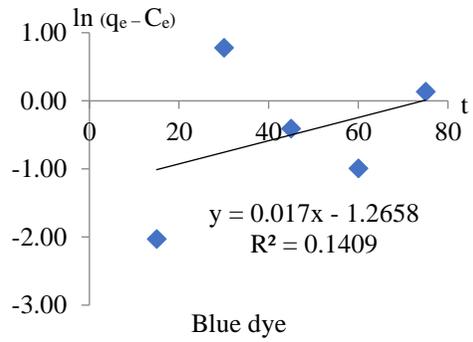


Fig. 5. Pseudo-first-order model of dye adsorption.

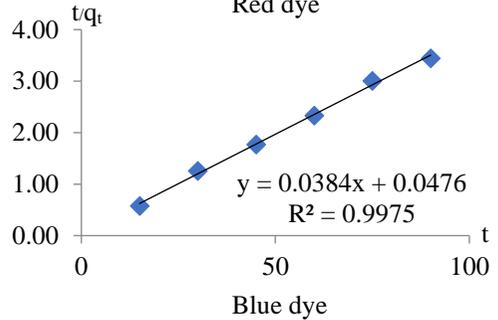
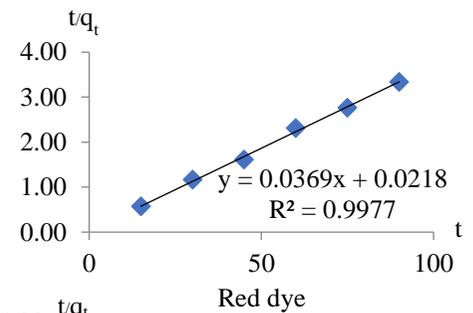


Fig. 6. Pseudo-second order model dye adsorption.

adsorption sites to remove up to ~26 mg of dye per gram of zeolite and reduce the dye concentration to acceptable levels. Thus, zeolite can effectively reduce pollution problems caused by several types of dyes. The measured rate constants enable us to infer how fast the waste water can flow over the adsorbent for any given quantity of adsorbent. From our data, a full economic model, including needed adsorbent quantities and allowable flow rates, can be built to achieve satisfactory results.

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