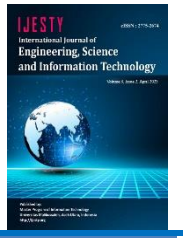
International Journal of Engineering, Science & InformationTechnology (IJESTY)
Volume 3, No. 2 (2023) pp. 25-30
ISSN 2775-2674 (online)
Website: http://ijesty.org/index.php/ijesty
DOI: https://doi.org/10.52088/ijesty.v1i4.431
Research Paper, Short Communication, Review, Technical Paper



Methyl Orange Absorption Using Chitosan from Shrimp Skin as an Adsorbent

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Manuscript received 3 April 2023; revised 16 April 2023; accepted 18 April 2023; Date of publication 19 April 2023

Abstract

The textile industry generally uses synthetic (artificial) dyes, methyl orange (MO), in coloring. This study investigated the adsorption of methyl orange (MO) dye with chitosan in a series of batch laboratory studies. The adsorption equilibrium study used a MO solution with a concentration of 10 to 50 mg/L with an adsorbent weight of 3 g put into an Erlenmeyer and shaken until the adsorption reached an equilibrium condition. Meanwhile, the adsorption kinetics used a MO solution with an initial concentration of 10 and 20 mg/L with a volume of 100 mL and an adsorbent weight of 3 g. The solution was adjusted to pH 2. Effective operating parameters such as pH, initial concentration of dye (C0), and contact time at adsorption have been investigated. The results showed that the adsorption capacity of methyl orange (MO) dye from chitosan increased with an increasing acid content, and it was found that a solution of pH 2 was the optimal pH value for MO adsorption. The adsorption parameters for the Langmuir and Freundlich isotherms were determined by nonlinear regression. The Langmuir isotherm model best explained the equilibrium data; this was indicated by the high correlation coefficient (R2) value, which was 0.9595. The maximum adsorption capacity was 0.1297 mg/g. Adsorption kinetics can be successfully applied to pseudo-second-order kinetic models. The pseudo-second-order model results show that the adsorption process is controlled by chemical sorption (chemisorption).

Keywords: *Adsorbent, Adsorption, Chitosan, Methyl Orange.*

1. Introduction

The growth of the textile industry, progressing and developing rapidly will, of course, impact the increasing pile of waste produced in volume and type. Uncontrolled industrial waste continues to be discharged into water bodies, causing pollution to fill nature[1].
Adsorption is the best alternative to overcome dye contamination. The increasing need for and use of activated charcoal in industries has resulted in a relatively high price increase, so the researchers have switched their research to cheaper adsorbents that can be produced from waste materials. Hence this study used an adsorbent using chitosan from shrimp shells, and the adsorbate used was methyl orange. Methyl orange is an azo dye with the chemical formula $C_{14}H_{14}N_3NaO_3S$ which has low solubility in water and can be removed like colloidal particles. Methyl orange has been widely applied in textile industries that cause harm to the environment, especially rivers around the industry location [2].
Chitosan has several potential uses in daily life. The use of chitosan has been identified as hydrogels, wound dressing, biomaterials, cosmetics, and wastewater treatment [3]–[7]. Chitosan has been widely used for adsorption. Using chitosan as pollutant removals such as metals, dyes, and pharmaceuticals are based on its properties of large surface area, pore diameters, and existing functional groups[8].
There have been several identified potential alternative natural sources of adsorbents. Crab shells, fly ash, water hyacinth root, molasses, alginate, and other sources [3], [9]–[12]. Shrimp shell, usually wasted in the culinary restaurant, has the potential for waste treatment use. Amongst the use of shrimp shells is its application as chitosan raw material for the biosorbent role. Shrimp shell-based chitosan as a biosorbent has been examined for heavy metals and organic waste treatment from the environment[13]. Shrimp shell was used as chitosan raw material in adsorbing copper [14]. [15] utilized shrimp shell-based chitosan in iron adsorption.
This study aimed to study the adsorption mechanism using the Langmuir and Freundlich isotherm models for MO absorption using chitosan adsorbents. In addition, it also calculates the rate constant of the adsorption kinetics tested using pseudo-first-order and pseudo-second-order models.

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2. Materials and Methods

2.1. Materials

The materials used in this study were chitosan with a size of 100 mesh. Methyl orange (MO) solution as mother liquor with a concentration of 50 mg/L (50 ppm) was made with distilled water as the solvent required for this study. MO solutions of 10 mg/L to 50 mg/L were prepared and adjusted to the pH conditions until the adsorption process.

2.2. Methods

Research on the absorption of methyl orange by chitosan to find the best pH conditions in the absorption process was carried out in a 250 mL Erlenmeyer containing 100 mL of MO solution with a concentration of 50 mg/L, with the pH varied from 2 to 9. Adsorbent weighing 3 grams was put into Erlenmeyer. Furthermore, the sample that has been filled in a 250 mL Erlenmeyer is placed in a shaker, shaken at 250 rpm at room temperature, and carried out for 2 hours. Then the sample was filtered using a centrifuge and tested using UV/Vis at a wavelength of 420 nm.

For equilibrium adsorption, MO solution was used with an initial concentration of 10 to 50 mg/L with a volume of 100 mL at pH 2. Then the adsorbent weighing 3 grams was put into the Erlenmeyer, then shaken until the adsorption conditions reached equilibrium.

The MO concentration at equilibrium, qe (mg/g), can be calculated using (1)[16]:

$$qe = \frac{V\,(C_o - C_e)}{m} \quad (1)$$

where C0 (mg/L) is the initial concentration of MO in the liquid phase, Ce (mg/L) is the concentration of MO in the liquid phase at equilibrium, V (mL) is the total volume of the MO solution and m (g) is the weight of the adsorbent.

Experimental data for this research sorbates were evaluated through nonlinear regression analysis using two kinetic models (pseudo-first order and pseudo-second order) and two equilibrium models (Langmuir and Freundlich). Nonlinear regression was used to analyze experimental data using the Solver add-in function in Microsoft Excel.

Adsorption isotherms describe the volume or weight of a substance adsorbed as a function of the pressure or concentration of the adsorbate at a constant temperature.

The Langmuir isotherm model describes the monolayer coverage of molecules that adsorb onto the surface of the adsorbent. It is assumed that once the adsorbent site is covered with dye molecules, no further adsorption occurs. It also shows that all adsorption sites have equivalent energy. The Langmuir isotherm model in its nonlinear form using (2)[17].

$$qe = \frac{C_e K_L}{1 + K_L C_e} \quad (2)$$

where qe is the adsorption capacity of the adsorbent (mg/g) at equilibrium, Ce is the adsorbate concentration (mg/L) in solution at equilibrium, and KL is the Langmuir equilibrium adsorption constant (L/mg).

The Freundlich isotherm model is based on the assumption that adsorption occurs on a heterogeneous surface. The Freundlich equation [17] is shown as (3)

$$qe = K_F C_e^{1/n} \quad (3)$$

where KF is the Freundlich constant associated with adsorption capacity and 1/n is the heterogeneity factor. The large value of the adsorption capacity of K_F, indicates the adsorption capacity. Good adsorption can be concluded when the value of 1/n ranges between 0 and 1.

Meanwhile, adsorption kinetics is vital because it provides essential information about reaction rates and control mechanisms[17].

For kinetic adsorption using a solution with an initial concentration of MO 10 and 20 mg/L with a volume of 250 mL, with an adsorbent weight of 1 gram, a solution pH of 2, and carried out at room temperature. Then shaken with a rotational speed of 250 rpm at certain intervals, samples were taken and tested using UV/Vis. The adsorption kinetics test was evaluated using two kinetic models: the pseudo-first-order model and the pseudo-second-order model.

Pseudo-first order suggests an absorption mechanism preceded by diffusion across the boundary. The shape of the nonlinear model is described as (4).

$$qt = q_e^{(1-ekt)} \quad (4)$$

where qe and qt are the amount of dye adsorbed (mg/g) at equilibrium and time t (min), respectively, and k1 (min−1) is the pseudo-first-order rate constant. The pseudo-first-order equation assumes the adsorption of one adsorbing molecule to an active site on the surface of the adsorbent. The pseudo-second-order kinetic model is based on the assumption that adsorption follows a second-order kinetic mechanism. The model describes an absorption process controlled by chemisorption. The shape of the nonlinear model is defined as (5).

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

where qe and qt are the amount of adsorbed dye (mg/g) at equilibrium and time t (min), respectively, and k2 (g/mg min) is the pseudo-second-order rate constant.

3. Results and Discussions

3.1. pH Effect

pH value of the MO solution plays an essential role in the entire adsorption process because variations in pH lead to variations in the surface properties of the adsorbent and, therefore, the degree of ionization. As shown in Figure 1, shows that the adsorption capacity of MO increased at pH two by 0.135 mg/g. The lowest absorption capacity was obtained at pH 6, 0.035 mg/g. Absorption processes that use chitosan as an adsorbent are usually obtained at the optimum pH, which ranges from pH 2-6, reported by previous researchers such as[18]. This is due to the protonation of the chitosan fibers as an adsorbent at low pH values where H+ ions provide a strong electrostatic attraction between the chitosan surface and the dye molecules leading to maximum adsorption[19]. Hence the following experiment in this study was carried out at pH two as the optimal pH.

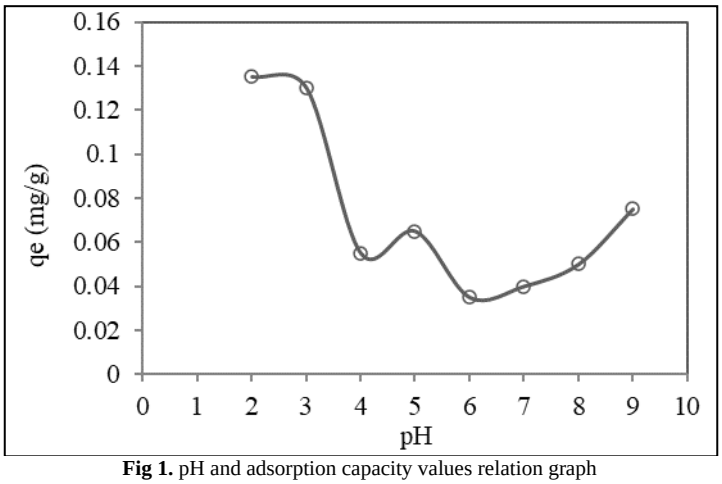

Fig 1. pH and adsorption capacity values relation graph

3.2. Adsorption Equilibrium

Absorption capacity testing is carried out to determine the time equilibrium is reached by an adsorbent used.

Experimental data from MO adsorption with chitosan were analyzed using nonlinear isotherms. The description of the magnitude of MO absorption of chitosan is illustrated by a graph of the importance of the adsorbate loading (qe) versus the equilibrium concentration (Ce), as shown in Figure 2 obtained using (2). In the Langmuir equation, if 0 < RL < 1, it can be stated that adsorption is favorable, RL > 1 is unfavorable, R_L = 1 is linear adsorption, and RL = 0 means irreversible.

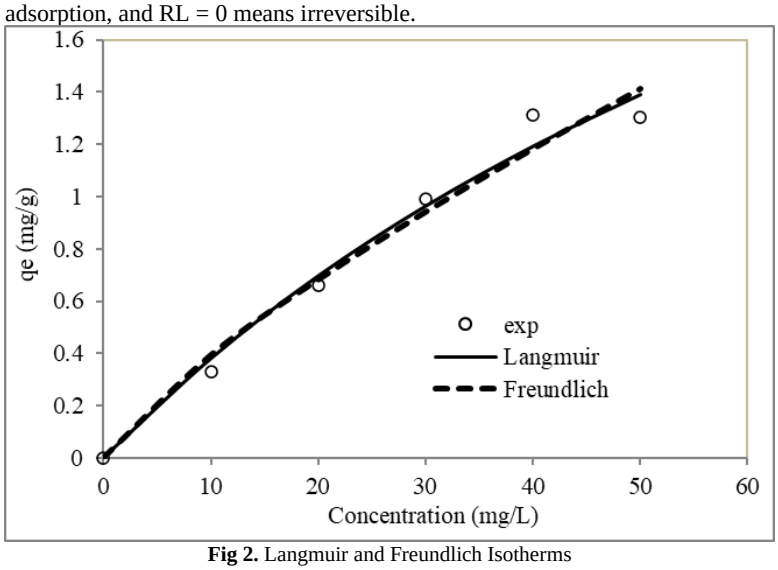

Fig 2. Langmuir and Freundlich Isotherms

Figure 2 shows that the Langmuir model can describe experimental data for all data concentrations compared to the Freundlich model. This can be shown by the high value of the correlation coefficient (R^2) in Table 1, which is 0.9595. Figure 2 shows that the absorption process of methyl orange with chitosan is more suitable for the Langmuir model than Freundlich.

Table 1. Langmuir and Freundlich Equations Parameters

Equilibrium Model	Equations	Parameters	Results
Langmuir	$q_e = (K_L Ce)/(1 + K_L Ce)$	K_L (L/mg)	0,0419
		SSE	0,0270
		R^2	0,9595
		R_L (L/g)	0,3231
		q_m (mg/g)	0,1297
Freundlich	$qe = K_F\ Ce^{1/n}$	K_F (L/g)	0,0631
		SSE	0,5369
		R^2	0,9474
		1/n	1,2585

Figure 2 depicts a plot between concentration (mg/L) vs. qe (mg/g). Meanwhile, the suitability of the isotherm (favorable) for the adsorption process expressed in the form of a balance parameter (RL) was also considered in this study. The magnitude of the value of the balance parameter (R_L) is between 0 to 1[19]. Table 1 shows the value of the RL is 0.3231, which indicates that the absorption process of methyl orange (MO) with chitosan is included in the good category.

The Freundlich model shown in Figure 2 is illustrated using equation (3), where the absorption load on the adsorbent (qe) can be calculated by optimizing the KF and n values from equation (3). Figure 2 also shows that the Freundlich model line starts from a concentration of 30 mg/L to 50 mg/L. There is a slight deviation compared to the Langmuir model; this indicates that the Freundlich model is only able to implement at low concentrations[20], while the Langmuir model is suitable for all concentrations data. Hence it is not surprising that the correlation coefficient for the Langmuir model is higher than that for the Freundlich model.

3.3. Adsorption Kinetics

Adsorption kinetics facilitates the adsorption process by controlling chemical and physical factors[21]. To understand the mechanism and kinetic equations are used. In this study, two kinetic models were used, namely, pseudo-first order and pseudo-second order kinetic models, to explore the relationship between the amount adsorbed and reaction time.

3.3.1. Pseudo First Order Model

A series of experiments were carried out at different initial concentrations, namely, 10 and 20 mg/L at 30°C and pH 2. The research results are shown in Figure 3 that the adsorption rate increases rapidly at the initial stage but slows down at later stages until it reaches equilibrium. The absorption curve obtained is smooth and continuous toward saturation, indicating the formation of a monolayer of adsorbate on the surface of the adsorbent[22]. The fast adsorption upon initial contact can be attributed to the availability of active sites, and the slow adsorption of MO dye may be due to the pore diffusion of the solute into the bulk of the adsorbent. The equilibrium time for the adsorption of MO on chitosan for various adsorption concentrations was found at a contact time of 35 minutes, which indicates that the equilibrium time does not depend on the initial concentration of the adsorbate.

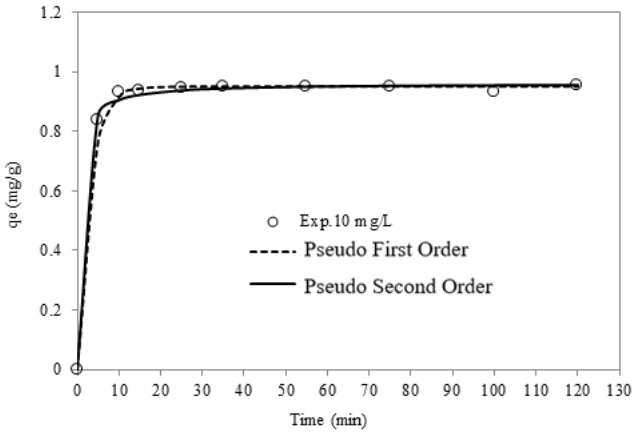

Fig 3. 10 mg/L Adsorption Kinetics

The model line is shown in Figure 3 (qe versus t plot). The qe and k1 for the first-order pseudo-kinetic model are obtained by optimizing using Solver-add in, which is in Microsoft Excel. Parameter values in (3), such as reaction rate constant (k_1), correlation coefficient value (R^2), and qe (experimental and calculated) values, are summarized in Table 2, ranging from 0.8134 to 0.9496. In addition, the experimental qe values (qe, exp) do not correspond to the calculated values (qe, cal), as shown in Table 2. This indicates that MO's adsorption kinetics on chitosan do not follow the pseudo first order kinetic model; therefore, diffusion does not control the adsorption kinetics events.

Table 2. Adsorption Kinetics Parameters with varying initial MO Concentrations

Conc (mg/L)	Pseudo First Order				Pseudo Second Order			
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (1/min)	R^2	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (mg/g.min)	R^2
10	0,9532	0,9516	0,3281	0,9496	0,9532	0,9609	1,6764	0,9796
20	0,9200	0,9047	0,1827	0,8134	0,9200	0,8053	2,9825	0,9777

3.3.2. Pseudo Second Order Model

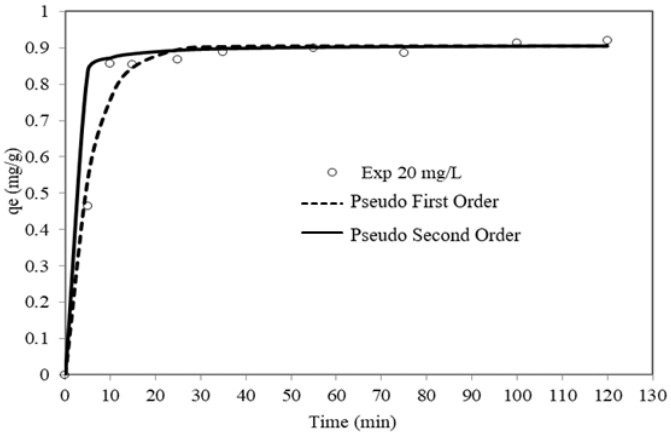

Fig 4. 20 mg/L Adsorption Kinetics

The model line shown in Figure. 4 (qe versus t plot) is described using (5). The k2 and qe were determined by optimization and are presented in Table 2 with the corresponding correlation coefficients. This model is more likely to predict behavior across experimental adsorption data. This pseudo-second-order kinetic model shows good agreement between the observed and calculated qe values , as presented in Table 2. In addition, the corresponding correlation coefficient (R^2) for the pseudo-second-order kinetic model is more significant than 0.97 for all MO concentrations. This implies that the adsorption process is controlled by chemisorption.

4. Conclusion

Chitosan made from shrimp shells is suitable as an adsorbent and is effective for removing MO from aqueous solutions (artificial waste). MO dye has a strong absorption capacity on the chitosan surface, indicated by the high a_L value of 0.3231 L/g. The adsorption parameters for the Langmuir and Freundlich isotherms were determined by nonlinear regression. The Langmuir isotherm model best explained the equilibrium data; this was indicated by the high correlation coefficient (R2) value, which was 0.9595.
The maximum adsorption capacity was obtained at 0.1297 mg/g. Adsorption kinetics can be successfully applied to pseudo-second-order kinetic models. The pseudo-second-order model results show that the adsorption process is controlled by chemical sorption (chemisorption), with a correlation coefficient (R^2) greater than 0.97, and the value of qe,exp is very close to qe,cal.

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