

ADSORPTION KINETICS OF TARTRAZINE ON CHITOSAN: COMPARISON OF LINEAR AND NON-LINEAR METHODS

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ABSTRACT

Adsorption kinetics for tartrazine on chitosan have been done at optimum pH to determine the kinetically dimensions, to compare the linear and non-linear methods and to predict a mechanism of adsorption. The chitosan which used is the product of chemical deacetylation from commercial chitin. Tartrazine can be adsorbed on chitosan at an optimum pH of 9.0. At this pH, the adsorption systems followed the nonlinear method of pseudo-first-order kinetics model with the adsorption rate constant of 0.01821/ min and the adsorption capacity of 2.682 mg/g. The adsorption mechanism that occurred in this process was studied using the diffusion film from the beginning until the equilibrium was reached.

Keywords: Adsorption Kinetics, Chitosan, Nonlinear Method, Tartrazine

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INTRODUCTION

Dyes are commonly applied to increase the attractiveness and packaging of the food, medicine, cosmetics, children's toys, and electronics industries. The use of dyes in the Indonesian industry will continue to grow along with the establishment of five prioritized manufacturing sectors by Indonesia Government through Making Indonesia 4.0, including the food and beverage industry, textile and clothing, automotive, electrical and chemical.¹ For the Asian region, Indonesia is the third-largest user of dyes, after China and India. Indeed, the waste will be generated and can inhibit the sunlight transmission leading to the reduction of photosynthetic activity, particularly for the living organism on the bottom of the water body.² Besides, the presence of dyes and the degradation products can be toxic and induce the gene mutations.³ The waste will also cause aesthetic problems in the aquatic environment. In some cases, the low concentration of dyes, even less than 1 ppm, can provide enough color.⁴ This problem is getting worst since some dyes are biologically difficult to decay. Therefore, the removal of dyes is highly required.

The conventional methods to remove dyes from industrial waste involve various techniques such as biological treatment, membrane technology, coagulation, and oxidation.^{5,6,7} Adsorption is a good alternative method to overcome dye contamination.^{2,3,8} The process will be more effective and efficient if the adsorbent is appropriate and is obtained from the waste of other processes. Bhatia et al⁷ in his review discussed various inexpensive adsorbents from agricultural waste to adsorb dyes. Chitin (Fig.-1a) which is the abundant biopolymer in nature after cellulose and chitosan derivatives (Fig.-1b) is an alternative adsorbent that has been widely employed to adsorb phenol^{9,10}, heavy metals¹¹⁻¹⁵, and dyes.^{16,17-21} Besides the thermodynamic aspects such as adsorption isothermal, the kinetic study should be also evaluated to determine how quickly the adsorption process occurs, the factors that affect the adsorption rate, and the mechanism of the adsorption process.²²

Tartrazine (Fig.-2) is an azo dye that is still widely used in food, candy, medicine, cosmetics, textiles, and electroplating.¹⁹ Tartrazine can cause allergic problems, poisons, trigger hyperactivity, and behavioral problems. It also causes asthma, migraines, eczema, thyroid cancer, and lupus.²³ According to Kumar²⁴, the pH of wastewater is a substantial factor in the adsorption process dyes on chitosan since amino groups will be protonated at low pH so that they can be attacked by the anionic dyes. In this study, the kinetic

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adsorption of tartrazine dyes on chitosan obtained from the deacetylation of commercial chitin will be reported. The comparison between linear and nonlinear kinetics methods will be also evaluated. To date, the approach used in solving the problem of adsorption kinetics is a linear method which is the result of the transformation or restoration of the nonlinear kinetics equation. In fact, the data processing with linear equations as a result of the transformation from nonlinear equations will give structural errors between the actual results and the calculated results and ignore the various errors and normal assumptions of the least-squares standard.^{25,26}

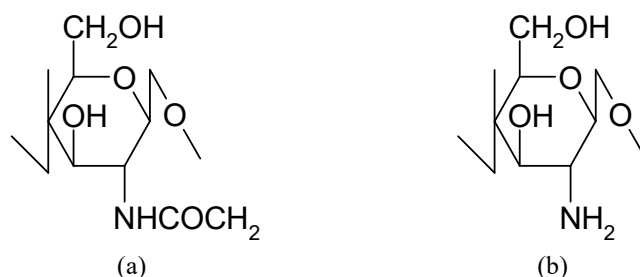


Fig.-1: The Structure of Repeat Unit (A) Chitin And (B) Chitosan

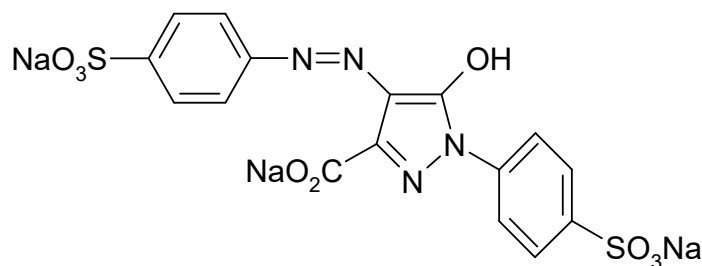


Fig.-2: The Molecular Structure of Tartrazine

EXPERIMENTAL

Materials and Tools

The materials used were chitin (Aldrich), tartrazine (Merck), hydrochloric acid (Merck), sodium hydroxide (Merck), and Whatman filter paper. Chitosan was obtained from deacetylation of the commercial chitin (Aldrich) according to the No and Meyers methods²⁷ and had an 80.11% deacetylation degree and molecular weight of $9.64 \times 10^4 \text{ g/mol}$ ²⁸.

The tools used were laboratory glassware, shaker (IKA Labortechnik), UV-Vis spectrophotometer (Shanghai No.3 Analytical Instrument Factory), pH-meter (Hanna) and analytical balance (Adam Equipment).

General Procedure

Determination of Optimum Adsorption pH

0.5 g of chitosan and 50 ml of tartrazine solution 50 ppm (C_0), which was dissolved in pH-adjusted-distilled water (3.0; 5.0; 7.0; 9.0; and 10.5) were introduced into 5 Erlenmeyer flasks. The pH was adjusted by the addition of hydrochloric acid and sodium hydroxide solutions. Then, the mixture was shaken on the shaker for 6 h with stirring speed on a scale of 100. The mixture was separated to refine with Whatman filter paper 40 and the concentration of solution after adsorption (C_e) was then determined based on a standard curve that had been made with a standard concentration of 5.0; 10.0; 15.0; 25.0 and 50.0 ppm. The adsorption capacity (Q_e) was calculated using Equation 1.

$$Q_e = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

This experiment was carried out in triplicate. The optimum pH value will be used for the next experiment.

Determination of Order and Adsorption Rate Constant

In 7 Erlenmeyer, 50 ml of tartrazine solution (50 ppm) and 0.5 g of chitosan were mixed in distilled water (at optimum pH) according to the previous experiment. The Erlenmeyer was shaken using the shaker at stirring speed on a scale of 100. After 30, 60, 90, 120, 180, 240 and 360 minutes of shaking, the Erlenmeyer was removed, filtered with Whatman 40 filter paper and determined the concentration after adsorption (C_e). The experiment was carried out in triplicate. The amount of tartrazine adsorbed by chitosan at time t (X) was determined based on Equation 2 where V is the volume of the tartrazine solution and m is the mass of chitosan.

$$X = \frac{(C_0 - C_e) * V}{m} \quad (2)$$

RESULTS AND DISCUSSION

Optimum Adsorption pH

The kinetic adsorption of tartrazine dyes on chitosan is strongly influenced by pH so that optimum pH is significantly required. The pH of a solution is a substantial factor for regulating the adsorbent surface load and the degree of ionization of the adsorbate in solution.¹⁹ The results showed that the optimum pH for the tartrazine adsorption on chitosan was 9.0 (Fig.-3). The results were different from the theory which stated that the amino groups will be protonated at low pH so that they can be attacked by the anionic dyes.²⁴ It was probably is due to the high solubility of chitin at leading to the low adsorption capacity. According to Annadurai et al²⁹, the ability of the adsorption of dyes will increase with increasing pH value. In Fig.-3, after reaching the optimum pH the ability to adsorb dyes tends to decrease. Tartrazine not only can form the ionic bond, but also covalent bonds, coulomb bonds, hydrogen bonds or van der Waals weak forces with adsorbents since it has -OH, -COONa, -SO₃Na, and -N=N- functional groups.⁵ It allowed the formation of these bonds between tartrazine and chitosan at pH 9.0.

Order and Adsorption Rate Constant

The kinetic study of tartrazine adsorption on chitosan (Fig.-4) showed that the amount of tartrazine adsorbed on chitosan increased and reached equilibrium at 120 minutes. It is different from the adsorption system between methylene blue dyes with chitosan adsorbent which up to 360 minutes which has not yet reached equilibrium.²⁸ It was probably due to differences in cooperation between the adsorbate and the adsorbent. As a consequence, it is difficult to determine the amount of adsorbate that can be adsorbed by the adsorbent when equilibrium occurs (X_e) because it requires a longer experiment time. The adsorption kinetics models can overcome both linear and nonlinear methods.

There are two models for studying the adsorption kinetics namely pseudo-first-order Lagergren model (P1OLM)³⁰ and pseudo-second-order Ho model (P2OHM).^{31,32} In general, the P1OLM is expressed as Equation (3), the integral between $t = 0$ to $t = t$ and $X = 0$ to $X = X_e$ will give Equation (4) with X (mg/g) is the number of adsorbates adsorbed by grams of adsorbent at time t and $k_{l,ads}$ are the first-order reaction rate constant of the Lagergren model. Equation (4) is a linear method for the P1OLM and can be rearranged into Equation (5) which is a nonlinear method.²³

$$\frac{dX}{dt} = k_{l,ads} (X_e - X) \quad (3)$$

$$\ln (X_e - X) = \ln X_e - k_{l,ads} t \quad (4)$$

$$X = X_e (1 - e^{-k_{l,ads} t}) \quad (5)$$

The P2OHM are based on the assumption that the adsorption follows a second-order mechanism which can be expressed as Equation (6) which is integrated between $t = 0$ to $t = t$ and $X = 0$ until $X = X_e$ will give Equation (7) which is nonlinear method and if rearranged in a linear method will be Equation (8) - Equation (11) with $k_{2,ads}$ are the second-order adsorption reaction rate model Ho^{5,23,25} as shown in Table-1.

$$\frac{dX}{dt} = k_{2,ads}(X_e - X)^2 \quad (6)$$

$$X = \frac{k_{2,ads} X_e^2 t}{1 + k_{2,ads} X_e t} \quad (7)$$

Table-1: The Forms of The Linear Method Equation Adsorption Kinetics of the P2OHM

Type	Forms of linear method equation	Plot	No. Equation	Parameters
Type-1	$\frac{t}{X} = \frac{1}{k_{2,ads} X_e^2} + \frac{1}{X_e} t$	t/X vs t	8	$X_e = 1/M; k_{2,ads} = M^2/C$
Type-2	$\frac{1}{X} = \left(\frac{1}{k_{2,ads} X_e^2} \right) \left(\frac{1}{t} \right) + \frac{1}{X_e}$	1/X vs 1/t	9	$X_e = 1/C; k_{2,ads} = C^2/M$
Type-3	$\frac{1}{t} = \left(k_{2,ads} X_e^2 \right) \left(\frac{1}{X} \right) - \frac{k_{2,ads} (X_e)^2}{X_e}$	1/t vs 1/X	10	$X_e = -M/C; k_{2,ads} = C^2/M$
Type-4	$\frac{X}{t} = -\frac{k_{2,ads} (X_e)^2}{X_e} X + k_{2,ads} X_e^2$	X/t vs X	11	$X_e = -C/M; k_{2,ads} = M^2/C$

Information: X_e = the amount of adsorbate was adsorbed at equilibrium (mg/g); X = the amount of adsorbate was adsorbed at a certain time (mg/g); $k_{2,ads}$ = the adsorption rate constant of P2OHM (g/(mg minute)); t = time (minute); C = intercept; M = slope

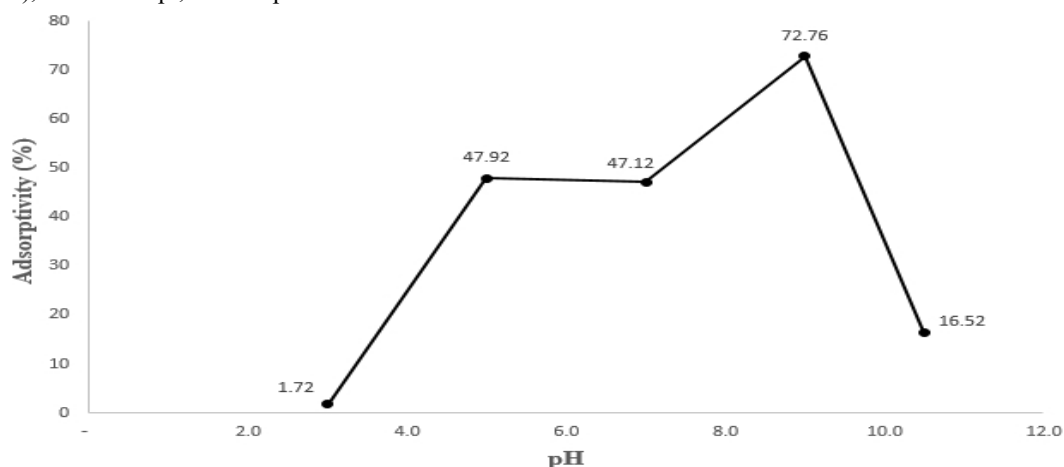


Fig.-3: The Ability of Adsorption Or Adsorptivity of Tartrazine by Chitosan at Various Phs

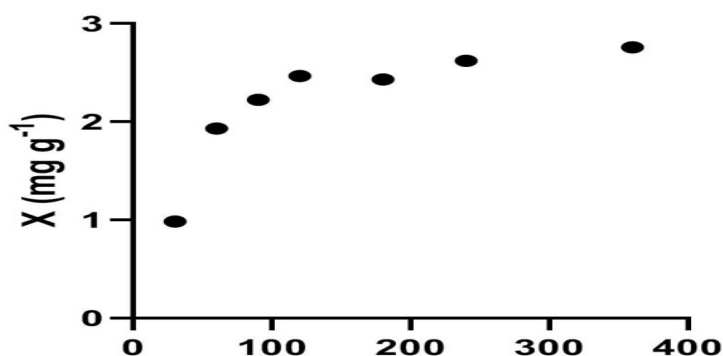


Fig.-4: Graph of The Amount of Tartrazine Adsorbed by Chitosan at Some Time of Adsorption

Linear Method of Adsorption Kinetics

Based on Equation 4, there were three independent variables to explain the P1OLM including time (t), number of adsorbates adsorbed at time t (X), and the amount of adsorbate adsorbed when equilibrium is reached (X_e). Therefore, to obtain a linear equation that satisfies the experimental data, a trial and error method was carried out by varying the X_e value which gives the highest linear regression (R^2) value. Fig. 5 was the best trial result obtained from the adsorption data between tartrazine and chitosan. The X_e value chosen for the trial method was that the X_e value approaches the equilibrium state according to Fig. 4, which was approximately 2.79 mg/g. Based on Fig. 5, the calculated X_e was 1.847 mg/g and $k_{1,ads}$ were 0.01094/min. To prove whether the tartrazine adsorption kinetics on chitosan follows the P1OLM, the R^2 value must exceed 95%. Additionally, the calculated X_e ($X_e = \exp(\text{intercept})$) must be close to the experimental X_e . It was found that the calculated X_e was 1.847 mg/g and there was a difference of around 33.80%.

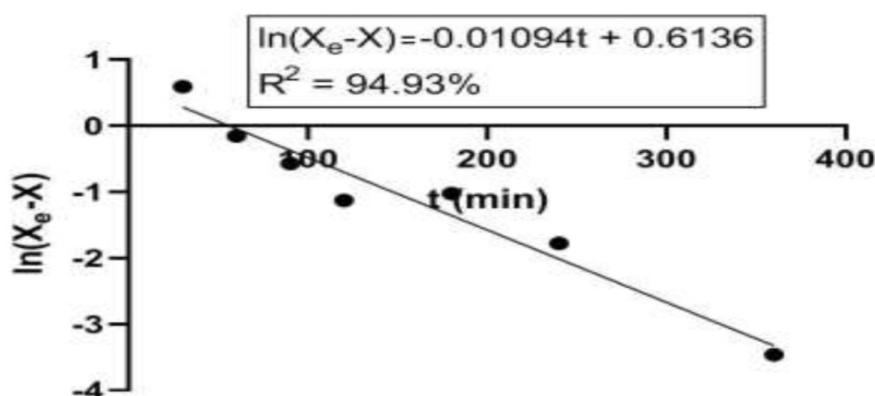


Fig.-5: The Graph Linear Method of Adsorption Kinetics P1OLM with Tried X_e is 2.79 mg/g.

The linear method of adsorption kinetics of P2OHM type-1, type-2, type-3, and type-4 for tartrazine adsorption on chitosan gave X_e , $k_{2,ads}$, and R^2 values based on Equation 8 to Equation 11 as shown in Fig.-6 and Table 2. Based on the R^2 value showed in Table 2, it can be stated that the experimental data of tartrazine adsorption on chitosan follows the linear method of adsorption P2OHM type-1 with $k_{2,ads}$ of 7.10×10^{-3} mg/g minute and X_e of 3.125 mg/g. The results supported the previous research²⁸ on the adsorption of methylene blue on chitosan with $k_{2,ads}$ of 0.154 g/mg minute and X_e for 2.22 mg/g. The difference in the value of $k_{2,ads}$ and X_e between the two adsorption systems was probably due to the differences in the adsorbate used, where the structure of tartrazine which is greater than that of methylene blue. The larger the adsorbate molecule, the lower the adsorption rate constant ($k_{2,ads}$) and the amount of adsorbate adsorbed at equilibrium (X_e). Whereas the lowest R^2 value was obtained in the linear method of adsorption of P2OHM type-4 as also obtained in the previous studies.^{5,22} However, to further statistically ascertain whether there is a difference between the X value of the experimental result (X_{exp}) and the X value calculated (X_{cal}), the average percentage error (APE) test, the χ^2 (chi) test, and the determinant coefficient (r^2) test^{25,26,33-36} must be done by Equation (12) - Equation (14).

$$APE = \frac{\sum_{i=1}^N |X_{exp} - X_{cal}| / X_{exp}}{N} \times 100\% \quad (12)$$

$$\chi^2 = \sum \frac{(X_{exp} - X_{cal})^2}{X_{exp}} \quad (13)$$

$$r^2 = \frac{\sum (X_{cal} - \overline{X_{exp}})^2}{\sum (X_{cal} - \overline{X_{exp}})^2 + \sum (X_{cal} - X_{exp})^2} \quad (14)$$

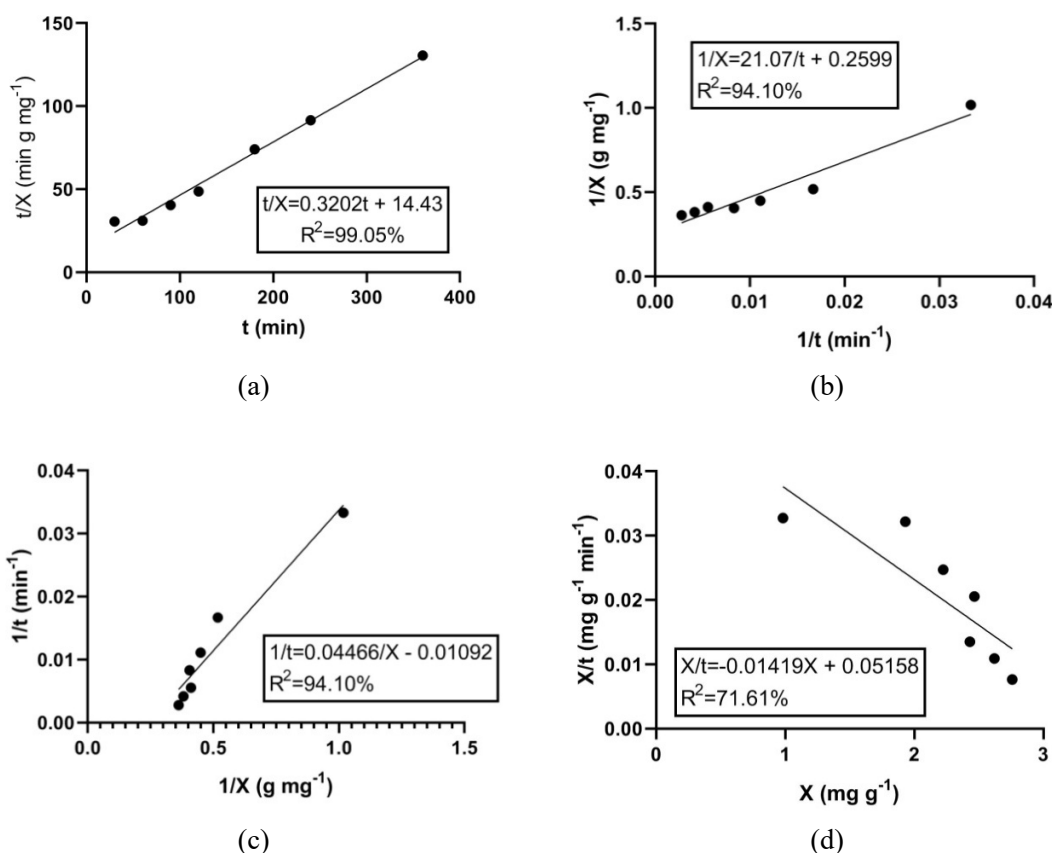


Fig.-6: Graph Linear Method of Adsorption Kinetics P2OHM(a) type-1, (b) type-2, (c) type-3 and (d) type-4 for Adsorption System of Tartrazine on Chitosan

Table-2: Kinetics Parameters for the Linear Method of Adsorption Kinetics P2OHM type-1, type-2, type-3, and type-4 for Adsorption System of Tartrazine on Chitosan.

Linear method of adsorption kinetics P2OHM	X_e (mg/g)	$k_{2,ads}$ (g/mg min)	R^2 (%)
Type-1	3.125	7.10×10^{-3}	99.05
Type-2	3.861	3.18×10^{-3}	94.10
Type-3	4.400	2.27×10^{-3}	94.10
Type-4	3.643	3.84×10^{-3}	71.61

The data compared were X_{exp} (Fig.-4) with calculation data based on $k_{2,ads}$ and X_e values obtained from each linear method of adsorption kinetics of P1OLM and P2OHM (Fig.-6 and Table-2) as shown in Table 3. The results of the calculation of statistical parameters for the data in Table-3 were presented in Table-4. There are four conditions that must be met to state that an adsorption kinetics method is best suited to the experimental conditions^{34,35,36}, such as (1) the experimental X value must close to the X value of all adsorbate concentrations, (2) the r^2 value must be maximum, (3) the χ^2 value must be minimum, and (4) the APE value must be less than 10%. Based on Table-4, if we only considered the APE value and the value of χ^2 , the linear method of adsorption kinetics P2OHM type-1 was the best approach. However, the method did not have maximum r^2 value because it only reached 92% or less than 95%. On the other hand, if we only considered the r^2 value, the linear method of adsorption kinetics P2OHM type-4 was the best approach. However, as discussed earlier that type-4 has the lowest R^2 value so that it was also not suitable for the adsorption of tartrazine on chitosan. Therefore, based on these four criteria and the values in Table-4 and Table-2, the five linear methods of adsorption kinetics were not suitable for tartrazine adsorption systems by chitosan.

Table-3: Comparison of the X Value of the Experimental Result (X_{exp}) and the X Value Calculated (X_{cal}) Based On The Values of k and X_c Obtained on Table 2 for The Linear Method of Adsorption Kinetics of P1OLM and P2OHM

t (min)	X_{exp} (mg/g)	X_{cal} (1-lin)* (mg/g)	X_{cal} (21-lin)* (mg/g)	X_{cal} (22-lin)* (mg/g)	X_{cal} (23-lin)* (mg/g)	X_{cal} (24-lin)* (mg/g)
30	0.9828	0.7782	1.2488	1.0393	1.0144	1.0769
60	1.9310	1.3393	1.7845	1.6378	1.6488	1.6624
90	2.2241	1.7439	2.0822	2.0268	2.0829	2.0304
120	2.4655	2.0357	2.2718	2.3000	2.3987	2.2830
180	2.4310	2.3978	2.4992	2.6582	2.8236	2.6075
240	2.6207	2.5861	2.6309	2.8827	3.1048	2.8069
360	2.7586	2.7349	2.7773	3.1486	3.4426	3.0394

*Information: (1-lin) for linear method of adsorption kinetics of P1OLM, (21-lin) for linear method of adsorption kinetics of P2OHM type-1, (22-lin) for linear method of adsorption kinetics of P2OHM type-2, (23-lin) for linear method of adsorption kinetics of P2OHM type-3, and (24-lin) for linear method of adsorption kinetics of P2OHM type-4

Table-4: Statistical Parameters Between the X value of the Experimental Result (X_{exp}) with the X Value Calculated (X_{cal}) Based on Table-3 for linear methods of adsorption kinetics of P1OLM and P2OHM

Linear Methods of Adsorption Kinetics	APE (%)	χ^2 test	r^2
P1OLM	13.43	0.4036	0.8962
P2OHM type-1	7.54	0.1095	0.9167
P2OHM type-2	10.00	0.1790	0.8845
P2OHM type-3	12.35	0.3767	0.8240
P2OHM type-4	9.16	0.1314	0.9556

Nonlinear Method of Adsorption Kinetics

Equation (5) and (7) can be used to explain the nonlinear method of adsorption kinetics P1OLM and the P2OHM. Ho²⁵ and Kumar²² used trial and error methods with Microsoft Excel® to determine the pseudo-second-order reaction rate constants by optimizing experimental data on nonlinear adsorption kinetics. On the other hand, Subramanyam and Das³⁶ used the Prism Graph Pad Primer 5.0 program to determine the parameters for the nonlinear method of adsorption isotherm. As it is known, the nonlinear equation for the Langmuir adsorption isotherm was similar to the nonlinear equation for the adsorption kinetics of the Ho model. The use of the Graph Pad Prism program was easier, faster and more accurate than the trial and error method. The results of determining the kinetic parameters for the nonlinear method of kinetics adsorption P1OLM and P2OHM for the adsorption tartrazine on chitosan using the Pad Graph Prism program version 8.0 were presented in Fig.-7 and Table-5.

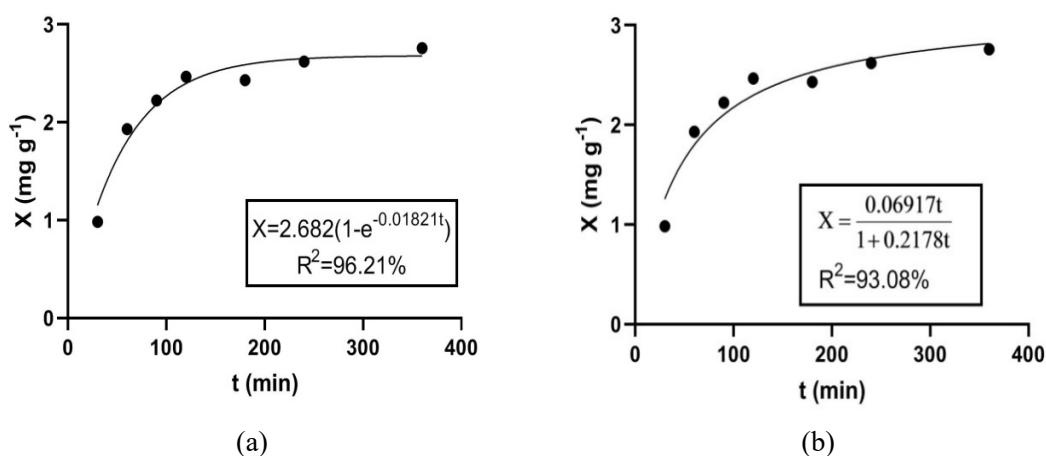


Fig.-7: The Graphs of The Relation X with Time (t) Using The Nonlinear Method Of Tartrazine Adsorption Kinetics on Chitosan for (a) P1OLM and (b) P2OHM

Table-5: Kinetics Parameters for the Nonlinear Method of Adsorption Kinetics P1OLM and P2OHM for Adsorption System of Tartrazine on Chitosan

Nonlinear Method of Adsorption Kinetics	The Adsorption Rate Constant	X_e (mg g ⁻¹)	R^2 (%)
P1OLM	0.01821 m ⁿ⁻¹	2.682	96.21
P2OHM	6.858 x 10 ⁻³ g/mgm	in 3.1758	93.08

Based on the value of R^2 in Table-5, the nonlinear method of kinetics adsorption P1OLM was more suitable than the nonlinear method of kinetics adsorption P2OHM. However, to further ascertain whether there was a difference between the X of the experimental result (X_{exp}) and the calculated X value (X_{cal}), statistical tests were conducted. The data tested were the results of calculations on Equation 5 (for P1OLM) and Equation 7 (for P2OHM) where each of the adsorption rate constant values and X_e were obtained in Table-5 and the results were shown in Table-6. The calculated statistical parameters for the data in Table-6 were presented in Table-7.

Table-6: Comparison of the X value of The Experimental Result (X_{exp}) and the X Value Calculated (X_{cal}) Based on the Values of k and X_e Obtained in Table-5 for the Nonlinear Method of Adsorption Kinetics of P1OLM and P2OHM

t (min)	X_{perc} (mg/g)	X_{hit} (1-nonlin)* (mg/g)	X_{hit} (2-nonlin)* (mg/g)
30	0.9828	1.1289	1.2550
60	1.9310	1.7826	1.7996
90	2.2241	2.1612	2.1039
120	2.4655	2.3804	2.2982
180	2.4310	2.5808	2.5321
240	2.6207	2.6481	2.6678
360	2.7586	2.6782	2.8189

*Information: (1-nonlin) for the nonlinear method of adsorption kinetics of P1OLM and (2-nonlin) for the nonlinear method of adsorption kinetics of P2OHM

Table-7: Statistical Parameters Between the X value of the Experimental Result (X_{exp}) with the X value Calculated (X_{cal}) Based on Table 6 For Nonlinear Methods of Adsorption Kinetics of P1OLM and P2OHM

Nonlinear Method of Adsorption Kinetics	APE (%)	χ^2 test	r^2
P1OLM	5.57	0.0497	0.9751
P2OHM	7.83	0.1086	0.9432

Based on Table-5, Table-7 and the four statistical test criteria^{34,35,36}, the most suitable approach method for the adsorption of tartrazine on chitosan was the nonlinear method of adsorption kinetics P1OLM since it has R^2 above 95%, APE which was less than 10%, the most minimum χ^2 test, and the maximum r^2 . This nonlinear method of adsorption kinetics of P1OLM had adsorption rate constant ($k_{l, ads}$) of 0.01821/min and the amount of tartrazine adsorbed at equilibrium (X_e) of 2.682 mg/g. These values can be directly obtained from the nonlinear equations as shown in Fig.-7a, without recalculating the amount as in the other equations (see the formula in the parameter column Table-1). This nonlinear method of the first-order Lagergren model has also obtained in the adsorption malachite green dye on oil palm trunk fiber³⁷ and the adsorption of methylene blue dye on board bean peels.³⁸ Indeed, this model is still rarely found in adsorption systems and until now there are no known properties of the adsorption system that make a model better than others.³⁸

Adsorption Mechanism

The adsorption mechanism of a solution consists of four stages: (a) the process of diffusion of solute from the bulk phase to the boundary layer around the adsorbent particles (bulk diffusion or film diffusion), (b) the diffusion process from the boundary layer to the surface of the adsorbent particles (external diffusion), (c) the diffusion from the surface to the internal side of the adsorbent (surface diffusion or pore diffusion),

and (d) the retrieval processes consisting of physical-chemical adsorption, ion exchange, precipitation or complex formation.^{39,40} Hameed and El-Khaiary³⁸ stated that there are three processes since the stages (b) and (c) were combined and the adsorption process (stage d) usually takes place very quickly from the other two stages. Therefore, the overall adsorption rate was controlled by film diffusion (stage a) or intraparticle diffusion (stages b and c) or both. Even there was no reasonable mechanism for the P1OLM adsorption process⁴¹, Hameed and El-Khaiary^{37,38} tried to explain the pseudo-first-order adsorption mechanism with the Weber intraparticle diffusion approach⁴² based on Equation 15 where X was the number of adsorbates adsorbed (mg/g) at time t , k_i is the diffusion-intraparticle constant (mg/g min^{0.5}), and c is intercept.

$$X = k_i t^{0.5} + c \quad (15)$$

If the c value is zero, the adsorption rate is determined by the intraparticle diffusion (stage b and c) for the entire adsorption period. However, the plot of X vs $t^{0.5}$ usually showed more than one linear part, and if the gradient of the first part is not equal to zero, then the film diffusion or stage (a) was as a stage of determining of reaction rate from the beginning. Fig.-8 showed the relationship of diffusion-intraparticle tartrazine by chitosan which has two straight lines.

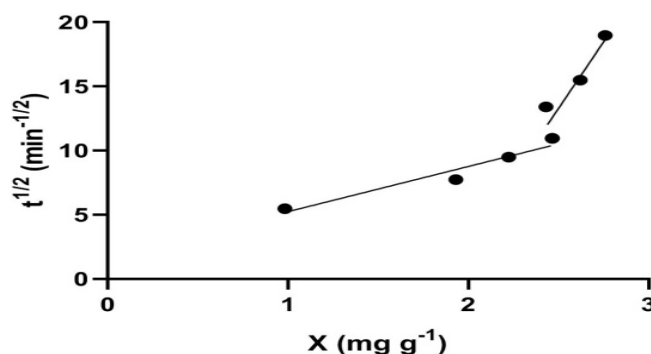


Fig.-8: The Relationship of Diffusion-Intraparticle Tartrazine By Chitosan

The first part started from the beginning to 100 min and the second was from the 100 min until the equilibrium. It showed that the adsorption rate was determined by the diffusion of the film (stage a) from the beginning to the equilibrium. It was possible for a short time before the equilibrium was reached, the adsorption rate determined by intraparticle diffusion, but the 30-minute time interval does not seem sufficient to see this. The similar results were observed for the initial malachite green concentrations of 200 and 250 mg/L, while at concentrations of 25, 50, 150, and 300 mg/L were initially controlled by film diffusion up to 55-71 min then changed to intraparticle diffusion.³⁸ It indicated that the determining stage of the adsorption rate was also influenced by the initial adsorbate concentration. Many studies have found that the adsorption system was determined by the diffusion of boundary layers or film diffusion (stage a) characterized by a dilute concentration of adsorbate, poor stirring, and small particle size of the adsorbent. On the other hand, the adsorption system was determined by the adsorption rate intraparticle diffusion (stages b and c) were characterized by the high concentrations of adsorbates, good stirring, and large particle size.^{37,43}

CONCLUSION

Chitosan produced from commercial chitin with a degree of deacetylation of 80.11% and the average relative molecular weight based on the viscosity was 9.64×10^4 g/mol can adsorb tartrazine dyes at optimum pH of 9.0. The adsorption kinetic model followed the nonlinear method of adsorption of the P1OLM with adsorption rate constant of 0.01821/min and the amount of tartrazine adsorbed when the equilibrium occurred was 2.682 mg/g. The adsorption mechanism that occurred in this process was determined by the diffusion stage of the film from the beginning until the equilibrium reached.

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