Removal of Methyl Orange from Synthetic Wastewater onto Chitosan-Coated-Montmorillonite Clay in Fixed-Beds

C. Umpuch and S. Sakaew

Abstract— *The removal of methyl oragne from aqeous solution onto chitosan-coated-montmorillonite (CTS/MMT) was studied in this work by using fixed bed adsorption column. Experiments were carried out as a function of inlet methyl orange concentration (C_0: 50-200 mg/L), liquid flow rate (Q: 3.60 - 9.25 mL/min) and mixed sand-clay bed height (H: 15-25cm). The breakthrough characteristics of the adsorption were investigated. The breakthrough point appears faster with increasing liquid flow rate and inlet methyl orange concentration, but more slowly with increasing the bed height. It was found that the highest bed capacity of 7.34 mg/g was obtained at the condition: 200 mg/L inlet methyl orange concentration, 15 cm bed height and 3.60 mL/min flow rate. The adsorption data were fitted to three well-established fixed-bed adsorption models namely, Adam's-Bohart, Thomas and Yoon-Nelson models. The results fitted well to the Thomas and Yoon-Nelson models with coefficients of correlation $R^2 \geq 0.9415$. The adsorption test shows that CTS/MMT can be used as effective adsorbent for adsorption of the mtheyl orange using fixed-bed adsorption column.*

Keywords— **Methyl orange, chitosan-coated-montmorillonite, adsorption, fixed-beds.**

1. INTRODUCTION

Presently, textile industries are much larger scale-up to increase the amount of products. An azo dye such as methyl organe, which contains at least one azo bond (-N=N-) bearing aromatic rings, is the most common dye used due to their advantages such as bright colors, excellent color fastness and ease of applications [1]. Many azo dyes are toxic to some organisms and may cause direct destruction of creatures in water. They are hardly biodegradable in the natural stream codition. Azo dyes are highly soluble in water, their removal from effluent is difficult by conventional physicochemical and bilological treatment methods [2]. The removal of methyl orange from wastewater by adsorption technique using low-cost meterial could be an alternative method to handle this problem.

Montmorillonite clay (MMT) is a natural matter, low-cost and high spport in Thailand. It is a larmina structure with 2:1 silica. The clay inner layer composes of an alumina (Al_2O_3) complex octahedral sheet, which is sanwhiched by two silica (SiO_4) tetrahedral sheets. The substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Fe^{2+} for Al^{3+} in the octahedral layer results in a net negtive charge. In nature, the permanant negative charge on clay surface and lamella interlayer is compensated naturally by accomulation of cation Na^+, or Ca^{2+} on the layer surfaces. The MMT is water swellable which is due to the proton can be loaded in the interlayer resulting in larger basal spacing. The adsorption capacity of cations dye onto the clay is high due to electrostatic interaction between the negative layer charge and cationic dye molecules, for example, natural MMT can adsorb high amount of cationic dye such as methylene blue with the monolayer adsorption capacity of 322.6 mg dye/g clay [3]. Although high amount of cationic dye loaded on MMT was observed, anionic dye uptake on the MMT is very small because of electrostatic replusion. The use of modified MMT for anionic dyes has been widely considered in recent years by a number of researches [4], [5]. The coated catioic surfacant on the clay surface colud affect the clay structure which echances adsorption capacity to methyl organe [5]. The MMT activated by hydrochloric acid promotes the uptake of methyl orange on the modified clay as compared to the untreated MMT [6]. It can be mentioned that the modified clays display higher dye adsorption capacity than that of the original clay.

Chitosan (CTS) is the N-deacetylated derivative of chitin and the second most plentiful natural biopolymer. As a well-known sorbent, CTS is widely used for the removal of heavy, transition metals and dyes because the biopolymer chain of CTS contains amine group ($-NH_2$) and hydroxyl group (-OH) which can bind with cationic and anionic molecules [7]. Therefore, the CTS is a good adsorbent for methyl orange adsorption. On the other hand, CTS has some limitation that is the weak mechanical property and low specific gravity so it swells and floats when it is dissolved in water. To improve this limitation, it can be immobilized on the MMT surface to form a composite such as CTS/MMT. Therefore, the objective of this research is to study adsorption of methyl oragne onto CTS/MMT in fixed-bed column. The important design parameters such as inlet concentration of methyl orange solution, flow rate of fluid and column bed height were investigated. The breakthrough curves for the adsorption of methyl orange were analyzed using Adam's-Bohart, Thomas and Yoon-Nelson models. Further, modeling on the adsorption dynamics of the fixed bed was presented. Finally, the correlation between

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the model and the experimental data were compared.

2. RESEARCH METHODOLOGY

2.1 Materials

The methyl orange ($C_{14}H_{14}N_3NaO_3S$) obtained from Asia Pacific Specialty Chemicals Co. Ltd., is a monovalent anionic dye with molecular weight of 327.33 g/mol. The dye stock solution was prepared by dissolving accurately weight methyl orange in distilled water to meet 1 g/L of the dye concentration. The experimental solutions were obtained by dilution of the dye stock solution in accurate proportions to needed inlet concentrations. The chemical structure of methyl orange is shown in Fig.1. CTS ($C_{12}H_{24}N_2O_9$) obtained from Aldrih Chemistry has molecular weight of 340.33 g/mol.

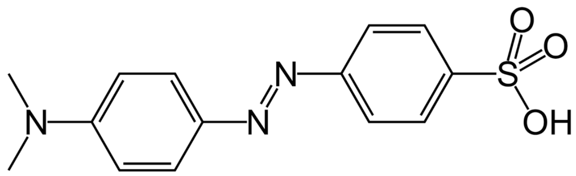

Fig.1. Molecular Structure of the Methyl Orange [5]

The MMT used was supplied by Thai Nippon Chemical Industrial Co. Ltd., Thialand. The chemical composition of MMT in weight percent is 56-60% of SiO_2, 16-18% of Al_2O_3, 5-7% of Fe_2O_3, 2.4-3% of Na_2O, 1.5-2% of MgO, 1.9-2.1% of CaO, 0.3-0.5% of K_2O and 1.2-1.5% TiO_2. The cation exchange capacity (CEC), data from the supplier, is 80 meq per 100 grams of MMT. The chemicals and clay were used without furthur purification.

2.2 Preparation of chitosan-coated-montmorillonite

An amount of 1 g of MMT dissolved in 100 mL distilled water and 100 mL of 2 g/L CTS solution were added into a batch reactor. The mixing was done by stirring at constant speed 200 rpm for 1 h at room temperature (25ºC). The pH of the suspension was adjusted to 7.0-7.5 by adding 0.1M NaOH and/or 0.1M HCl solutions and left it 30 min for gel formation. The formed composite was filtrated and washed with distilled water and then dried at 40ºC for 12 h. The dried clay was ground and sieved to 200 mesh sieve to obtain particle size in range of 300-600 µm. The CTS adsorbed onto MMT was confirmed by using CHNS-analyzer**.**

2.3 Column investigation

The CTS/MMT clay was mixed with quart sand at 2% by weight of adsorbent and then it was loaded into the glass column (1.2 cm inner diameter and 40 cm in height). Glass wool was inserted in the column as support. The column was loaded with different initial methyl orange concentrations, different flow rates and different mixed clay-sand bed heights as listed in Table 1. The effluent samples were continuously collected at the bottom of the column every 5 min in order to obtain breakthrough curve and the collected time was noted to determine the mean liquid flow rate. The dye concentration was analyzed by using UV-Vis-spectrophotometer at maximum absorbance wave length of 536 nm. The experiments were carried out at temperature of 25±1°C without pH adjustment.

2.4 Analysis of fixed-bed column data

The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristic for determining the operation and the dynamic response of an adsorption fixed-bed column. The breakthrough curve shows the behavior of dye removed from the aqueous solution in a fixed-bed column and is usually in term of adsorbed methyl orange concentration (C_{ad}), the initial methyl orange concentration (C_0), outlet methyl orange concentration (C_t) or normalized concentration defined as the ratio of outlet methyl orange concentration to inlet methyl orange concentration (C_t/C_0) as a function of time or volume of effluent for a given bed height. Effluent volume can be calculated by multiplying total flow rate (Q: mL/min) and total flow time (t_{total}: min).

The total adsorbed methyl orange quantity (maximum column capacity) or q_{total} was determined by integrating area under curve of the plot between C_{ad} (mg/L) versus t (min) multiplied by mean flow rate velocity (mL/min). The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (C_{ad}: mg/L) versus t (min) plot can be used to find the total adsorbed methyl orange quantity (maximum column capacity). Total adsorbed methyl orange quantity q_{total} (mg) in the column for a given feed concentration and flow rate is calculated as:

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} \, dt \qquad (1)$$

Equilibrium uptake q_e (mg/g) or maximum capacity of the column is determined by division of the total amount of adsorbed (q_{total}) per gram of adsorbent (w) at the end of total flow time.

3. RESULTS AND DISCUSSION

3.1 Breakthrough characteristics and adsorption capacities

A plot between the effluent volumes against the time was constructed. It was found that the plot was linear line with correlation coefficients of $R^2 \geq 0.9999$ showing that no blocking of mixed clay-sand in the column. The liquid mean flow rate velocities (Q) are shown in Table 1.

Fig. 2 shows the effect of a variation of the inlet methyl orange concentration of 50 to 200 mg/L on the adsorption characteristic was carried out using a fixed bed height and a solution flow rate. The normalized concentration (C_t/C_o) initially increases with time t and then remains constant. Moreover, it was observed that the slope of breakthrough curve obtained at 50 mg/L initial dye concentration was steeper than those 100 mg/L and 200 mg/L, respectively. At lower inlet dye concentrations, breakthrough curves were dispersed and the breakthrough points were reached slower. This can be described that a lower concentration gradient causes a slower methyl orange transport with a small diffusion coefficient or mass transfer coefficient. The larger inlet concentration provides steeper breakthrough curve and faster breakthrough point which is a result from the greater concentration gradient promoting the saturation rate. As the inlet methyl orange concentration increases, the methyl orange loading rate increases, so does driving force or mass transfer increase, which in a decrease in the adsorption zone length [8].

Table 1. Column Data Parameters obtained at Different Inlet Methyl Orange Concentrations, Bed heights and Flow Rates

C_0 (mg/L)	H (cm)	Q (mL/min)	t_b (min)	V_b (mL)	q_{total} (mg)	q_e (mg/g)
50	15	3.60	1.78	3.79	2.24	3.73
100	15	3.60	2.72	9.29	3.26	5.44
200	15	3.60	2.10	7.59	4.41	7.34
100	20	3.60	2.28	8.21	3.78	4.72
100	25	3.60	2.97	8.21	4.21	4.21
100	15	7.20	1.93	10.7	2.67	4.45
100	15	9.20	1.43	13.19	1.87	3.12

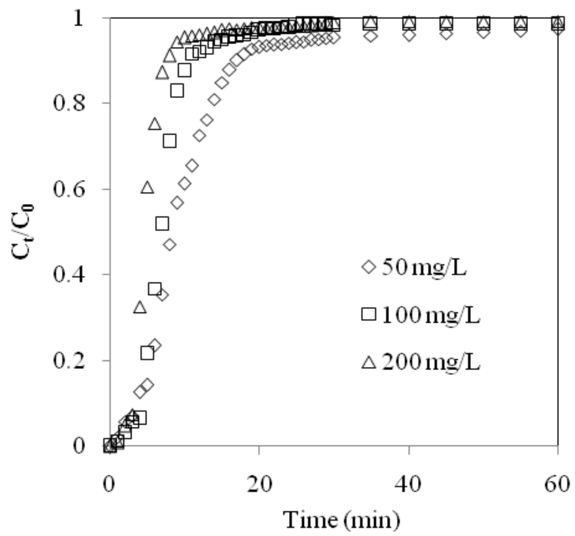

Fig.2. Breakthrough Curves for Methyl Orange Adsorption at Different Initial Concentration (15cm Bed Height and 3.6 mL/min).

Fig. 3 shows the breakthrough curve of methyl orange adsorption on the mixed clay-sand bed with variation of three flow rates such as 3.60, 7.20 and 9.20 mL/min. It was observed that breakthrough generally occurred faster with higher flow rate. Breakthrough time reaching saturation was increased significantly with a decreased in the flow rate. At low flow rate, the inlet methyl orange has more time to contact with bed resulting in higher capacity adsorption of methyl orange in column. It can be described that at higher flow rate the rate of mass transfer gets increase with flow rate leading to faster saturation. At a higher flow rate, the adsorption capacity was lower due to insufficient residence time of the solute in the column and diffusion of solute into the pores of the adsorbent, and therefore, the solute left the column before equilibrium reached.

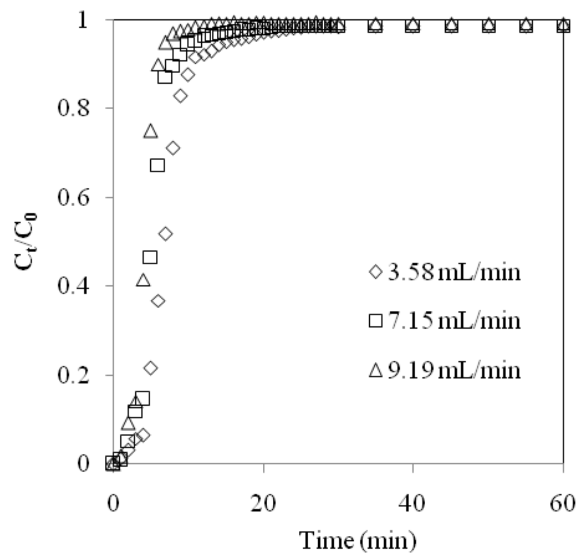

Fig.3. Breakthrough Curves for Methyl Orange Adsorption at Different Flow Rates (100 mg/L Initial Methyl Orange Concentration and 15cm Bed Height).

Fig. 4 shows the breakthrough curve of methyl orange adsorption on the mixed clay-sand bed with different bed heights of 15, 20 and 25 cm (0.6g, 0.8g and 1.0g). The breakthrough increases with increasing the bed height. As the bed height increases, methyl orange had more time to contact with the bed resulting in higher adsorption capacity of methyl orange in the column. The slope of breakthrough curve decreased with increasing bed height, which results in a broadened mass transfer zone. High adsorption capacity was observed at the highest bed height due to an increase in the surface area of adsorbent, which provided more binding sites for the adsorption.

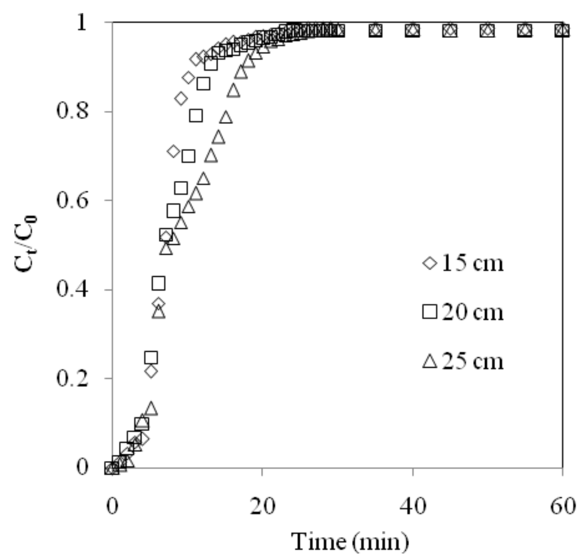

Fig.4. Breakthrough Curves for Methyl Orange Adsorption at Different Bed Height (100 mg/L Initial Methyl Orange Concentration and 3.6 mL/min).

Table 1 shows not only the liquid mean flow rate velocities but also the breakthrough characteristics, adsorption capacity and exhausted time, of methyl orange in the mixed CTS/MMT-sand clay beds at different inlet methyl orange concentration, different flow rate and different bed length. The breakthrough point (the position at C_t/C_0 = 0.05) appears faster with increasing liquid flow rate and initial methyl orange concentration, but more slowly with increasing the bed height. The highest of breakthrough time (t_b) was 2.97 min which obtained at condition: 100 mg/L inlet methyl orange concentration, 25 cm bed height and 3.60 mL/min flow rate. The highest breakthrough volume (V_b) was 13.19 mL which obtained at condition: 100 mg/L inlet methyl orange concentration, 15 cm bed height and flow rate of 9.20 mL/min. The highest bed capacity (q_e) was 7.34 mg/g obtained at the condition: 200 mg/L methyl orange concentration, 15 cm bed height and flow rate of 3.60 mL/min.

3.2 Modelling of Brakthrough curves

It is necessary to fit the adsorption data using established models and subsequently determine noticeable parameters associated with these models to determine their influence for optimization of the fixed-bed adsorption process.

3.2.1The Adam's-Bohart model

Adam's-Bohart model [9] established the fundamental equations describing the relationship between C_t/C_0 and t in a continuous system. The Adam's-Bohart model was applied to experimental data for the description of the initial part of the breakthrough curve. The expression is following:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{AB}C_0t - k_{AB}N_0\left(\frac{Z}{F}\right) \tag{2}$$

where C_0 and C_t (mg/L) are the inlet and effluent methyl orange concentration, k_{AB} (L/mg.min) is the kinetic constant, F(cm/min) is the linear velocity calculated by dividing the flow rate by the column cross section area, Z(cm) is the bed depth of column and N_0 (mg/L) is the saturation concentration. A linear plot of $\ln(C_t/C_0)$ against time (t) was determined values of k_{AB} and N_0 from the intercept and slope of the plot (Figure not shown).

Table 2. Adam's – Bohart Parameters at Different Conditions Using Linear Regression Analysis

C_0 (mg/L)	H (cm)	Q (mL/min)	k_{AB}x10^3 (L/mg min)	N_0 (mg/L)	R^2
50	15	3.60	9.048	94.410	0.9128
100	15	3.60	5.462	182.907	0.9049
200	15	3.60	5.377	220.652	0.9033
100	20	3.60	6.289	118.848	0.9261
100	25	3.60	8.170	90.162	0.9530
100	15	7.20	9.036	121.962	0.8727
100	15	9.20	10.440	99.738	0.8939

After applying Adam's-Bohart model to experimental data, a linear relationship between $\ln(C_t/C_0)$ and time (t) according to Eq.(2) was constructed for the relative concentration (C_t/C_0) up to 0.5, i.e, 50% breakthrough. For all breakthrough curves, respective values of N_0, and k_{AB} were calculated and presented in Table 2 together with correlation coefficients (R^2>0.8727). The values of k_{AB} decrease with inlet methyl orange concentration and solution flow rate, but it increases with bed height. This shows that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in the column [10]. Although the Adams-Bohart model provides a simple and comprehensive approach to running and evaluating sorption-column tests, its validity is limited to the range of conditions used.

3.2.2Thomas mode

Thomas model [10] assumes plug flow behaviour in the bed, and uses Langmuir isotherm for equilibrium, and second-order reversible reaction kinetics. This model is suitable for adsorption processes where the external and internal diffusion limitations are absent. The linearized form of Thomas model can be expressed as follows:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th}q_0w}{Q} - k_{Th}C_0t \tag{3}$$

where k_{Th} (mL/min.mg) is the Thomas rate constant; q_0 (mg/g) is the equilibrium methyl orange uptake per g of the adsorbent; w (g) is the mass of adsorbent, Q (mL/min) is the flow rate and total time (min) stands for flow time. The value of C_t/C_0 is the ratio of outlet and inlet methyl orange concentrations. A linear plot of $\ln[(C_0/C_t)-1]$ against time (t) was employed (figure not shown) to determine values of k_{Th} and q_0 from the intercept and slope of the plot.

Table 3. Thomas Model Parameters at Different Conditions Using Linear Regression Analysis

C_0 (mg/L)	H (cm)	Q (mL/min)	k_{Th}x10^3 (L/mg min)	q_0 (mg/g)	R^2
50	15	3.60	9.750	2.489	0.9797
100	15	3.60	7.343	4.137	0.9629
200	15	3.60	6.270	5.600	0.9608
100	20	3.60	7.349	2.984	0.9794
100	25	3.60	8.359	2.489	0.9822
100	15	7.20	10.117	3.173	0.9415
100	15	9.20	11.462	2.624	0.9601

The column data were fitted to the Thomas model to determine the Thomas rate constant (k_{Th}) and maximum solid-phase concentration (q_0). The determined coefficients and relative constants were obtained using linear regression analysis according to Eq.(3) and the results are listed in Table 3. It is found that the determined coefficients (R^2) are among 0.9415 to 0.9822. The values of k_{Th} and q_0 are presented in Table 3. As flow rate increases, the value of q_0 decreases but the value of k_{Th} increases. As the inlet concentration increases, the value of q_0 decreases while the value of k_{Th} increases. The reason is that the driving force for adsorption is the concentration difference between the methyl orange on the adsorbent and the methyl orange in solution [8]. As the bed heights increase, the value of q_0 increases significantly while the value of k_{Th} decreases significantly. Thus, lower flow rate, lower initial methyl orange concentration and higher bed heights would increase the adsorption of methyl orange on the bed column. The Thomas model is suitable for adsorption processes where the external and internal diffusions will not be the limiting step [10].

3.2.3The Yoon-Nelson model

Yoon and Nelson [11] developed a model based on the assumption that the rate of decrease in the probability of adsorption of adsorbate molecule is proportional to the probability of the adsorbate breakthrough on the adsorbent. The Yoon-Nelson is a linearized model for a single component system i expressed as:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - k_{Th}\tau \qquad (4)$$

where k_{YN} (1/min) is the rate velocity constant, τ (min) is the time required for the relative concentration region up to 0.5. A linear plot of $\ln[C_t/(C_0\text{-}C_t)]$ against sampling time (t) according to Eq.(4) gives the values of k_{YN} and τ from the intercept and slope of the plot (figure not shown). The values of K_{YN} and τ are listed in Table 4. The rate constant K_{YN} increases and 50% breakthrough time τ decreases with flow rate and inlet methyl orange concentration. An increase of bed height, the values of τ increases while the values of K_{YN} decrease. Table 4 indicates that τ values from the calculation are significantly different from the experimental results.

Table 4. Thomas Model Parameters at Different Conditions Using Linear Regression Analysis

C_0 (mg/L)	H (cm)	Q (mL/min)	K_{YN} (L/mg min)	τ (min)	R^2
50	15	3.60	0.488	8.283	0.9797
100	15	3.60	0.729	6.943	0.9629
200	15	3.60	1.245	4.700	0.9608
100	20	3.60	0.741	6.578	0.9794
100	25	3.60	0.841	6.874	0.9822
100	15	7.20	1.020	5.245	0.9415
100	15	9.20	1.160	4.322	0.9601

4. CONCLUSIONS

The fixed-bed adsorption system was found to perform better with lower inlet methyl orange concentration, lower feed flow rate and higher mixed clay-sand bed height. The breakthrough point appears faster with increase of liquid flow rate and initial methyl orange concentration. The highest bed capacity of 7.34 mg/g was obtained at the condition: 200 mg/L inlet methyl orange concentration, 15 cm bed height and 3.60 mL/min flow rate. The fixed-bed column adsorption system containing mixed CTS/MMT-sand is effective to removal methyl orange from aqueous solution. The column experimental data were analyzed by the Adam's-Bohart, Thomas and Yoon-Nelson models. For methyl orange adsorption, the column data were fitted well to the Thomas and Yoon-Nelson models.

The use of MMT modified with other chemicals, for example, cationic surfactant and strong acid might be further studied for the pollution control.

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