

# Clamshell As Biosorbent – Fixed Bed Adsorption Evaluation of Calcined Clamshells as Biosorbent for The Column Adsorption of Methyl Orange Dye From Liquid Phase

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## Abstract

The wastewater discharged from textile, dyeing, leather and paper industries contains hazardous dye which is the main source of water pollution, leading to water quality degradation. In this study, the clamshell or known as *Orbicularia Orbiculata* by its scientific name was used as low-cost adsorbent to remove methyl orange (MO) from aqueous solution. The clamshell was activated through thermal treatment to produce the calcined clamshells biosorbent for this adsorption study. The calcined clamshell was characterized by using scanning electron microscope (SEM) and Fourier Transform Infrared (FTIR) spectroscopy. The effect of bed height, initial dye concentration and contact time were investigated in the column adsorptive study. As a result, the optimum adsorption condition for methyl orange achieved the maximum removal percentage of 96.65% at the bed height of 10 cm, initial dye concentration of 10 mg/L and contact time of 10 minutes. The removal percentage increased with the increasing of bed height; however, the opposite trend was observed for initial dye concentration and contact time. The kinetic studies were evaluated by employing the pseudo-first-order model, pseudo-second order, Thomas model and Yoon-Nelson model. Pseudo-second-order model and Yoon-Nelson model were found to be well-fitted the dynamic behavior of adsorption of methyl orange onto the calcined clamshells. The results obtained from this study suggested that clamshells can be an effective adsorbent in the treatment of dye-bearing wastewater.

**Keywords:** *Biosorbent, Calcined clamshell, Column adsorption, Low-cost adsorbent and Methyl orange*

## 1. Introduction

Synthetic dye is a widely used substance in the various industries such as textile and leather, to impart bright and attractive colors on various finishing products for the enhancement of its esthetic values. Due to the high usage of these substances, the presence of multiple types of dyes in the water bodies were unavoidable. Methyl orange with its IUPAC name of sodium 4-[(4-dimethylamino) phenyldiazonyl] benzenesulfonate, is a common azo anionic dye that is extensively used in the textile, printing and paper industry. Methyl orange is a synthetic dye which is very soluble in water, which appeared as bright orange when dissolved in water. Methyl orange consists of two aromatic groups and the azo groups ( $-N=N-$ ) (Table 1) that makes it highly toxic and carcinogenic (Wu et al., 2021). As it does not degrade easily in the water, it contributes to one of the main pollutants from the dyeing industry and becomes harmful to the environment (Yang et al., 2017). Therefore, the removal of methyl orange from the water is a challenging and urgent issue for the dyeing industry.

There are several methods developed for the removal of dye from the water, namely

photodegradation proposed by Rafaie et al. (2017), advanced oxidation proposed by Kumar et al. (2017), ion exchange method proposed by Grelluk & Hubicki (2011) and ozonation proposed by Quan et al. (2017). Besides, adsorption is also being studied to remove dye from water through the surface reaction on the adsorbent. The application of adsorption in removing dye from wastewater was reported to be cost-effective, easy-operated and environment friendly especially when bio-adsorbent is employed for the dye removal (Inthapanya et al., 2019).

As one of the effective methods to remove methyl orange from the water, adsorption is studied in-depth to improve its removal efficiency. Different effective adsorbents were characterized by high affinity and large surface area can be used in the dye adsorption process such as activated carbon and zeolite. However, the application of these adsorbents is expensive and has regeneration issues especially in the developing countries (Zamparas et al., 2021). Therefore, to overcome these shortcomings, the application of low-cost adsorbents with high efficiency, such as fly ash, chitosan, fruit shell and calcite-based clamshell in methyl orange removal are necessary to be focused on. In addition, these

adsorbents are also present in abundance with high availability as it can be easily obtained from the domestic wastes. Reusing these materials as an adsorbent is very crucial in reducing the waste needed to be disposed of through incinerators or landfills to minimize environmental pollution.

Clamshells are produced in large quantities due to the rapid increase in clamshell cultivation in Malaysia. However, most of the waste clamshells are usually dumped at the shoreline or roadside that brought adverse environmental impacts such as pollution of coastal fisheries and unpleasant odor due to the decomposition of organic matters on the shells (Jović et al., 2019). Therefore, the study on the use of calcined clamshells as an adsorbent for methyl orange removal at optimal condition is critical to solve the waste problem of aquaculture while improving the quality of water to achieve environmental sustainability.

## 2. Methodology and Experiment Setup

### 2.1 Preparation of Adsorbent

The clamshells collected at local market (Serdang, Malaysia) were washed to remove the contaminants by using a non-ionic detergent. Then, the washed

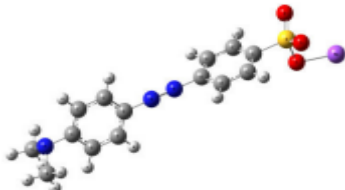
clamshells were dried under the sun for 24 hours. The dried clamshells were crushed and ground into small powder by using a grinder, followed by sieving the bulk sample into the desired particle size of smaller than 2 mm diameter. These clamshells powder was placed in the furnace at 800°C for 2 hours for the calcination (heat treatment) process. The calcined clamshells powder was then cooled to room temperature, ready to be used for the experimental work.

### 2.2 Preparation of Methyl Orange Stock Solution

The methyl orange stock solution was prepared by dissolving 0.1 g of methyl orange powder into the 1 L deionized water to prepare 100 mg/L of methyl orange solution. Dilution was performed by adding the specific amount of water into a specific amount of the methyl orange stock solution to prepare the following dye solution concentration; 10 mg/L, 15 mg/L, 20 mg/L and 30 mg/L. Equation [1] provided the calculation in identifying the exact amount of water required to dilute the methyl orange stock solution into desired concentration.  $C$  is the concentration of methyl orange in the solution while  $V$  is the volume of the solution. Table 1 shows the 3D structure and general properties of the methyl orange dye.

$$C_1V_1 = C_2V_2 \quad [1]$$

**Table 1** Structure and Properties of Methyl Orange Dye

Chemical formula	3D structure	Molecular weight	Maximum wavelength
$C_{14}H_{14}N_3NaO_3S$		327.33 g/mol	464 nm

### 2.3 Characterization of Adsorbent

The raw and calcined clamshells before adsorption experiment were characterized by using Scanning Electron Microscopy (SEM) at the following magnification: 3000, 5000 and 10,000 times to observe and compare the surface morphology of the raw and calcined clamshells. In addition, the raw and calcined clamshells before and after adsorption experiment were sent for characterization using Fourier-transform infrared spectroscopy (FTIR) to investigate their respective functional groups present on the adsorbent material.

### 2.4 Column Adsorption Experimental Setup

The methyl orange feed solution was contained in a beaker, at which a peristaltic pump was used to transport the methyl orange solution from a beaker and pumped to the top of the column to flow through the adsorption column. The clamshell powder was placed in the column with a glass wool fixed at the bottom of the column. The effluent from the column was then collected in a separate beaker. The

withdrawal point of water samples was located at the exit of the column. The concentration of the methyl orange in the samples extracted from the effluent of the adsorption column was determined by using the UV-visible spectrophotometer (model- UVILine 9400) at the wavelength of 469 nm.

In this experiment, the effect of bed height, initial dye concentration and contact time were analyzed. The adsorption time was executed for 10 minutes of time intervals until the equilibrium was attained. The effect of bed height was investigated by varying the adsorbent bed height in the following range, 5 cm, 8 cm, and 10 cm at a constant initial dye concentration of 30 mg/L. The solutions with different initial dye concentrations which are 10, 15, 20 and 30 mg/L were fed to the column at a constant adsorbent bed height optimized from the result of effect of bed height.

The following parameters namely the removal efficiency, the total quantity of dye adsorbed in the column,  $q_{total}$  and total quantity of dye fed to the column,  $m_{total}$  were calculated by using Equation [2]

and Equation [3], where  $C_0$  is initial methyl orange concentration,  $Q$  is the flow rate of methyl orange

$$q_{total} = \frac{QC_0}{1000} \int_{t=0}^{t=t} \left(1 - \frac{C_t}{C_0}\right) dt \quad [2]$$

$$m_{total} = \frac{C_0 Q t_{total}}{1000} \quad [3]$$

The removal efficiency and adsorption capacity ( $q_e$ ) will be then calculated by using Equation [4] and Equation [5] respectively.

$$Removal\ efficiency = \frac{q_{total}}{m_{total}} \times 100\% \quad [4]$$

$$q_e = \frac{q_{total}}{w} \quad [5]$$

### 2.5 Adsorption Kinetic Studies

The pseudo-first-order model and pseudo-second-order model were employed to determine the rate-limiting steps in the adsorption of methyl orange onto calcined clamshells. Pseudo-first-order model assumed that the amount of solid uptake with time and difference in saturation concentration is directly proportional to the rate of change of the solute

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad [6]$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad [7]$$

In addition, the mathematical models of Thomas model and Yoon-Nelson models were investigated as well to analyse the behaviour of adsorbent-adsorbate system of this adsorption process. Thomas model assumed the Langmuir kinetics adsorption-desorption without axial dispersion is derived with the rate driving forces that obeys second-order reversible kinetics. In contrast, the properties of the adsorbate, type and properties of

$$\ln\left(\frac{C_t}{C_0} - 1\right) = \frac{K_{th} q_e x}{Q} - K_{th} C_0 t \quad [8]$$

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = K_{YN} t - K_{YN} \tau \quad [9]$$

## 3. Result and Discussion

### 3.1 Characterization of Adsorbent

The surface morphology on the adsorbent were carried out using the scanning electron microscope (model: Tescan Vega3) at magnification of 3000, 5000 and 10000 times for raw and calcined clamshell before adsorption shown as Figure 1 to investigate the difference in morphology of these two types of shells. It was observed that the surface of the raw clamshell was rough and disordered with very low porosity grains. In contrast, the surface of

feed to the column in mL/min and  $t$  is adsorption time.

uptake (Sahoo & Prelot, 2020). In contrast, pseudo-second-order model suggested that the rate of adsorption is based on the adsorption capacity instead of the concentration of adsorbate. The linear equations of pseudo-first-order model and pseudo-second-order model were shown as Equation [6] and Equation [7] respectively.

adsorbent used were not included in the Yoon-Nelson model. This model assumed that rate of probability adsorption for each adsorbate and probability of adsorbate breakthrough is proportionate to the rate of decrease in the probability of adsorption (Patel, 2019). The linear equation of Thomas model and Yoon-Nelson model could be expressed as Equation [8] and Equation [9].

calcined shell was smoother with more porous structure, proving that the thermal decomposition had been successfully modified the surface properties of the adsorbent (Nordin et al., 2015). As reported by Hazri & Nasir (2020). The increment of pore diameter was also observed after the calcination of mussel shells. This was probably due to the expansion of grains and the formation of microcracks after the high temperature heating process (Ahmed, 2022).

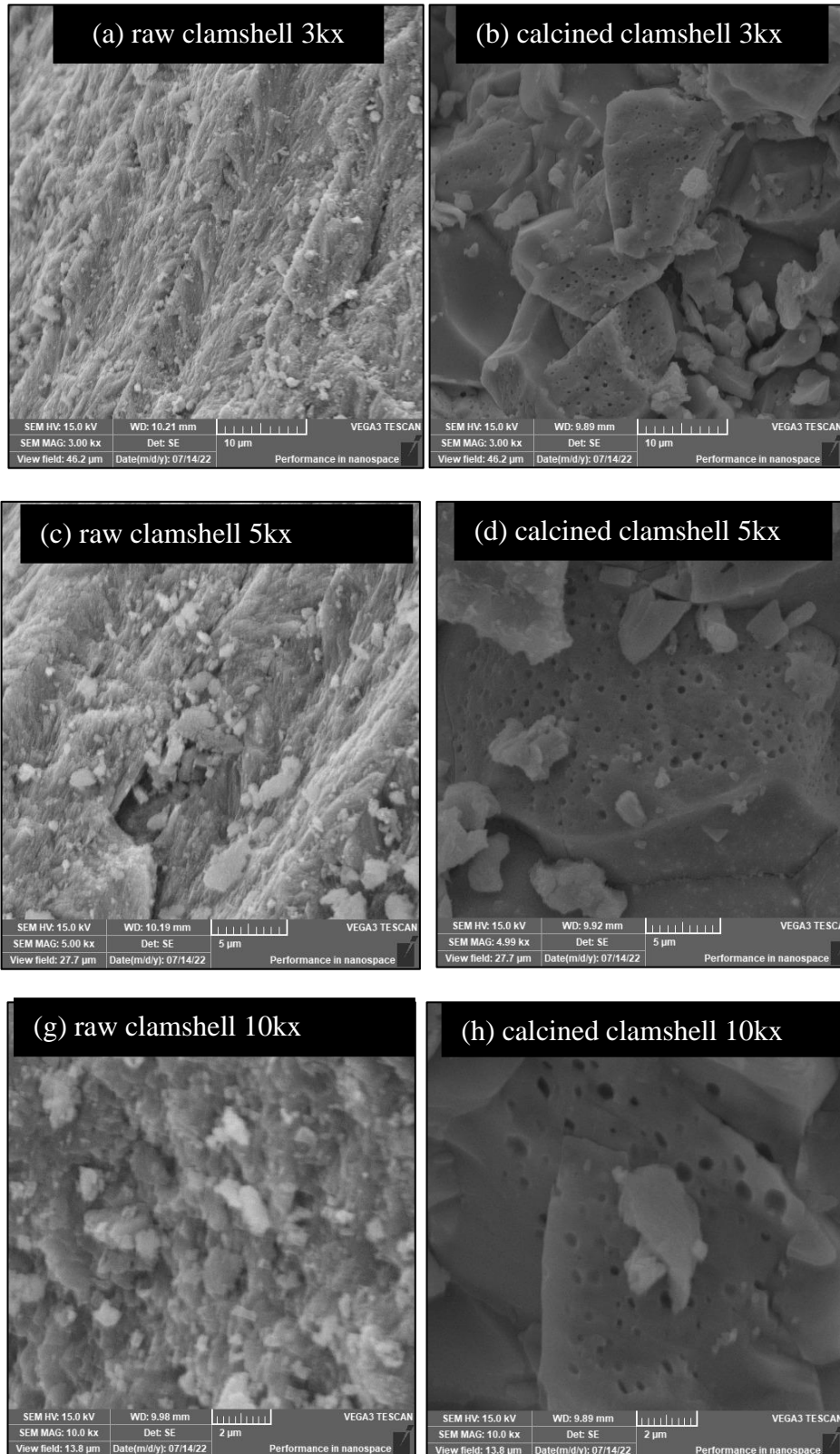


Figure 1. SEM Image of Raw and Calcined Clamshells Before Adsorption

Figure 2 showed the FTIR spectrum for calcined shells before and after the adsorption has taken place. The results showed a medium absorption band at  $707.65\text{ cm}^{-1}$  indicating the presence of carbonate ion being attached to calcium (Khiri et al., 2016). Two strong bands at  $868.95\text{ cm}^{-1}$  and  $1399.65\text{ cm}^{-1}$  were observed which corresponded to

the asymmetric C–O bond vibration of calcite that was probably due to the formation of calcium carbonate species upon carbon dioxide adsorption on calcium oxide (Aitlaalim et al., 2020). Upon completion of the adsorption process, the significant absorption band at  $868.95\text{ cm}^{-1}$  has been shifted to  $868.61\text{ cm}^{-1}$ ,  $707.65\text{ cm}^{-1}$  was shifted to  $706.54\text{ cm}^{-1}$

and  $1399.65\text{ cm}^{-1}$  was shifted to  $1385.95\text{ cm}^{-1}$ . The shifting of these band and reduction in their intensity(s) was probably due to the interaction of these functional group with MO dye molecules. A weak peak at  $1226.7\text{ cm}^{-1}$  had appeared indicating

the presence of C-N functional group from the aromatic amine. This showed that the methyl orange molecules had successfully adsorbed and strongly suggest chemical interaction occurred between dye and calcined clamshells biosorbent.

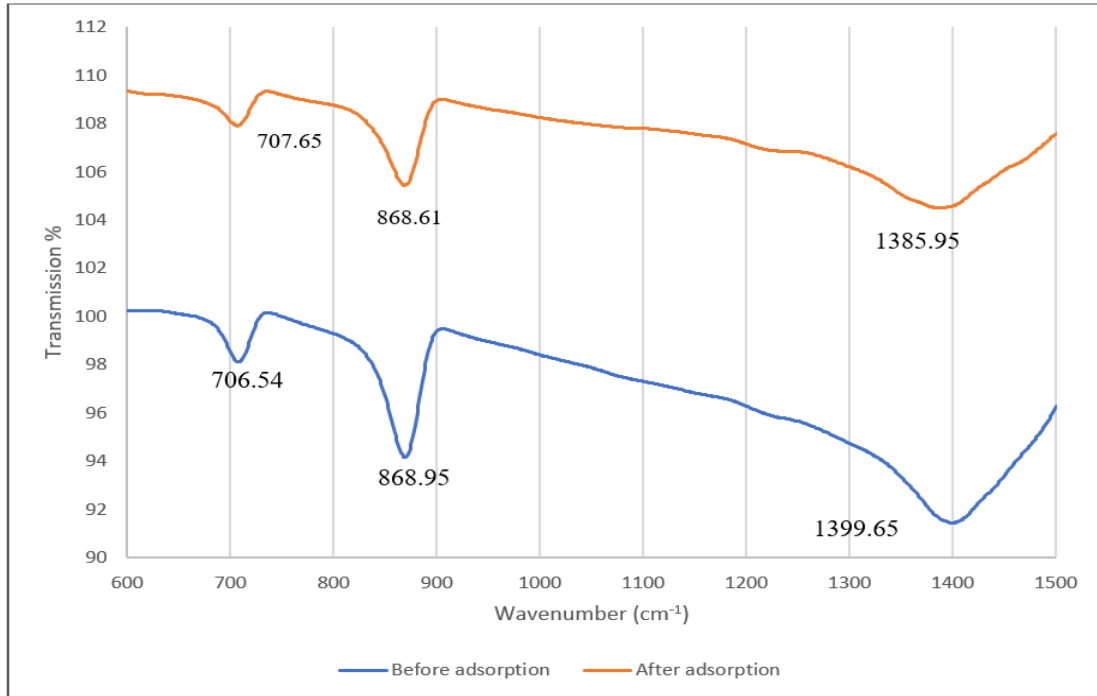


Figure 2. FTIR Spectrum for Calcined Clamshells Before and After Adsorption

### 3.2 Effect of Bed Height and Contact Time

Figure 4 showed that the methyl orange removal efficiency increased with increasing bed height at any time. When the bed height increased from 5cm to 10cm, the removal efficiency increased from 69.783% to 93.027% at 10<sup>th</sup> minutes. This trend was also agreed by the previous researches reported by Tejada-Tovar et al. (2021) and Mohanta et al. (2021). This phenomenon could be attributed to the increment in surface area of adsorbent that provided higher binding sites or adsorption sites for adsorbate when the bed height increased (Patel and

Vashi, 2012). For the same influent concentration of methyl orange, the dye molecules could interact with more adsorbent and adsorbed onto the adsorbent. Eventually, the removal efficiency would increase with higher adsorbent bed height. Besides, the removal efficiency decreased with increasing contact time. This was due to the reduction in the number of active sites available for adsorption process when more and more adsorbates were adsorbed but same concentration of methyl orange solution was still provided.

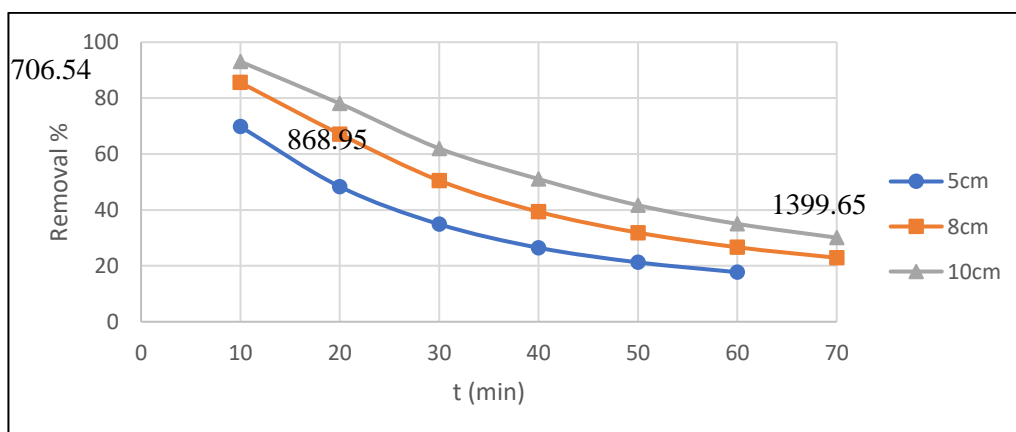


Figure 3. Graph of Removal Percentage versus Time at Different Bed Height

Moreover, the effect of bed height of calcined shell could also be investigated through breakthrough curve shown as Figure 4. It was observed that the breakthrough time increased as the bed height increased. The exhaustion time for 5 cm bed height was observed to be 60 minutes and 70 minutes for both 8 cm and 10 cm bed height. As the bed height increased, the mass transfer zone was broadened and binding sites for adsorbate increased and therefore increased the breakthrough time and exhaustion time (Hiremath and Theodore, 2017).

Although the exhaustion time for 8cm and 10cm bed height were observed to be the same, the breakthrough curve for 8cm bed height was obviously steeper than that of 10cm bed height. The lower the steepness of breakthrough curve, the more extended the exhaustion time (Chowdhury et al., 2014). An earlier exhaustion time was observed for 8cm bed height if the time interval for sample collection was smaller. This was also the reason that 5cm bed height had the highest inclination which was a curvilinear curve.

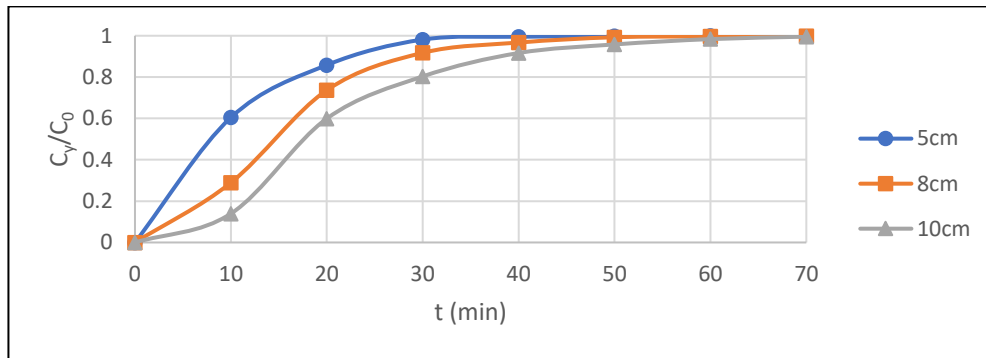


Figure 4. Breakthrough Curve at Different Bed Height for Calcined Shell

### 3.3 Effect of Initial Dye Concentration

The adsorptive performance of calcined clamshells biosorbent for various initial MO concentrations are presented in Figure 5. From Figure 5, the removal efficiency was observed to decrease from 96.65% to 93.03%, as the initial concentration increased from 10 mg/L to 30 mg/L at contact time of 10<sup>th</sup> minutes. The effect of initial methyl orange concentration was more obvious at contact time of 70<sup>th</sup> minutes where the removal efficiency decreased from 44.61% to 30.07% when initial concentration increased from 10 mg/L to 30 mg/L. This can be due to a constant and limited number of binding sites was provided when the initial dye concentration increased. At lower initial concentration, the ratio of initial number of anion to accessible binding sites was low and hence the removal efficiency was high. At higher initial concentration, this ratio became higher and

more residual anions remained in the solution, therefore, the removal efficiency was lower (Gorzin & Abadi, 2018). This effect could also be analysed through breakthrough curve shown as Figure 6. The breakthrough curve showed that the higher the initial methyl orange concentration, the shorter the breakthrough time and exhaustion time. This phenomenon was majorly due to higher saturation rate of the binding sites on the adsorbent due to higher driving force for mass transfer provided by higher initial methyl orange (Cao et al., 2015). In contrast, at low initial methyl orange concentration, the transport of methyl orange molecules to the adsorbent surface was slower due reduced mass transfer driving force and diffusion coefficient (López-Cervantes et al., 2018). This could also prove that diffusion process is concentration dependent (Han et al., 2008).

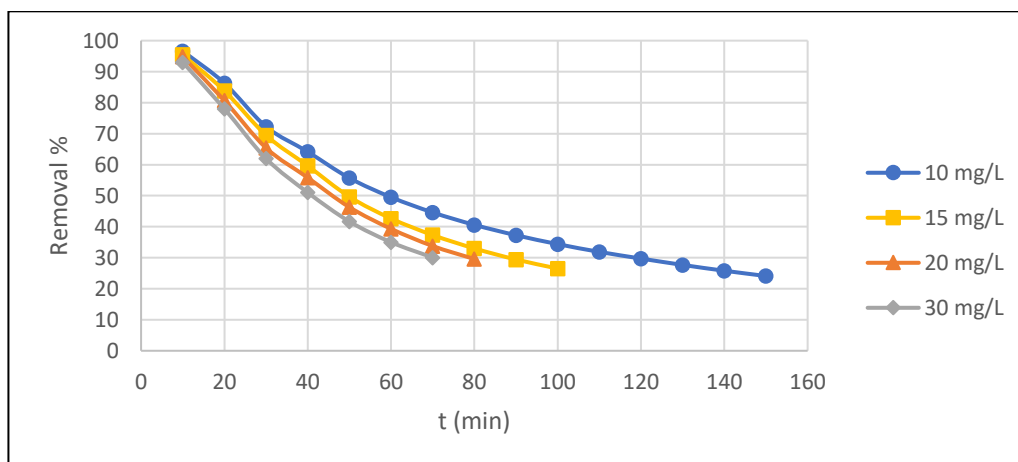


Figure 5. Removal Efficiency at Different Initial Methyl Orange Concentration

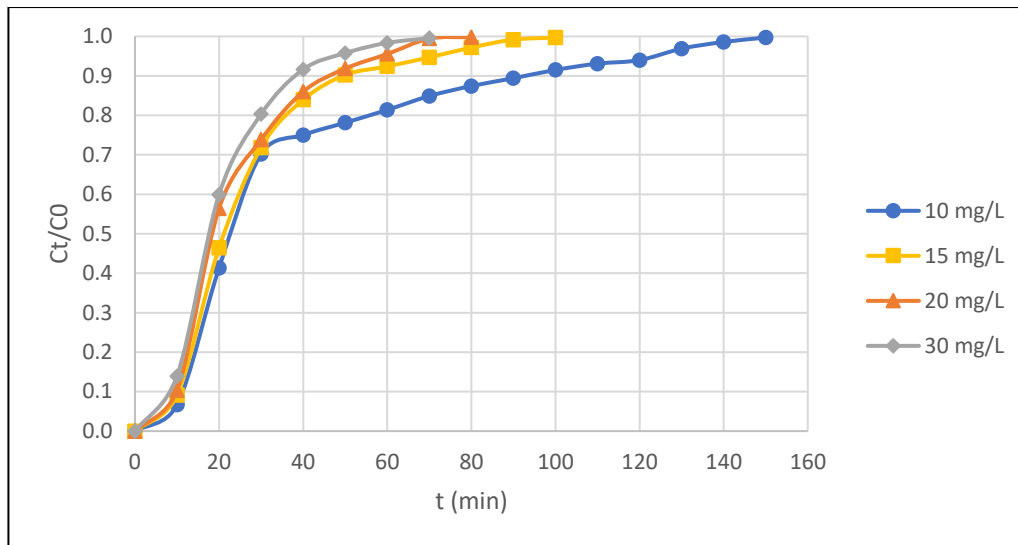


Figure 6. Breakthrough Curve at Different Initial Methyl Orange Concentration

### 3.4 Adsorption Kinetic Studies

Figure 7 and Figure 8 showed the linear plot of pseudo-first order and pseudo-second-order model respectively, and the constants calculated from these linear fittings are presented in Table 2 and 3. As evinced from Table 2 and Table 3, it showed that pseudo-first order model had regression coefficient ranging from 0.8872 to 0.9991 while pseudo-second order model had regression coefficient all above 0.98 (0.9863 to 0.998). This result proved that pseudo-second order model was in good agreement with the experimental data. Besides, the theoretical

$q_e$  and experimental  $q_e$  was found to be closer in pseudo-second order model than pseudo-first order model. Therefore, it could be concluded that pseudo-second order model was appropriate to be employed to depict the methyl orange removal mechanism by calcined shells, in which the rate-limiting step of this adsorption process is chemisorption (Sahoo & Prelot, 2020). Similar findings was also reported in previous literatures such as Inthapanya et al. (2019) which utilized the calcined oyster shell to remove Acid Green 25.

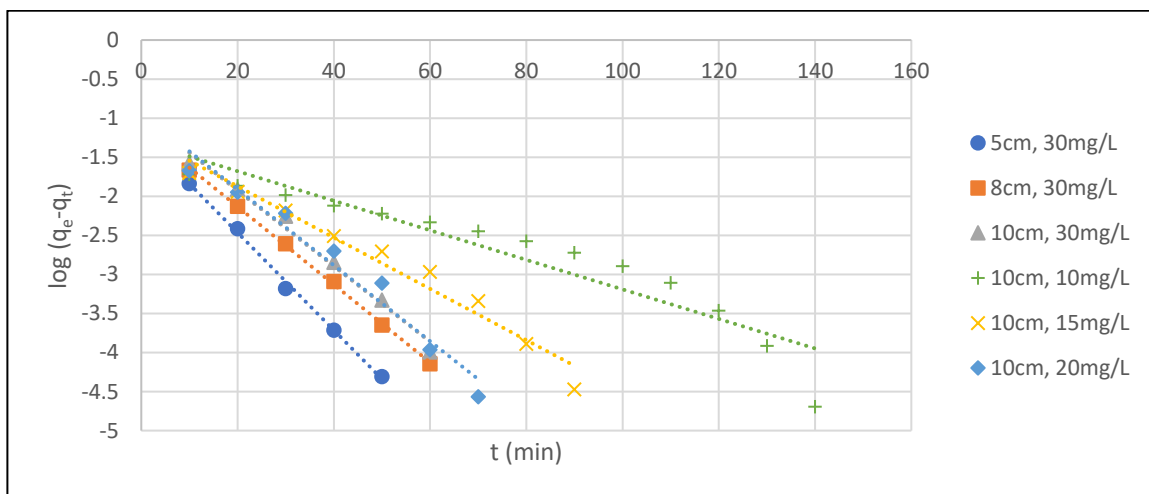


Figure 7. Linear Plot of Pseudo-first Order Model

Table 2 Analysis Result of Pseudo-first-order Model Kinetic

Bed height (cm)	Initial concentration (mg/L)	Theoretical $q_e$ (mg/g)	Experimental $q_e$ (mg/g)	$k_1$ (L/min)	$R^2$
5	30	0.0608	0.0425	0.1437	0.997
8	30	0.0731	0.0463	0.1149	0.9991
10	30	0.1101	0.0476	0.1115	0.9847
10	10	0.05	0.026	0.0435	0.8872
10	15	0.0608	0.0309	0.0755	0.9666
10	20	0.1151	0.0354	0.1119	0.9624

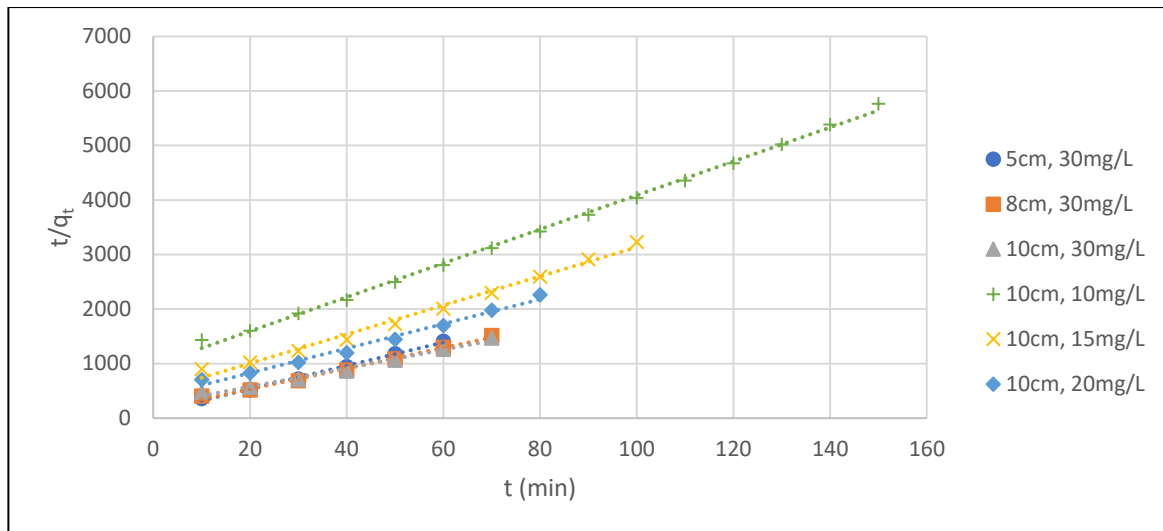


Figure 8. Linear Plot of Pseudo-Second-Order Model

Table 3 Analysis Result of Pseudo-Second-Order Model

Bed height (cm)	Initial concentration (mg/L)	Theoretical $q_e$ (mg/g)	Experimental $q_e$ (mg/g)	$k_2$ (L/min)	$R^2$
5	30	0.0468	0.0425	4.2569	0.9957
8	30	0.0529	0.0463	2.2941	0.9922
10	30	0.0593	0.0476	1.179	0.9863
10	10	0.0321	0.026	0.998	0.998
10	15	0.0376	0.0309	1.4972	0.9898
10	20	0.0444	0.0354	1.3409	0.9863

### 3.5 Column Adsorption Dynamic Model

Figure 9 and Figure 10 showed the linear plot of Thomas model and Yoon-Nelson model respectively, while Table 4 and 5 depict their corresponding model parameters and correlation coefficients. The results were in good agreement with these two models with a high regression coefficient value. The Thomas model from Table 4, the theoretical  $q_e$  was very close to the experimental  $q_e$ , indicating high accuracy of prediction of  $q_e$  can be done by using Thomas model. Besides, the theoretical  $q_e$  increased from 0.03 to 0.0464 mg/g when bed height increased from 5 cm to 10 cm. When initial methyl orange concentration increased from 10 mg/L to 30 mg/L,  $q_e$  increased from 0.0269 to 0.0476 mg/g. Therefore, it was proved that the adsorption capacity increased with increasing bed height and initial dye concentration.

The value of  $k_{TH}$  was observed to decrease from 5.5701 to 3.7208 mg/g/min when bed height increased from 5 cm to 10 cm. This trend was same as the result described by Patel (2019). As the initial dye concentration is low (<20 mg/L),  $k_{TH}$  increased from 4.2794 to 5.5281 mg/g/min and start decreasing when initial dye concentration increased from 20 mg/L to 30 mg/L. This was probably due to the limitation that the Thomas model was derived based on the second order kinetics, however the adsorption process was probably controlled by mass transfer but not only the chemical reaction Aksu & Gönen (2004). This discrepancy may lead to error

under certain conditions. Therefore, it can be said that Thomas model might not be suitable to be used for all conditions provided in this adsorption. For Yoon-Nelson model,  $k_{YN}$  decreased from 0.1598 to 0.1099  $\text{min}^{-1}$  while  $\tau$  (50% breakthrough time) increased from 7.505 to 20.5 minutes when bed height increased from 5 cm to 10 cm (Table 5). When initial methyl orange concentration increased from 10 mg/L to 30 mg/L,  $k_{YN}$  increased 0.0402 to 0.1099 but  $\tau$  decreased from 32.1866 minutes to 20.5 minutes. Therefore, it was proved that  $k_{YN}$  decreased while  $\tau$  increased with increasing bed height and decreasing initial concentration. The same trend was also obtained and reported from the study of column adsorption in removing Acid Yellow 17 dye by utilizing the tamarind seed powder Patel & Vashi (2012). The value of theoretical and experimental  $\tau$  were close when the regression coefficient was higher than 0.96.

From all the results above, it could be seen that although from Thomas model and Yoon-Nelson model same regression coefficient was obtained for all conditions, only the parameters in Yoon-Nelson model such as Yoon-Nelson constant as well as the 50% breakthrough time were obtained in the same trend as many other literatures. Therefore, it could be concluded that Yoon-Nelson model could describe the column adsorption of methyl orange onto the clamshells better at any condition, in which the rate of decrease in the probability of adsorption was proportionate to the rate of probability of

adsorption of adsorbate molecules and the probability of adsorbate breakthrough. While Thomas model was more suitable to be used to describe the column adsorption process at higher initial dye concentration (>20 mg/L) and at any bed

height, in which the adsorption followed Langmuir kinetics adsorption-desorption that the rate driving forces obeys second-order reversible kinetics and no axial dispersion.

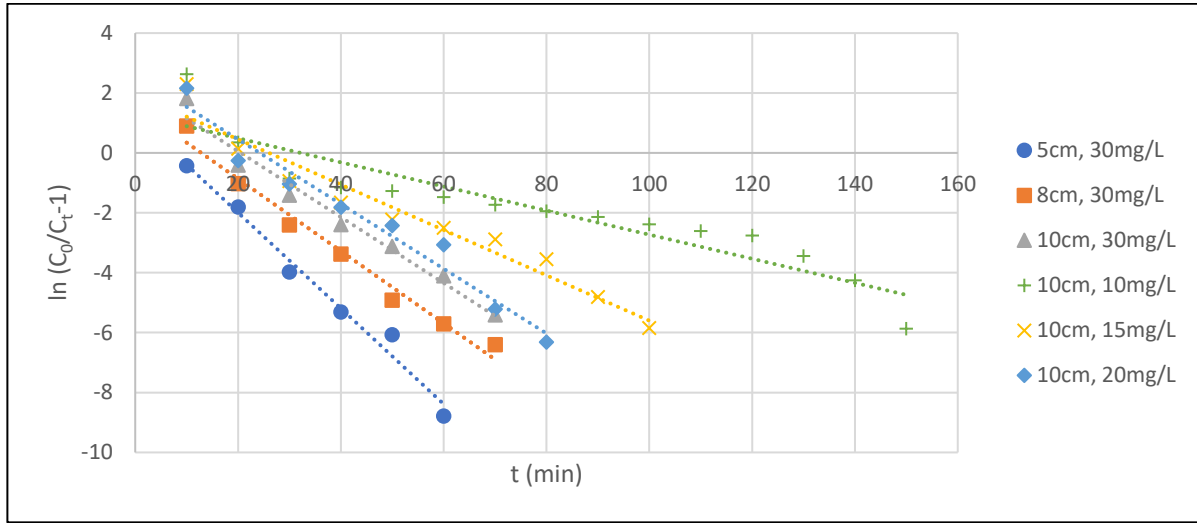


Figure 9. Linear Plot of Thomas Model

Table 4 Analysis Result of Thomas Model

Bed height (cm)	Initial concentration (mg/L)	$k_{TH}$ (mL/mg/min)	Theoretical $q_e$ (mg/g)	Experimental $q_e$ (mg/g)	$R^2$
5	30	5.5701	0.03	0.0425	0.9809
8	30	4.1015	0.0364	0.0463	0.9787
10	30	3.7208	0.0464	0.0476	0.9607
10	10	4.2794	0.0269	0.026	0.8548
10	15	4.9699	0.0303	0.0309	0.9447
10	20	5.5281	0.0362	0.0354	0.9735

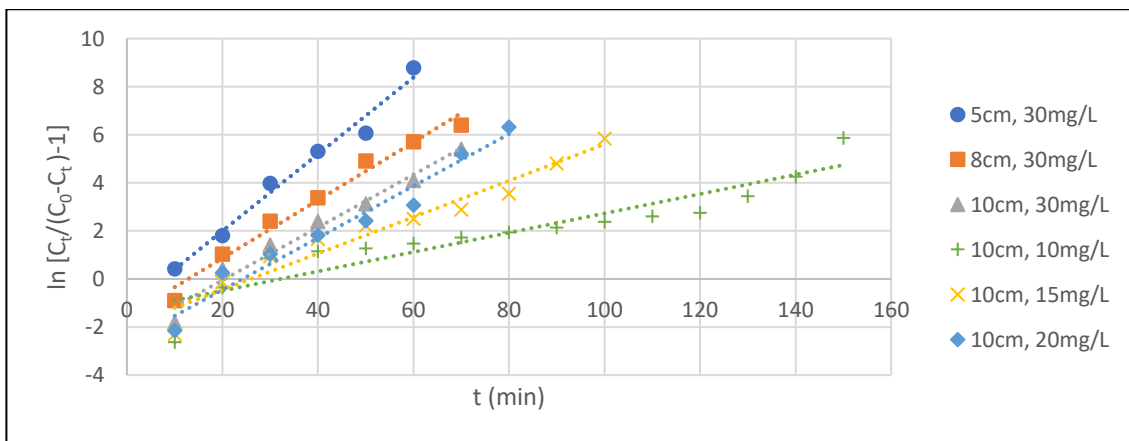


Figure 10. Linear Plot of Yoon-Nelson Model

Table 5 Analysis Result of Yoon-Nelson Model

Bed height (cm)	Initial concentration (mg/L)	$k_{YN}$ (min <sup>-1</sup> )	Theoretical $\tau$ (min)	Experimental $\tau$ (min)	$R^2$
5	30	0.1598	7.505	7.9	0.9809
8	30	0.1206	12.8391	14.6	0.9787
10	30	0.1099	20.5	17.61	0.9607
10	10	0.0402	32.1866	22.63	0.8548
10	15	0.0757	25.9881	18.32	0.9447
10	20	0.108	24.2111	21.12	0.9735

#### 4. Conclusion

It can be summarized that calcined clamshell can be used as an effective adsorbent for the removal methyl orange from the aqueous solution. The methyl orange removal efficiency onto the prepared calcined clamshells biosorbent was observed to increase with increasing bed height and decreasing contact time and initial dye concentration. The highest removal efficiency of 96.648% was achieved at adsorbent bed height of 10 cm and initial methyl orange concentration of 10 mg/L at contact time of 10<sup>th</sup> minutes. For kinetic studies, pseudo-second order model was found to fit the experimental data well. It could be concluded that the adsorption process of methyl orange onto the clamshells was chemisorption process. In addition, the adsorption process also obeyed the Yoon-Nelson model. The result of characterization through the SEM analysis at various magnification showed that calcined clamshells had more porous and smoother surface than raw clamshells, thus favoured the uptake of the adsorbate. The FTIR spectroscopy proved that there was transformation of calcium carbonate to calcium oxide during the calcination. The experimental data well fitted the pseudo-second order kinetic model, indicating that the adsorption is a chemisorption process. In addition, Yoon-Nelson kinetic model best describe the column adsorption studies at any condition in comparison to the Thomas model which well fitted at the initial dye concentration higher than 20 mg/L of any bed height.

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