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Removal of green 40 from aqueous solutions by adsorption using organo-corn straw

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Abstract

The objective of this study was to investigate the adsorption characteristics of green 40 on organo-corn straw which was prepared by means of adsolubilization in batch tests and fixed bed column experiments. The batch tests were studied as functions of contact times (t), initial pH solutions (pH_0), and initial dye concentrations (C_e). The adsorption reached equilibrium within 5 h and the amount of the dye adsorbed decreased with increases in pH_0. The adsorption isotherm followed Langmuir and Freundlich isotherms and the kinetic data obeyed the pseudo-second order kinetic model. The fixed bed experiments were carried out as functions of inlet dye concentrations, liquid flow rates, and bed heights. The breakthrough point appeared faster with increases in liquid flow rates and inlet dye concentrations, but presented more slowly with increases in bed heights. It was found that the highest adsorption capacity of 152.75 mg/g was obtained under the condition of inlet dye concentration of 200 mg/L, bed height of 16 cm, and flow rate of 3.5 mL/min. The adsorption data were fitted to three well-established fixed-bed adsorption models, Adams-Bohart, Thomas, and Yoon-Nelson models with good coefficients. The results showed that organo-corn straw can be used as an effective biosorbent for the removal of green 40 from wastewater.

Keywords : Green 40, Adsolubilization, Organo-corn straw, Adsorption, Batch tests, Fixed-bed column

1. Introduction

Local fabric products such as hand-woven silk and hand-woven cotton produced in many rural areas in Thailand have received attention from many customers around the world. Villagers earn income in addition to that from their agricultural activities from the sale of their fabric products. According to high product demand, villagers group themselves into household-scale textile industries to increase their production capacities. There are over a hundred textile industries at the household scale in Ubon Ratchathani province. Dyeing the fabric is an important step to make it attractive. Organic dyes are normally used due to their bright colors, excellent color fastness, and ease of application [1]. These dyes are highly soluble in water and do not biodegrade well in natural stream conditions because of their high resistance to heat, light, and structural complex. Accumulation of organic dyes in nature causes a reduction of the penetration of light into the water body, resulting in polluted water which is unsightly and strong smelling. Furthermore, many organic dyes are contaminated with toxic heavy metals and may cause direct harm to humans and organisms via natural streams. Treatment of colored effluent is difficult by conventional physical, chemical, and biological treatment methods [2]. Treatment that is cheap, efficient, and simple is what is required.

Biosorption is an emerging technique for water treatment that involves the binding of contaminants on the surface with easily available biomaterials. The capacity of biosorbents can be enhanced by various treatments [3-4]. Adsolubilization technology, which is a process to form admiclle of surfactant on the external surface of adsorbent for altering surface properties from hydrophilic to organophilic, has been proven to be effective [3]. As biosorption mainly takes place on the biomass surface, surfactant adsolubilized on the biosorbent surface is an effective approach for enhancing the biosorption capacity to organic molecules including organic dyes [5]. Green 40 is an organic dye manufactured in Thailand and its major constituents are carbon and hydrogen which are very cheap and available in many local markets near Ubon Ratchathani University. It is one of the most used organic dyes in the dyeing process in this region. This research used corn straw in the preparation of organo-corn straw by means of adsolubilization.

Corn is one of the major agricultural products in Thailand and there is a plentiful, inexpensive, and renewable supply of its straw left in the fields after the harvesting season each year. Batch adsorption tests are usually carried out to investigate adsorption capacity and adsorption behavior of organic dyes on the modified biosorbent. Factors affecting biosorption include contact times, initial pH solutions, and initial dye concentrations. In practical uses, immobilization of the cationic surfactant on a supporting or immobilizing material is also tested to remove dyes from effluents [6]. The immobilization systems provide advantages over free-form biosorbents. These include ease of regeneration and reuse of the biomass, easier solid-liquid separation, and minimal

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clogging of continuous flow systems [7]. Batch adsorption taken places in a closed system containing a desired amount of adsorbent contacting with a certain volume of adsorbate solution, while dynamic adsorption usually occurs in an open system where adsorbate solution continuously passes through a column packed with adsorbent. For column adsorption, the breakthrough curve is a very important because it provides predominant information for the design of a column adsorption system for practical application [8]. Factors affecting adsorption in fixed-bed column include initial dye concentrations, bed heights and feed flow rates [9].

The objective of this research was to study the biosorption potential of organo-corn straw in batch tests and fixed bed columns. In the batch tests, biosorption was investigated as functions of contact times, initial pH solutions, and initial dye concentrations and adsorption isotherm and kinetic models were also conducted for data correlation. In the fixed bed experiments, the important design parameters such as inlet concentrations of green 40 solutions, flow rates of fluid, and column bed heights were investigated. The breakthrough characteristics of the biosorption of green 40 on the organo-corn straw were analyzed using Adams-Bohart, Thomas, and Yoon-Nelson models.

2. Material and methods

2.1. Dye solutions

The organic dye, green 40 was purchased from a local market near Ubon Ratchathani University [10]. The IR-spectra of green 40 dye showed that the dye contains two categories of active functional groups which are carboxyl and hydroxyl groups which are hydrophilic part and long chain alkyl group which is hydrophobic part which has been reported in previous study [11]. The dye stock solution was prepared by dissolving accurately weighed green 40 in distilled water to obtain 1 g/L of the dye solution. The dye solutions studied were prepared by dilution of the dye stock solution in accurate proportions to the desired initial concentrations.

2.2. Preparation of organo-corn straw

Raw corn straw which was also purchased from a local market near Ubon Ratchathani University was prepared by washing with distilled water several times to remove dust and other impurities. It was then dried at a temperature of 40°C in an air circulating oven until its weight was constant. The corn straw was crushed and shredded in a blender for about 15 min and sieved (50 mesh) to obtain a particle size below 297 µm [12]. The organo-corn straw was prepared by treating 1.0 g of the corn straw with 100 mL of 1000 mg/L tetradecyltrimethyl ammonium bromide surfactant ($C_{17}H_{38}NBr$) purchased from the Merck Chemical Company (Germany). The cationic surfactant structure was shown in Figure 1. Mixing took place at 200 rpm for 15 min at room temperature using an orbital shaker. Afterwards, the organo-corn straw particles were filtrated with GF80 filter (Whatman, UK), washed with distilled water several times to remove superficially retained surfactant, and dried in an oven at 40°C until the weight was constant (approximately 48 hr). To obtain more reproducible data, the organo-corn straw particles were sieved (50 mesh) before its use for the adsorption studies. Furthermore, all adsorbents were packed in plastic bags and stored in desiccators for further use.

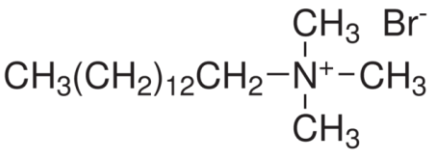

Figure 1 TMDA-Br structure

2.3. Batch tests

Since the percentages of green 40 removal of the corn straw and the organo-corn straw were 25.62% and 95.61%, respectively, which were obtained under a condition: 100 mL of solution volume, 200 mg/L dye solution, 0.1 g of adsorbent, 200 rpm agitation speed, and 24 hr shaking duration. Thus, only the organo-corn straw was used as biosorbent for further experiments. Batch adsorption tests were conducted as functions of contact times, initial pH solutions, and initial dye concentrations. First, to investigate the effect of contact times, a series of 250 mL Erlenmeyer flasks containing 100 ml of 200 mg/L dye solution was mixed with 0.1 g of the organo-corn straw. These flasks were plugged with parafilm to avoid evaporation and then horizontally shaken at 200 rpm. The samples were measured at intervals between 5 and 360 min. Second, to investigate the effect of initial pH solutions, 100 ml of 200 mg/L dye solution was mixed with 0.1 g of the organo-corn straw and placed in a 200 ml Erlenmeyer flask. The initial pH solution was adjusted between 2.0 and 10.0 by 0.01N NaOH and/or 0.01N HCl and then horizontally shaken at 200 rpm for 24 hours. Finally, to investigate the effect of initial dye concentrations, 0.1 g of the organo-corn straw was loaded into 100 ml of 50 to 250 mg/L initial dye solution and then horizontally shaken at 200 rpm for 24 hours to achieve equilibration (equilibrium time was obtained from the study of contact time). All samples were measured in the equilibrium condition. The dye concentration of all samples was analyzed by using UV-Vis-Spectrophotometer at a maximum absorbance wave length of 409 nm. The experiments were carried out at a temperature of 25±1°C without pH adjustment.

2.4. Fixed bed column experiments

Experiments in fixed bed columns (Figure 2) were then completed as functions of initial dye concentrations, flow rates, and bed heights. Fixed bed columns were prepared by inserting glass wool in an end of a glass column (1.2 cm inner diameter and 40 cm height) until 10 cm of glass wool height was obtained and then organo-corn straw was loaded into the other end of the glass column. The factors affecting include initial dye concentration (50-200 mg/L), flow rate (1.4-7 mL/min) and bed height (8-24 cm) are investigated. First of all, distillated water was pumped into the column by a diaphragm pump to measure the water permeability and then the dye solutions were fed into the column. The samples from the effluents from the columns were measured every 5 min until the effluents reached 90% of the initial dye concentration. Breakthrough characteristics and mean liquid flow rates were interpreted from the experimental data.

The breakthrough time (t_b), breakthrough volume (V_b), and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of biosorption in the fixed bed columns. The breakthrough curve shows the shape of mass transfer

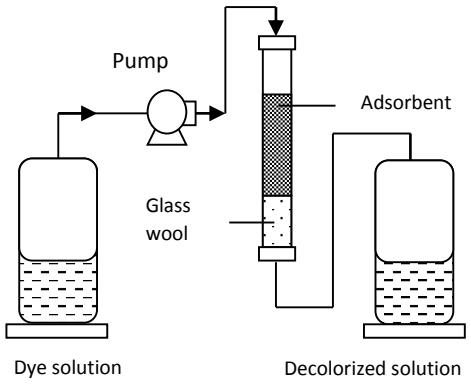

Figure 2 Column experimental set-up

zone occurring in the fixed bed columns and adsorption capacity is usually in terms of adsorbed dye concentration (C_{ad}), the initial dye concentration (C_0), outlet dye concentration (C_t) or normalized concentration defined as the ratio of outlet dye concentration to inlet dye concentration (C_t/C_0) as a function of time or volume of effluent for a given bed height. The effluent volume can be calculated by multiplying total flow rate (Q: mL/min) and total flow time (t_{total}: min). The total adsorbed dye quantity (maximum column capacity) or q_{total} was determined by integrating the area under curve of the plot between C_{ad} (mg/L) versus t (min) multiplied by the 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 dye quantity (maximum column capacity). The total adsorbed dye quantity q_{total} (mg) in the column for a given feed concentration and flow rate is calculated as:

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

The 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. A plot between the effluent volumes against time was constructed. The characteristic parameters obtained from breakthrough curves also presented in Table 1.

It was found that the plot of distillated water flow rate versus time was linear with correlation coefficients of $R^2 \geq 0.9999$ showing no blocking of liquid transferred through organo-corn straw in the column.

3. Research results and discussion

3.1. Effect of contact time

The effect of contact time on the dye uptake from the aqueous solution is depicted in Figure 3. The adsorption capacity of green 40 dye on the organo-corn straw rapidly increased in the first 10 min and maintained a slower increase until constant at 300 min (equilibrium time). The fast adsorption rate in the initial stage comes from the fact that there was a plentiful availability of active sites on the external surface of admicelle coated on the organo-corn straw surface so that dye molecules were solubilized on the admicelle surface easily and quickly. The slower sorption rate in the later stage can be explained as the dye molecules being diffused into the interior of the admicelle covering on the adsorbent surface. To ensure equilibrium, further experiments in the batch tests were left for 24 hours.

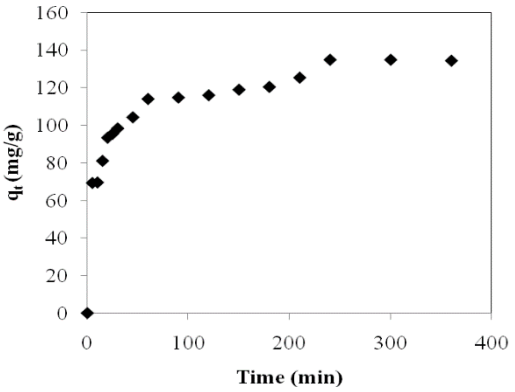

Figure 3 Effect of contact time on adsorption capacity of green 40 on organo-corn straw, C_0: 200 mg/L, pH 5.0

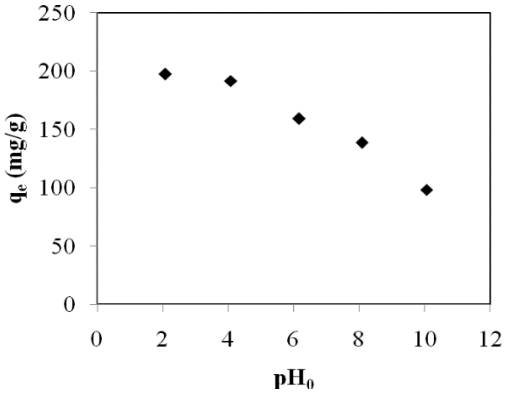

Figure 4 Effect of initial pH solution on the sorption of green 40 on organo-corn straw, C_0: 200 mg/L, pH: 2.0 – 10.0, Contact time: 24 hrs

3.2. Effect of initial pH solution

The adsorption capacity of green 40 on the organo-corn straw steadily decreased with increases in the pH solution as depicted in Figure 4. The high decrease is probably attributed to the dissociation of functional groups in the alkali medium. Green 40 contains three functional groups including carboxyl, hydroxyl and long chain alkyl groups involving the adsorption [11]. The carboxyl and hydroxyl groups of the green 40 interacts with at the positively fixed charges of external surface of admicelle due to electrostatic interactions so that the increase of hydroxide ions portion causes higher competition of conjugated bases (dissociated functional groups) and the active sites of adsorbent. On the other hand, the dye molecules and the conjugated bases are of different hydrophobicity. The two hypothetical explanations could be sufficiently given for the decrease of dye uptake at high solution pH. The hypothetical schematic diagram which purposed interactions between green 40 and organo-corn straw purposed is shown in Figure 5. Therefore, the dye adsorbed by the organo-corn straw should be highly pH dependent. Furthermore, these results also show that green 40 can be removed from the dye-loaded adsorbent in an alkali medium after the adsorption at low solution pH terminated.

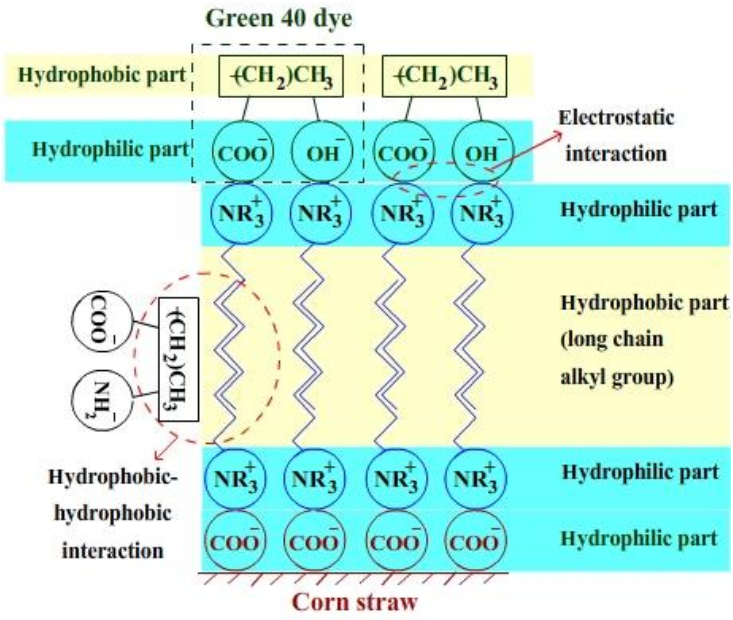

Figure 5 Schematic diagram for interactions between green 40 and organo-corn straw

3.3. Kinetic studies

The kinetic data are usually fitted by well-known established kinetic models such as the pseudo-first order kinetic model and pseudo-second order kinetic model. The pseudo-first order model proposed by Lagergren [13] is expressed in the form

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{2}$$

where q_e and q_t are the adsorption capacity (mg/g) of dye at equilibrium and at a time t respectively, and k_1 is the constant rate for pseudo-first order adsorption (L/min). After integration and application of initial condition $q_t = 0$ at $t = 0$, equation (2) becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t) \tag{3}$$

The best fit to kinetic data to equation (3) revealing that the external mass transfer through a boundary layer is the rate of limiting step. The pseudo-second order equation proposed by Ho [14] can be written as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

where k_2 is the constant rate for pseudo-second order adsorption (g/(mg.min)). For the initial condition $q_t = 0$ at $t = 0$, the integrated form of equation (4) becomes

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

The best fit to kinetic data to equation (5) indicating that the formation of interaction between adsorbate and adsorbent on the external surface of adsorbent is the rate of limiting step.

Table 1 Kinetic model parameters and correlation coefficients

Model	Parameter	Value
	q_e(exp) (mg/g)	134.32
Pseudo-first order model	k_1 (1/min)	0.0093
	q_e(cal) (mg/g)	59.70
	R^2	0.8104
Pseudo-second order model	k_2 (g/(mg.min))	0.000634
	q_e(cal) (mg/g)	137.0
	R^2	0.9996

The parameters of the kinetic models are given in Table 1. The experimental adsorption capacity q_e (exp) is the highest one at equilibrium stage obtained directly from the Fig. 3. Poor correlation of the kinetic data with the pseudo-first order kinetic equation was observed. Normally, the pseudo-first order equation was well fitted for the data obtained at the initial stage of the batch experiment. A good correlation between the kinetic data and the pseudo-second order equation was found. The formation of hydrophobic-hydrophobic interaction between dye molecules and the adsorbent were found on the external surface of the biosorbent. The hydrophobic-hydrophobic interaction is a phenomenon in which nonpolar substances to aggregate in aqueous solution and exclude water molecules.

This step takes the longest time compared to other steps, also known as the rate of limiting step. The results showed that the kinetic data were well described by the pseudo-second order ($R^2 = 0.9996$) indicating chemical sorption could be involved in the adsorption process.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{(k_L . q_m)} \tag{6}$$

3.4. Adsorption isotherms

The adsorption isotherm is the plot of adsorption capacity versus dye concentration at the equilibrium stage. Adsorption isotherms developed by Langmuir and Freundlich [15] were commonly used to fit the equilibrium data. Langmuir isotherm is related to the sorption taking place at specific homogeneous sites within the adsorbent. Freundlich isotherm is based on the assumption of a heterogeneous surface with a non-uniform heat distribution of the sorption along the surface. The linear equations of Langmuir isotherm is shown below where q_m is monolayer capacity or limiting sorption (mg/g) and k_L is Langmuir constant (L/mg). The parameters can be evaluated from the slope and intercept of the linear plat of C_e/q_e against C_e.

The linear equation of Freundlich isotherm is

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (7)$$

where k_F is Freundlich characteristic constant $(mg/g)(L/g)^{1/n}$ and 1/n is the heterogeneity factor of adsorption. The parameters can be obtained from the intercept and slope of the linear plat of ln q_e against ln C_e respectively.

The adsorption isotherms of green 40 which are a relationship between q_e and C_e are shown in Figure 6. The adsorption capacity of the green 40 increased with equilibrium concentration. The equilibrium data obtained were fitted to the Langmuir and Freundlich models. The isotherm constants and correlation coefficients for the adsorption of green 40 on the organo-corn straw are listed in Table 2. According to the correlation coefficients r^2, it can be seen that the system followed both the Langmuir and the Freundlich isotherms. This suggests that the monolayer and/or multilayer coverage on the adsorbent surface took place.

3.5. Fixed bed column adsorptions

Figure 7 shows the effect of inlet green 40 concentrations of 50 to 200 mg/L on the breakthrough curves in a fixed bed with a bed height of 16 cm and a flow rate of 3.5 mL/min. It was observed that the normalized concentration (C_t/C_0) initially increased with time t and then remained constant. The breakthrough time of 50 mg/L initial dye concentration was the longest compared to that of 100 mg/L and 200 mg/L respectively. This may be because the lower inlet concentration caused a smaller driving force so that the mass transfer rate from the liquid phase to the solid surface was small. Higher inlet dye concentrations have higher mass transfer and the faster breakthrough time is because of the faster saturation rate. This results in a shorter mass transfer zone length [16-18]. Therefore, the faster breakthrough point appearance was a result of increased inlet dye concentration.

Figure 8 shows the breakthrough curve of green 40 adsorption on the organo-corn straw with different bed heights of 8, 16, and 24 cm (0.2, 0.4, and 0.6 g) and an inlet dye concentration of 100 mg/L and a flow rate of 3.5 mL/min. The breakthrough time increased with an increase in the bed height due to a higher bed height that gave a higher amount of organo-corn straw and more binding sites for the adsorption. This resulted in a broadened mass transfer zone. Higher adsorption capacity was observed at the higher bed height due to an increase in the surface area in the fixed bed column.

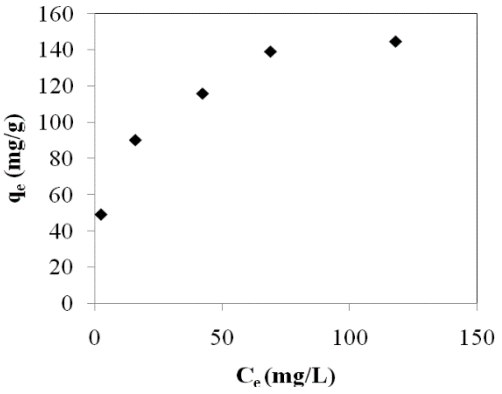

Figure 6 Adsorption isotherm of the sorption of green 40 on organo-corn straw, C_0: 50-200 mg/L, pH 5.0

Table 2 Isotherm constants and correlation coefficients

Model	Parameter	Value
Langmuir isotherm	q_m (mg/g)	156.25
	k_L(L/g)	15.36
	r^2	0.9944
Freundlich isotherm	k_F ((mg/g)(L/g)$^{1/n}$)	38.87
	n	3.46
	r^2	0.9879

Breakthrough curves of green 40 adsorbed on the organo-corn straw in fixed beds at different flow rates of 1.4, 3.5, and 7.0 mL/min were investigated with an inlet dye concentration of 100 mg/L and bed height of 16 cm as depicted in Figure 9. It was observed that the breakthrough time appeared faster with increased flow rates. At a lower flow rate, the inlet dye molecules had a longer time in contact with the fixed bed in the column resulting in closer equilibrium adsorption stage. At a higher flow rate, the adsorption capacity was lower due to shorter contact time in the column and the dye molecules leaving the fixed bed column before reaching the equilibrium stage.

Table 3 shows not only the experimental conditions in fixed bed columns but also the breakthrough characteristics, total adsorption capacity (q_{total}), and equilibrium dye uptake (q_e) of green 40 in the organo-corn straw under different conditions. The breakthrough point (the position at C_t/C_0 = 0.05) appeared faster with an increase in liquid flow rate and initial dye concentration, but slower with an increase in bed height. The highest of breakthrough time (t_b) and breakthrough volume were 220 min and 308 mL obtained under the conditions of an inlet dye concentration of 100 mg/L, bed height of 16 cm, and flow rate of 1.4 mL/min. The equilibrium bed capacity (q_e) was 152.75 mg/g obtained under the conditions of 200 mg/L green 40 concentration, 16 cm bed height, and flow rate of 3.50 mL/min. It was considered that inlet dye concentration was a main factor that caused the adsorption to reach the nearest equilibrium stage.

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

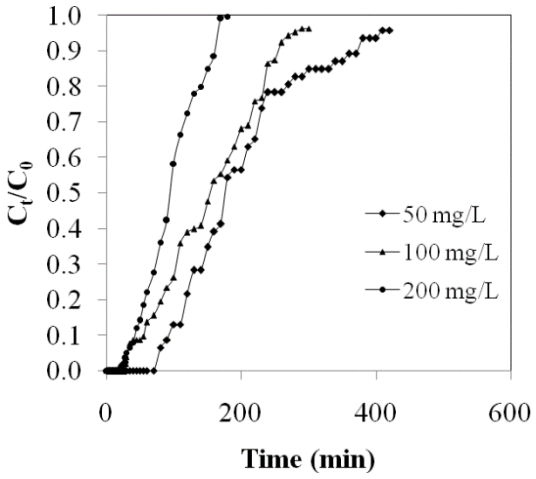

Figure 7 Effect of inlet dye concentration on breakthrough curve of the sorption of green 40 on organo-corn straw, Flow rate: 3.5 mL/min and Bed height: 16 cm

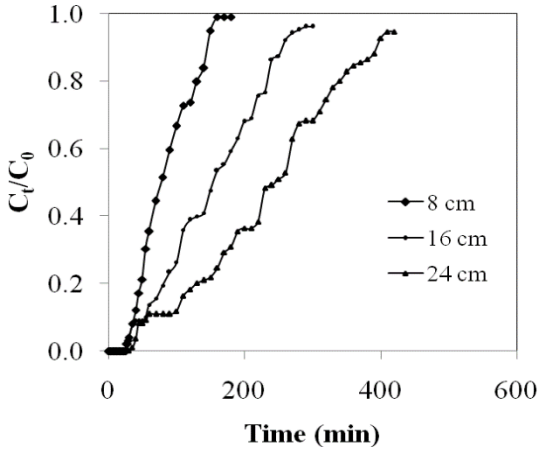

Figure 8 Effect of bed height on breakthrough curve of the sorption of green 40 on organo-corn straw, C_0: 100 mg/L and Flow rate: 3.5 mL/min

Table 3 Experimental conditions and characteristic parameters obtained from breakthrough curves and Adams-Bohart, Thomas and Yoon-Nelson model constants

Conditions	C_0 (mg/L)	50	100	200	100	100	100	100
	Height (cm)	16	16	16	16	16	8	24
	Flow rate (mL/min)	3.5	3.5	3.5	1.4	7.0	3.5	3.5
Breakthrough parameters	V_b (mL)	273	108.5	106.5	308	189	108.5	143.5
	t_b (mL)	78	31	30	220	27	31	41
	q_{total} (mg)	34.30	54.74	61.10	51.44	36.00	30.02	83.53
	q_e (mg/g)	85.75	136.85	152.75	128.60	90.00	150.10	139.22
Adams-Bohart model	k_{AB} (L/mg.min)	0.122	0.111	0.142	0.077	0.215	0.223	0.079
	N_0 (mg/L)	2,184	3,114	3,566	3,394	3,438	3,556	3,010
	r^2	0.7287	0.8422	0.8286	0.9078	0.7113	0.7302	0.8409
Thomas model	k_{Th} (mL/min/mg)	0.143	0.063	0.041	0.1	0.061	0.086	0.072
	q_0 (mg/g)	531	478	490	2,030	1,015	303	592
	r^2	0.9454	0.9752	0.9510	0.8688	0.9213	0.9485	0.9579
Yoon-Nelson model	k_{YN} (1/min)	0.0501	0.0222	0.0144	0.0149	0.0428	0.0150	0.0507
	τ (min)	87	155	239	420	83	199	97
	r^2	0.9439	0.9753	0.9530	0.9425	0.9195	0.9474	0.9635

In this work, three models were used namely Adams-Bohart, Thomas, and Yoon-Nelson models for kinetic studies in fixed bed columns. The Adams-Bohart model is used for the description of the initial part of the breakthrough curve. The expression is expressed as [19]:

$$\ln\left(\frac{C_t}{C_0}\right) = k_{AB}C_0 t - k_{AB}N_0\frac{Z}{F} \quad (8)$$

where k_{AB} is the kinetic constant (L/mg.min), F is the linear flow rate (mL/min), Z is the bed depth of column (cm), N_0 is the saturation concentration (mg/L), and t is time (min). Parameters describing the characteristic operations of the column (k_{AB} and N_0) were calculated using linear regression analysis according to equation (8). From a linear plot of ln (C_t/C_0) against time (t), values of k_{AB} and N_0 were determined from the intercept and slope of the plot (figure not shown).

After applying the Adams-Bohart model to experimental data, a linear relationship between ln (C_t/C_0) and time (t) according to equation (8) was observed. The parameters N_0, and k_{AB} were interpreted from the plot which are presented in Table 4 together with correlation coefficients (R^2 > 0.7113). The values of k_{AB} decreased with increases in dye

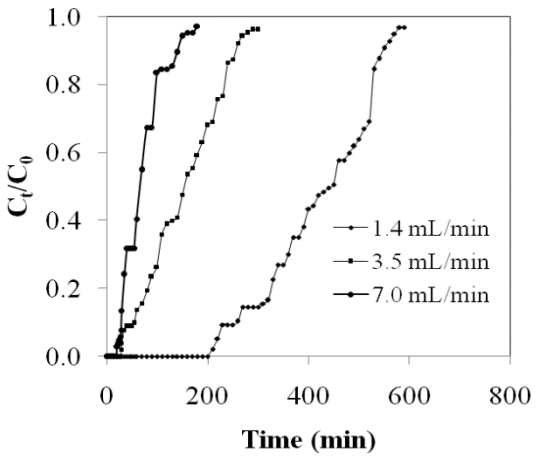

Figure 9 Effect of flow rate on breakthrough curve of the sorption of green 40 on organo-corn straw, C_0: 100 mg/L and Bed height: 16 cm

concentration and flow rate, but increased with increases in bed height. This showed that the overall kinetics system was dominated by external mass transfer in the initial part of adsorption in the column [20]. 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.

The Thomas model is known as the bed-depth-service-time (BDST) model [21]. The BDST approach is based on the irreversible isotherm model by Bohart and Adams [16]. This simplified-design model ignores both the intraparticle (solid) mass transfer resistance and the external (fluid-film) resistance directly. This means that the rate of adsorption is controlled by the surface reaction between the adsorbent and the unused capacity of the adsorbent. This expression of Thomas model for an adsorption column is given as follows:

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_{Th}q_0M}{Q}-\frac{k_{Th}C_0}{Q}V \qquad (9)$$

where k_{Th} is the Thomas rate constant (mL/min/mg), q_0 is the maximum adsorption capacity (mg/g), M is the total mass of the adsorbent (g), Q is volumetric flow rate (mL/min), and V is the throughput volume (mL). Parameters describing the characteristic operations of the column (k_{Th} and q_0) were calculated using linear regression analysis according to equation (9). From a linear plot of $\ln[(C_t/C_0)-1]$ against volume (V), values of k_{Th} and q_0 were determined from the slope and intercept of the plot (figure not shown).

The kinetic coefficient k_{Th} and the adsorption capacity q_0 are given in Table 4. Thomas rate constant k_{Th} is dependent on flow rate, initial dye concentration, and bed height. The maximum adsorption capacity q_0 decreased with an increase in flow rate and initial dye concentration but decreased with an increase in bed height. The results indicate that values of k_{Th} decreased with the increases in initial dye concentrations and flow rates and bed heights. This showed that the overall kinetics system was dominated by the surface reaction between the adsorbent and the unused capacity of adsorbent in the initial part of adsorption in the column [16]. High values of correlation coefficients ($r^2 > 0.8688$) indicated that the Thomas model fitted well to the experimental data.

Yoon and Nelson [22] developed a model based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent. The linearized Yoon-Nelson equation regarding to a single component system is expressed as:

$$\ln\left(\frac{C_0}{C_t}-1\right)=\tau k_{YN}-k_{YN}t \qquad (10)$$

where k_{YN} (1/min) is the rate constant, τ (min) is time required for 50% green 40 breakthrough, C_0 (mg/L) is initial dye concentration, C_e (mg/L) is equilibrium dye concentration in solution, and t (min) is time. A linear plot of $\ln[(C_0/C_t)-1]$ against time (t) was employed (figure not shown) to determine values of k_{YN} and τ from the intercept and slope of the plot.

The Yoon and Nelson model was fitted to investigate the breakthrough behavior of green 40 on organo-corn straw. A plot of $\ln[(C_0/C_t)-1]$ versus t gave a straight line with a slope of k_{YN}, and intercept of $-\tau k_{YN}$. The values of k_{YN} and τ obtained are also listed in Table 4. The results showed that the rate constant, k_{YN} decreased with an increase in inlet dye concentration, but increased with an increase in flow rate and bed height. Also, the time required for 50% breakthrough τ decreases with an increase in bed height and liquid flow rate but increases in initial dye concentration. High values of correlation coefficients ($r^2 > 0.9195$) indicated that Yoon and Nelson model fitted well to the experimental data. The decrease of k_{YN} with the increases in dye concentration, but increased with the increases in bed height and flow rate. This showed that the increase in initial dye concentration increases the competition between adsorbate molecules for the adsorption sites, which ultimately results in increased uptake rate [16].

4. Conclusion

Adsolubilization of corn straw with cationic surfactant alters the solubility of the biosorbent surface from hydrophilic to organophilic. Batch adsorption results showed that the adsorption capacity rapidly increased in the first 10 min and reached equilibrium within 5 h. The amount of the dye adsorbed decreased with increases in pH_0. The adsorption isotherm followed Langmuir and Freundlich isotherms. The kinetic data obeyed the pseudo-second order kinetic model indicating that the forming rate of hydrophobic-hydrophobic interactions on the biosorbent surface was the rate of limiting step. The results of fixed bed column experiments showed that the breakthrough point appeared faster with increases in liquid flow rate and bed height but were slower with increases in inlet green 40 concentrations. The highest bed capacity of 152.75 mg/g was obtained under the conditions of 200 mg/L inlet green 40 concentration, 16 cm bed height, and 3.6 mL/min flow rate. The column experimental data were analyzed by the Adams-Bohart, Thomas, and Yoon-Nelson models. For green 40 adsorption, the column data were fitted well to the Thomas and Yoon-Nelson models. The results exhibited that the organo-corn straw is effective in the removal of green 40 from aqueous solutions.

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6. References

[1] Yang XY, Al-Duri B. Application of branched pore diffusion model in the adsorption of reactive dyes on activated carbon. Chem Eng J 2001;83:1523.

[2] Chern JM, Huang SN. Study of nonlinear wave propagation theory-1-Dye adsorption theory-1-Dye adsorption by activated carbon. Ind Eng Chem Res 1998;37:253-257.

[3] Wibulswas R. Batch and fixed bed sorption of methylene blue on precursor and QACs modified montmorillonite. Separ Purif Technol 2004;39:3-12.

[4] Charuwong P, Kiattikomol R. Removal of organic compounds from aqueous solution by using montmorillonite clays and Oragno-clays. Suranaree J Sci Technol 2004;11:39-51.

[5] Jaruwong P, Aumpush J, Kiattikomol, R. Uptake of cationic and azo dyes by montmorillonite in batch and column systems. Thammasat Int J Sci Technol 2005;10(1):47-56.

[6] Teng MY, Lin SH. Removal of methyl orange dye from water onto raw and acid-activated montmorillonite in fixed beds. Desalination 2006;201:71-81.

[7] Wang L, Wang A. Adsorption characteristics of congo red onto the chitosan/ montmorillonite nanocomposite. J Hazard Mater 2007;147:979-985.

[8] Xu Z, Cai JG, PAN BC. Mathematically moding fixed-bed adsorption in aqueous systems. J Zhejiang Univ-Sci A (Appl Phys & Eng) 2013;14(3):155-176.

[9] Sivakumar P, Palanisamy PN. Packed bed column studies for the removal of Acid blue 92 and Basic red 29 using non-conventional adsorbent. Indian J Chem Technol 2009;16:301-307.

[10] Umpuch C, Jutarat B. Adsorption of organic dyes from aqueous solution by surfactant modified corn straw. Int J Chem Eng Appl 2013;4(3):134 -139.

[11] Umpuch C. Batch adsorption of organic dyes by Organo-bagasse: Carbon content, pH influence, kinetics and isotherms. IJE Transactions A: Basics 2015;28(4):507-515.

[12] Kuo KK, Acharya R. Fundamentals of Turbulent and Multiphase Combustion. New Jersey: John Wiley & Sons, Inc; 2012.

[13] Lagergren S, Svenska BK. About the theory of so-called adsorption of soluble substances. Vaternskapsakad Handlingar 1898;24(4):1-39.

[14] Ho YS, McKay G. Sorption of dye from aqueous solution by peat. Chem Eng J 1998;70:115-124.

[15] Umpuch C, Sakeaw S. Removal of methyl orange from aqueous solutions by adsorption using chitosan intercalated montmorillonite. Songklanakarin J Sci Technol 2013;35(4):451-459.

[16] Ahmad AA, Hameed BH. Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. J Hazard Mater 2010;175:298-303.

[17] Umpuch C, Sakeaw S. Adsorption characteristics of reactive black 5 chitosan intercalated montmorillonite. Desalin Water Treat 2015;53:2962-2969.

[18] Umpuch C, Jutarat B. Adsorption behavior of reactive black 5 on activated carbon prepared from sugarcane bagasse. UBU engineering journal 2012:5(2):10-21

[19] Umpuch C, Sakaew S. Removal of methyl orange from synthetic wastewater onto chitosan-coated-montmorillonite clay in fixed-beds. GMSARN International Journal 2012;6:175-180.

[20] Aksu Z, Gönen F. Biosorption of phenol by immobilized sludge in a continuous packed bed: prediction of breakthrough curves. Process Biochem 2004;39:599-613.

[21] Thomas HC. Heterogeneous ion exchange in flowing system. J Am Chem Soc 1944;66:1466-1664.

[22] Yoon YH. Application of gas adsorption kinetics. Part 1. A theoretical model for respirator cartridge service time. Am Ind Hyg Assoc J 1984;45:509-516.