



Batch Adsorption of Organic Dyes by Organo-bagasse: Carbon Content, pH Influence, Kinetics and Isotherms

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ABSTRACT

The affecting factors such as carbon content, contact time, solution pH and initial dye concentration on adsorption behavior of three organic dyes, blue21, yellow20, and green40 using organo-bagasse as a biosorbent were investigated. The organo-bagasse was prepared by adsolubilisation using tetradecyltrimethyl ammonium bromide. The precursor and organo-bagasse were characterized by elemental analysis, Brunauer-Emmett-Teller method, Fourier transform infrared spectroscopy, and scanning electron microscopy. A number of batch tests were carried out as functions of carbon content, contact time, initial pH solution, and initial dye concentration. The results showed that the adsorption capacity of green40 was the highest, followed by yellow 20 and then blue21. Adsorption of the organic dyes increased as the carbon content in the organic dyes increased. The adsorption of the three dyes reached equilibrium within 3.0 h and at this condition the adsorption capacities of blue21, yellow20, and green40 were 130.50, 166.55 and 174.81 mg/g, respectively. The maximum adsorption was obtained at pH 2.0. The kinetic data followed the pseudo-second order model indicating that the rate of interaction on the biosorbent surface was the rate limiting step. From the above results, the organo-bagasse was an effective adsorbent for the adsorption of the organic dyes.

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1. INTRODUCTION

Silk and cotton are famous local products of Thailand and have been manufactured in increasing quantities over the years. These products are handmade and commonly produced by small groups of villagers in rural areas. Selling these products provides income to villagers in addition to those derived from other agricultural activities. Synthetic dyes manufactured in Thailand are normally used in the dyeing process of these products because they are cheap and available in local markets. These synthetic dyes are preferred to natural dyes due to their bright and lasting colors, and high resistance to heat and light. However, after the dyeing process, much of the synthetic dyes usually find their way into nearby rivers and/or spaces under houses. High amounts of accumulated synthetic dyes in nature can cause serious environmental problems, for example,

contamination of underground water by polluted water of undesirable color and odor. Also, long-term exposure to these accumulated dyes can cause harm to humans, animals, and aquatic life [1]. Therefore, it is very important to treat such wastewater before discharge.

The treatment methods of these effluents should be cheap, simple, fast, and highly efficient. Adsorption is a simple separation method which is an adhesion of solutes from liquid to solid surfaces by creation of a thin layer of the adsorbate on the surface of the adsorbent [2-8]. Activated carbon derived from natural materials, such as bagasse, rice husk, corncobs, coconut shell, and fruit peel, is a very well-known adsorbent due to its high surface area available for adsorption and/or chemical reactions [9, 10]. However, activated carbon is expensive because high energy consumption is needed for the carbonization process and low re-utilization. Alternative ways to modify natural materials also exist to decrease the cost, for example, acid or base treatment, autoclave, and adsolubilisation with surfactant [11]. This study focused on adsolubilisation in which

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surfactant is formed as admicelle on the adsorbent surface because it is simple, cheap, and requires low energy consumption. Adsolubilisation causes the surface properties of adsorbents to change from hydrophilic to hydrophobic which enhances the adsorption capacity of the organic molecules [12-14].

Many natural materials have been selected for use as precursors for organo-biosorbents by means of adsolubilisation, for example, zeolite, alumina, natural polymers, celluloses, and clays [15, 16]. It has been reported that the organo-biosorbent enhances the adsorption capacity of organic molecules, synthetic dyes, toxic pollutants, and petrochemical products. Some researches showed that an increase of carbon content on the adsorbent surface causes an increase of the adsorption capacity for many solutes, for example, reactive dyes, organic dyes, heavy metals, and phenol [17-22]. On the other hand, another study showed that an increase of carbon content caused a decrease in the adsorption capacity of cationic dye such as methylene blue using organo-clays as adsorbent [23]. Research in this area has not proven conclusive or been well documented. In response to this situation, this study aimed to provide a better understanding of the effect of carbon content on the adsorption capacity of an organo-adsorbent. Bagasse is an agricultural residue that is generated in great quantities in many Thai industries and can be easily developed as a precursor and the surfactant adsolubilised on the surface of the bagasse is called 'organo-bagasse.' Adsorption using organo-bagasse is a cheap and simple process that could encourage villagers to treat the colored effluent before discharge, resulting in a reduction in water pollution. In this work, elemental analysis, Brunauer-Emmett-Teller (BET) method, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were used to characterize the organo-bagasse. In addition, there are reports that the carbon content can affect the adsorption capacity of organo-adsorbents regarding the organic molecules. Three organic dyes, blue21, yellow20, and green40, were examined. Also, the dye removal efficiency of organo-bagasse was determined by single-stage batch adsorption tests including kinetic study, adsorption isotherms, and the effect of initial pH solution.

2. EXPERIMENTAL

2.1. Materials Bagasse and three organic dyes, blue21, yellow20, and green40, were purchased from a local market near Ubon Ratchathani University, Thailand. The cationic surfactant studied was tetradecyltrimethylammonium bromide ($C_{17}H_{38}NBr$) purchased from the Merck Chemical Company, Germany.

The bagasse was first washed with distilled water to remove impurities and then dried at a temperature of 40°C in an air-circulating oven until the weight was constant. To have uniform modification and reproducible results, the bagasse was crushed and shredded in a blender for about 15 min and sieved to obtain a particle size below 300 µm, designated as raw bagasse. An amount of 1.0 g of the raw bagasse was treated with 100 mL of 1000 mg/L $C_{17}H_{38}NBr$ surfactant. Agitation took place at 200 rpm for 15 min at room temperature using an orbital shaker. Afterwards, the organo-bagasse 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. To obtain more reproducible data, the organo-bagasse particles were sieved (50 mesh) before use for adsorption studies. Furthermore, all adsorbents were packed in plastic bags and stored in desiccators for further use. The percentages of blue21, yellow20, and green40 removed by the organo-bagasse were higher than those of the precursor so that only the organo-bagasse was used as the biosorbent for the following experiments.

The carbon, hydrogen, and nitrogen contents of blue21, yellow20, and green40, the raw bagasse and the organo-bagasse were analyzed by a CHNS Analyzer (sulfur was not examined). The specific surface areas of the precursor and the modified adsorbent were measured by the use of an Automatic Surface Analyzer and N_2 gas was used as the adsorbate. FTIR spectroscopic analysis was used to determine the active functional groups of green40, blue21, yellow20, bagasse and organo-bagasse. The morphological features and surface characteristics of the biosorbents were obtained by the use of SEM.

2.2. Experimental Methods Batch adsorption tests were conducted in 250 mL Erlenmeyer flasks which contained 100 mL of the organic dye solutions. Firstly, the effect of contact time on the dye sorption was investigated. A series of 250 mL Erlenmeyer flasks containing 100 mL of the dye solutions were mixed with 0.1 g of the organo-bagasse. These flasks were closed with parafilm to avoid evaporation and then horizontally shaken at 200 rpm. The samples were measured at intervals between 5 to 360 min. Secondly, the effects of initial dye concentrations were studied. An amount of 0.1g of the organo-bagasse 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 ensure equilibration achieved. All samples were measured at the equilibrium condition. Finally, the effects of the initial pH solutions on the sorption were investigated. An amount of 100 mL solution of the organic dye of 200 mg/L and 0.1 g of the modified adsorbent was placed in a 250 mL Erlenmeyer flask. The initial pH solution was adjusted between 2.0 to 10.0 by 0.01M NaOH and/or

0.01M HCl and then horizontally shaken at 200 rpm for 24 hours. All samples of the batch experiments were filtrated through a glass microfiber filter which had pore size of 1.2 μm and thickness of 260 μm (Whatman, UK) to harvest the dye loaded adsorbent. Then, the free adsorbent solution was analyzed by a UV-Vis spectrophotometer to determine the remaining dye concentration. The maximum absorption wavelength of blue21, yellow20, and green40 were 535, 476, and 409 nm, respectively.

The equilibrium adsorption capacity (q_e : mg/g) was calculated from the expression in Equation (1):

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where C_0 (mg/L) is the initial dye concentration, C_e (mg/L) the equilibrium dye concentration, V (L) the volume of dye solution, and m (g) the amount of adsorbent.

3. RESULTS AND DISCUSSION

3. 1. Charactersization Results

The carbon, hydrogen, and nitrogen contents of the three organic dyes, the precursor, and the organo-bagasse were shown in Table 1. It was found that the major constituents of all samples were carbon which indicated those characterized samples were of a hydrophobic nature. The carbon content of green40 was the highest, followed by yellow20 and then blue21. The different dyes had different carbon contents, so the efficiencies of dye removal by the organo-bagasse were also different. Thus, hydrophobic-hydrophobic interaction could be one of interactions between the adsorbate/adsorbent.

N_2 adsorption-desorption isotherm of the raw bagasse and the organo-bagasse are provided in Figure 1. The isotherms were in accordance with the typical type II isotherm as defined by International Union of Pure and Applied Chemistry (IUPAC), showing the non-porous structure of the two biosorbents. The specific surface areas, analyzed by the BET method, for the raw bagasse and the organo-bagasse were 2.37 and 2.25 m^2/g , respectively; the slightly lower specific surface area of the organo-bagasse was due to the fact that the small internal surface area of the bagasse was lost by hindrance of surfactant film on the external surface of the organo-bagasse during adsolubilization. It is well documented that adsolubilization causes a lower specific surface area of the modified bio-sorbent [24]. Furthermore, the pore volume of the precursor and the organo-bagasse were 3.26×10^{-3} and 3.24×10^{-4} mL/g, respectively. The results suggested that the textural properties did not play an important role in the adsorption.

The IR spectra of the raw bagasse and organo-bagasse are shown in Figure 2. The spectral bands at 3,400 cm^{-1} (O-H stretching intramolecular hydrogen bonds), 2,921-2,890 cm^{-1} (asymmetric and symmetric – CH_2 of alkyl chain), 1,727 cm^{-1} (C-O stretching vibration for acetyl and ester linkages in lignin, hemicellulose, pectin etc.), 1,633 cm^{-1} (associated with the aromatic ring present in lignin and absorbed water), 1,244 cm^{-1} (C-O out of plane stretching due to the aryl group in lignin) are associated with the bagasse before the adsolubilization.

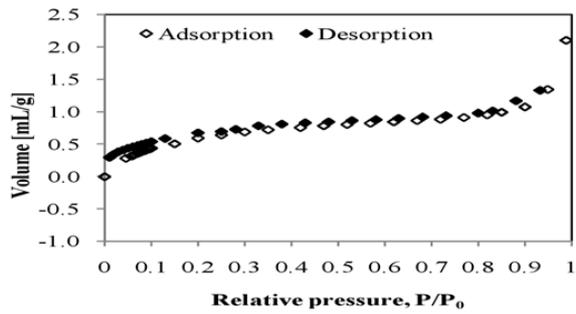
Normally, modification of adsorbent with cationic surfactant causes appearance of additional bands around 2,900-2,800 cm^{-1} indicating asymmetric and symmetric stretching vibration of – CH_2 of alkyl chain and band at about 1,600-1,200 cm^{-1} which assigned to vibration of trimethyl ammonium quaternary group $\text{CN}(\text{CH}_3)_3^+$ [25].

Since in this work the amount of $\text{C}_{17}\text{H}_{38}\text{NBr}$ was very small compared to those in other works [23-25], the two additional vibration bands (2,900-2,800 cm^{-1} and 1,600-1,200 cm^{-1}) could not be observed in the IR spectra of the organo-bagasse. Although, the IR spectra of the organo-bagasse was mostly similar to that of the precursor, there were some peaks of the bagasse at vibration bands of 923, 876 and 751 cm^{-1} which disappeared from the IR-spectra of organo-bagasse. This indicates that loading $\text{C}_{17}\text{H}_{38}\text{NBr}$ on the surface of the bagasse caused disappearance of some functional groups of the bagasse.

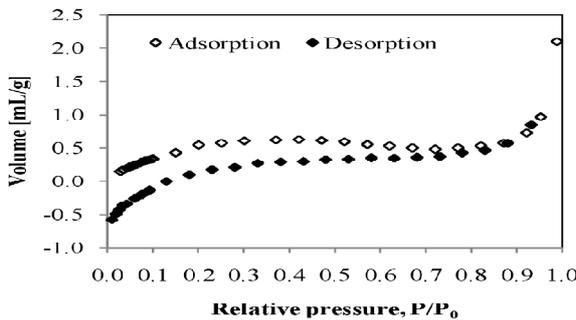
The IR spectra of the three organic dyes are shown in Figure 3. The spectral bands at 3,300-2,500 cm^{-1} (O-H stretching), 1,760-1690 cm^{-1} (C=O stretching), 1,320-1,000 cm^{-1} (C-O stretching) and 950-910 cm^{-1} (O-H bending) which are assigned to functional groups of carboxylic acids were associated with the three organic dyes. In addition, the spectral bands at 1,470-1,450 cm^{-1} (C-H bending), 1,370-1,350 cm^{-1} (C-H rocking) and 725-720 cm^{-1} (C-H rocking) which are assigned to alkyl groups of alkane were also associated with the three organic dyes. Thus, the three organic dyes contained carboxyl group as negatively hydrophilic active site and alkyl group as hydrophobic active site.

The morphologies of the raw bagasse and organo-bagasse are illustrated in Figures 4a and 4b, respectively. The external surface of the raw bagasse (Figure 4a) had a ridged profile which had several small warts. On the other hand, the surface of the organo-bagasse (Figure 4b) was coated by a thin smooth layer of the cationic surfactant.

The ridged profile on the surface of the raw bagasse was not observed. The difference between the raw bagasse and the modified one in the morphologies confirmed the cationic surfactant molecules adhering on the external surface of the raw bagasse.



(a)



(b)

Figure 1. The N₂ adsorption-desorption isotherms measured on the raw-bagasse (a) and the organo-bagasse (b)

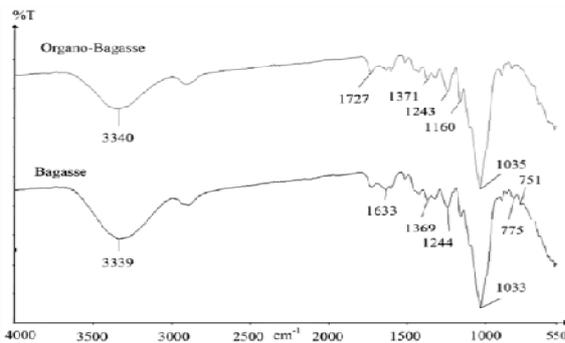


Figure 2. IR-spectra measured on the raw-bagasse and the organo-bagasse

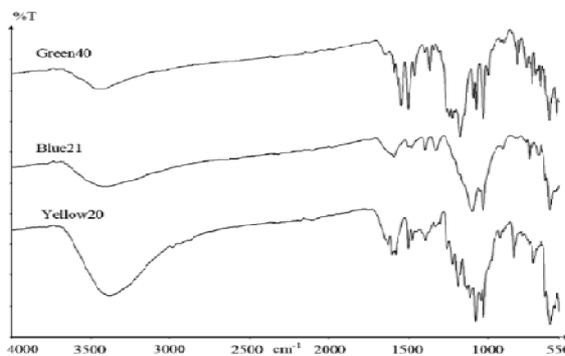
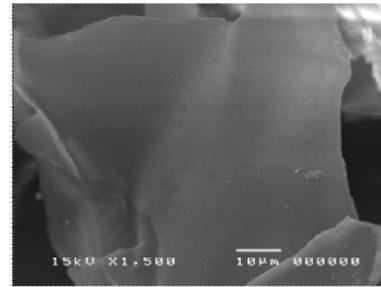
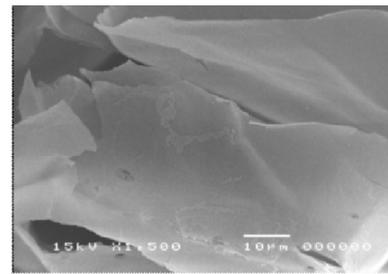


Figure 3. IR-spectra measured on the green40, blue21 and yellow20



(a)



(b)

Figure 4. SEM images of the raw-bagasse (a) and the organo-bagasse (b)

TABLE 1. Element content of organic dyes and biosorbents [16]

Sample	Element content (%)		
	C	H	N
Blue21	4.34	0.48	0.87
Yellow20	7.24	0.98	0.94
Green40	11.15	1.47	1.04
Raw bagasse	38.86	6.66	0.54
Organo-bagasse	40.71	7.05	0.88

3. 2. Adsorption Results

3. 2. 1. Effect of Contact Time The effect of contact time on the instantaneous adsorption capacities of blue21, yellow20, and green40 by the organo-bagasse is shown in Figure 5. The dye uptakes of all organic dyes on the organo-bagasse instantly increased in the first 5 min and then gradually increased with time until reaching a constant. The rapid rate in the initial stage was probably due to the abundant availability of active sites on the external surface of the organo-bagasse particles. The rate gradually increased in the later stages because of the reduction in available active sites. The saturation of organic dye molecules by the organo-bagasse was addressed at the final stage. The equilibrium time required for the adsorption of the blue21, yellow20, and green40 was approximately 3.0 hours. To ensure equilibrium, the agitation in the later adsorption experiments was run for 24 hours. The results showed that the adsorption capacity of green40 was the highest, followed by yellow20 and then blue21. In general, adsorption of the organic dyes increased as

the carbon content increased (Table 1). High carbon content can be a driving force for the retention of organic dyes.

3. 2. 2. Effect of pH The uptakes of the three organic dyes decreased with increase in the initial solution pH as depicted in Figure 6. The decrease in adsorption capacities of the blue21, yellow20, and green40 were probably attributed to two hypothetical explanations. First, the three organic dyes contain carboxyl groups which could bind with trimethyl ammonium quaternary group on the external surface of the admicelle. Thus, one of the interactions between three organic dyes and organo-bagasse could be electrostatic interaction. At acidic medium, there are many protons in the solution which did not inhibit the adsorption. On the other hand, in alkali medium there are many hydroxide ions which can competitively bind with positive amine group on the external surface of the admicelle. Second, the three organic dyes also had alkyl group which is a hydrophobic part. This alkyl group can bind with the long chain alkyl group in the interior of admicelle by hydrophobic-hydrophobic interaction. The adsorption depends on the solution pH; because, the dyes and the conjugated bases are of different hydrophobicity [26]. Therefore, the variation of amount of protons and hydroxyl ions in the solution affected the adsorption capacities of the dyes onto the organo-bagasse. The amount of blue21, yellow20, and green40 adsorbed to the organo-bagasse should be pH dependent.

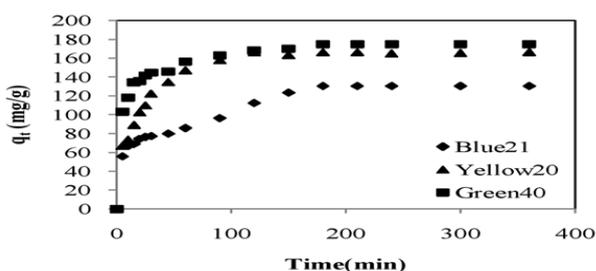


Figure 5. Effect of contact time on the organic dyes adsorption onto the organo-bagasse.

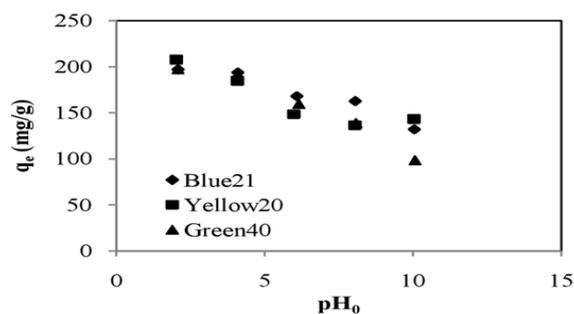


Figure 6. Effect of initial pH on the organic dyes adsorption onto the organo-bagasse.

3. 2. 3. Adsorption Kinetics To predict the sorption mechanisms, the kinetic data are usually fitted by the kinetic models such as pseudo-first order, pseudo-second order, and intra-particle diffusion models. The pseudo-first order model, proposed by Lagergren [27], is expressed in linear form as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

where q_e and q_t are the adsorption capacity (mg/g) of dye at equilibrium and at time t , respectively, and k_1 is the rate constant for pseudo-first order adsorption (L/min). The pseudo second order equation proposed by Ho [28] can be written in linear form as:

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 is the rate constant for pseudo-second order adsorption (g/(mg.min)).

The intra-particle diffusion equation [29] is expressed as:

$$q_t = k_i t^{0.5} + C \quad (4)$$

where k_i is the intra-particle diffusion rate constant (mg*min^{0.5}/g) and C is the intercept.

The best fit of kinetic data to Equation (2) reveals that the external mass transfer through a boundary layer is the rate limiting step. The best fit of kinetic data to Equation (3) indicates that the forming of interaction between the adsorbate and adsorbent on the external surface of adsorbent is the rate limiting step. The best fit of kinetic data to Equation (4) shows that the adsorbate diffusion into the interior of adsorbent is the rate limiting step.

The fitting parameters of the three kinetic models and the correlation coefficients are given in Table 2. Poor correlations of the kinetic data with the pseudo-first order kinetic and intra-particle diffusion models were observed. Normally, the pseudo-first order equation was well fitted for the data obtained at the initial stage of the batch experiment. On the other hand, the kinetic data were well described by the pseudo-second order equation ($r^2 \geq 0.9917$) indicating that the formation rate of adsorbate/adsorbent interaction on the external surface of the organo-bagasse was the rate limiting step. The chemical sorption could involved this sorption process. Furthermore, the calculated adsorption capacities (q_e) of green40, yellow20, and blue21 listed from the Table 2 are according to those observed in sections 3.2.1 and 3.2.2.

3. 2. 4. Determination of Adsorption Isotherm

The adsorption isotherms of the three organic dyes which are plots of q_e versus C_e are shown in Figure 7. The adsorption capacity initially increased and then reached a constant. The adsorption isotherms developed by Langmuir and Freundlich [30] were commonly used

to fit the equilibrium data. The Langmuir isotherm is related to the sorption occurring at specific homogeneous sites within the adsorbent. The 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 in Equation (5) and Freundlich isotherm in Equation (7) are shown below:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (5)$$

where q_m is the monolayer capacity or limiting sorption (mg/g) and K_L is the Langmuir constant (L/mg). The parameters can be evaluated from the slope and intercept of the linear plot of C_e/q_e against C_e . The essential characteristics of the Langmuir isotherm can be expressed by means of ' R_L ', a dimensionless constant referred to as the separation factor or equilibrium parameter [31]. The R_L is defined as:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (6)$$

This parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). As can be seen from Table 1, at all temperatures the R_L values were between 0 and 1.0, indicating that the adsorption of yellow20 onto the organo-bagasse was favorable.

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

where K_F is the Freundlich characteristic constant (mg/g)(L/g)^{1/n} and 1/n is the heterogeneity factor of adsorption. The parameters were obtained from the intercept and slope of $\ln q_e$ versus $\ln C_e$ of the linear plot, respectively.

Furthermore, the adsorption isotherms developed by Temkin and Dubinin-Radushkevich [30] were also used to fit the equilibrium data. The Temkin isotherm model [32] assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent-adsorbate interactions. The linear form of Temkin isotherm model is given by the equation:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (8)$$

where b is the Temkin constant related to the heat of sorption (J/mol), R is the universal gas constant, 8.314 J/mol.K, T is the temperature (K), and K_T is the Temkin isotherm constant (L/g) [33].

The Dubinin-Radushkevich (D-R) [34] equation is a semi-empirical equation where adsorption follows a pore-filling mechanism. It assumes that the adsorption has a multilayer character, involves van der Waals forces, and is applicable for physical adsorption processes. The linear form of D-R isotherm model is expressed as:

$$\ln(q_e) = \ln(q_s) - \beta \varepsilon^2 \quad (9)$$

where q_s is the maximum amount of adsorbate that can be adsorbed on adsorbent (mg/g), β is the constant related to free energy, and ε is the Polanyi potential which is defined as:

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (10)$$

The mean free energy (E) of the adsorption per molecule of adsorbate can be calculated using the following equation:

$$E = \frac{1}{(2\beta)^{1/2}} \quad (11)$$

The equilibrium data obtained were fitted to the Langmuir, Freundlich, Temkin, and D-R isotherm equations. The isotherm constants and correlation coefficients are listed in Table 3. Of the four adsorption isotherms, the experimental data was best fitted to the Freundlich isotherm model by consideration of the correlation coefficients, r^2 , which was the closest to 1.0.

The high correlation of the Langmuir isotherm model was observed ($r^2 \geq 0.9891$). The maximum monolayer coverages (q_{max}) of blue21, yellow20, and green40 were determined to be 250, 178.57, and 163.93 mg/g, respectively.

TABLE 2. Pseudo-first order, pseudo-second order, and intra-particle diffusion parameters

Model	Parameter	Value		
		Blue21	Yellow20	Green40
	q_e (exp) (mg/g)	130.50	166.55	174.81
Pseudo-first order model	k_f (1/min)	0.015	0.031	0.020
	q_d (cal) (mg/g)	88.90	126.46	70.94
	r^2	0.9043	0.9830	0.8944
Pseudo-second order model	k_2 (g/(mg.min))	3.93×10^{-4}	5.92×10^{-4}	2.32×10^{-4}
	q_d (cal) (mg/g)	136.99	172.41	178.57
	r^2	0.9917	0.9988	0.9996
Intra-particle diffusion model	k_i (mg/(g.min ^{1/2}))	5.88	7.28	5.81
	C (mg/g)	40.20	62.74	92.84
	r^2	0.8648	0.7451	0.5867

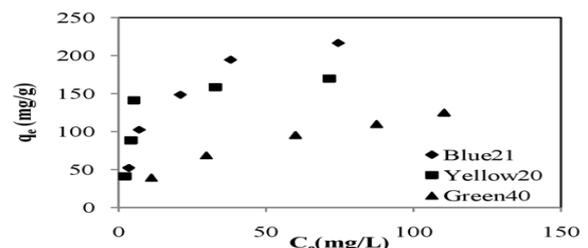


Figure 7. Adsorption isotherm of organic dyes onto the organo-bagasse.

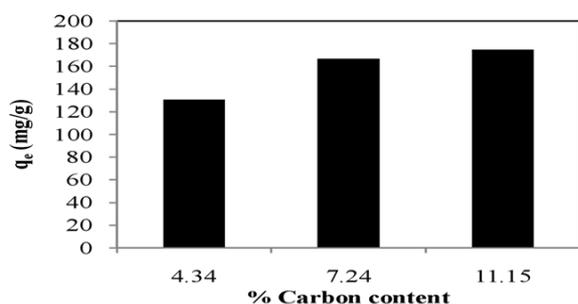


Figure 8. Relationship between adsorption capacities of organic dyes and carbon content in the organic dyes.

TABLE 3. Isotherm constants and correlation coefficients

Model	Parameter	Value		
		Blue21	Yellow20	Green40
Langmuir isotherm	q_m (mg/g)	250	178.57	163.93
	K_L (L/g)	0.0811	0.233	0.0256
	R_L	1.97×10^{-4}	9.60×10^{-5}	9.53×10^{-4}
	r^2	0.9964	0.9956	0.9891
Freundlich isotherm	K_F ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n}/\text{g}$)	35.90	50.89	12.36
	N	2.24	3.13	2.02
	r^2	0.9325	0.6566	0.9958
Temkin isotherm	K_T (L/g)	0.84	0.223	0.247
	b (kJ/mol)	46.23	78.90	67.97
	r^2	0.9878	0.7613	0.9883
Dubinin-Radushkevich isotherm	q_s (mg/g)	179.65	162.96	103.54
	E (J/mol)	388.08	583.21	150.76
	r^2	0.9175	0.9586	0.8622

The separation factor (R_L) was greater than 0 but less than 1.0, indicating highly favorable sorption for the three organic dyes by the studied organo-biosorbent. The monolayer capacity of blue21 was the highest, followed by yellow20 and then green40. These results are not consistent with those q_e which were observed in sections 3.2.1, 3.2.2, and 3.2.3, and this may be due to the not perfectly fitting of the experimental data to the Langmuir model. The deviation of the experimental data from the model may provide the insufficient well-fitting parameters.

The Freundlich isotherm described the isotherm data with high-correlation coefficients for blue21 and green40 but a low one was observed for yellow20. This suggested that the multilayer coverage on the adsorbent surface might also took place. The value of constant n was greater than unity, meaning that the repulsive forces between the adsorbate/adsorbate were involved in the system. This implied that the interaction between adsorbate/adsorbent was stronger than adsorbate/adsorbate repulsion [35]. Furthermore, the linear plot for the Temkin adsorption isotherm, which considers

chemisorption of an adsorbate onto the adsorbent [36], fitted well with a high correlation coefficient (Table 3). This further supported the findings that the adsorption of the organic dyes onto the organo-bagasse was a chemisorption process. The slope and intercept of plot of $\ln q_e$ versus ε^2 were used to calculate the D-R isotherm parameters β and q_s . The q_s value was consistent with the maximum adsorption capacity (q_e) value previously mentioned. The magnitude of the correlation coefficients for the D-R isotherm was as good as that of the Temkin isotherm model (Table 3). This suggested that the organic dyes adsorption by the organo-bagasse particles involved both chemical and physical processes.

3. 3. 3. Correlation of Carbon Content and Adsorption Capacity

The modification of bagasse with a cationic surfactant altered the surface properties of the precursor from hydrophilicity to hydrophobicity. Furthermore, the modification caused a decrease in BET surface area, formation of the trimethyl ammonium quaternary group and long chain alkyl group, and a change in morphology in the modified adsorbent. The adsorption of the blue21, yellow20, and green40 reached the equilibrium within 180 min. The adsorption capacity of green40 was highest, followed by yellow20 and then blue21.

Adsorption of the organic dyes increased as the carbon content increased (Figure 8), indicating that high carbon content can be a driving force for the retention of organic dyes. The kinetic data conformed to the pseudo-second order equation and the formation rate of adsorbate/adsorbent interaction was the rate limiting step. The sorption of blue21, yellow20, and green40 on the organo-bagasse depended on the initial solution pH. The adsorption isotherm followed the Langmuir, Freundlich, Temkin, and D-R isotherm equations showing that the blue21, yellow20, and green40 molecules formed a monolayer on the adsorbent surface. From the above results, the carbon content could be one of the affecting factors which can influence the adsorption behavior of three organic dyes on the organo-bagasse.

4. CONCLUSION

The cationic surfactant adsorbed on bagasse caused a presence of admicelle which is organophilic on the external surface of the precursor enhancing adsorption capacity to organic dyes. The characterization results shows that the modification caused a lowering in specific surface area, addition of new functional groups such as trimethyl ammonium quaternary group, and long chain alkyl group and an appearance of thin surfactant layer on the external surface of the organo-bagasse. The three organic dyes uptakes rapidly increased in the first

5 min and achieved equilibration at 180 min. The organo-bagasse sorbs organic dyes effectively in acidic solution (pH 2.0) and sorption of organic dyes is strongly pH dependent. The sorption process is well described by Langmuir, Freundlich, Temkin, and D-R equations. The kinetics study demonstrated that the adsorption kinetics followed pseudo-second order kinetic model. The adsorption capacities of organic dyes followed the order of green40>yellow20>blue21 which was attributed to their differences in carbon content. The adsorbed amount of organic dyes increased with increasing in carbon content indicating that carbon content can play an important role on the adsorption of organic dyes. From the above results, the organo-bagasse was an effective adsorbent for the removal of the organic dyes from synthetic effluents.

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7. REFERENCES

- Gong, J., Feng, J., Liu, J., Jiang, Z., Chen, X., Mijowska, E., Wen, X. and Tang, T., "Catalytic carbonization of polypropylene into cup-stacked carbon nanotubes with high performances in adsorption of heavy metallic ions and organic dyes", *Chemical Engineering Journal*, Vol. 248, (2014), 27-40.
- Nikzad, M., Movagharnjad, K., Najafpour, G.D. and Talebnia, F., "Comparative studies on effect of pretreatment of rice husk for enzymatic digestibility and bioethanol production", *International Journal E Transactions B: Applications*, Vol. 26, No. 5, (2013), 455-464.
- Zareie, C. and Najafpour, G., "Preparation of nanochitosan as an effective sorbent for the removal of copper ions from aqueous solutions", *International Journal of Engineering-Transactions B: Applications*, Vol. 26, No. 8, (2013), 829-836.
- Ghorbani, F., Sanati, A., Younesi, H. and Ghoreyshi, A., "The potential of date-palm leaf ash as low-cost adsorbent for the removal of Pb (II) ion from aqueous solution", *International Journal of Engineering-Transactions B: Applications*, Vol. 25, No. 4, (2012), 269-278.
- Radnia, H., Ghoreyshi, A., Younesi, H., Masomi, M. and Pirzadeh, K., "Adsorption of Fe (II) from aqueous phase by chitosan: Application of physical models and artificial neural network for prediction of breakthrough", *International Journal of Engineering-Transactions B: Applications*, Vol. 26, No. 8, (2013), 845-858.
- Anbia, M. and Ghaffari, A., "Modified nanoporous carbon material for anionic dye removal from aqueous solution", *International Journal of Engineering-Transactions B: Applications*, Vol. 25, No. 4, (2012), 259-268.
- Ghorbani, F., Younesi, H., Mehraban, Z., Celik, M.S., Ghoreyshi, A. and Anbia, M., "Aqueous cadmium ions removal by adsorption on aptms grafted mesoporous silica mcm-41 in batch and fixed bed column processes", *International Journal of Engineering Transaction B: Applications*, Vol. 26, No. 5, (2013).
- Sadrnezhad, S., Bagheri, N. and Mahshid, S., "Effect of si antioxidant on the rate of oxidation of carbon in MgO-C refractory", *International Journal of Engineering-Transactions B: Applications*, Vol. 24, No. 4, (2011), 357-366.
- Xiao, L., Zhang, S. and Huang, J., "Effective removal of organic dyes by tungstate oxide nanourchins", *Powder Technology*, Vol. 258, (2014), 297-303.
- Madrakian, T., Afkhami, A. and Ahmadi, M., "Adsorption and kinetic studies of seven different organic dyes onto magnetite nanoparticles loaded tea waste and removal of them from wastewater samples", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol. 99, (2012), 102-109.
- Crini, G., "Non-conventional low-cost adsorbents for dye removal: A review", *Bioresource Technology*, Vol. 97, No. 9, (2006), 1061-1085.
- Wang, Z., Liang, J. and Liang, Y., "Decolorization of reactive black 5 by a newly isolated bacterium bacillus sp. Yzu1", *International Biodeterioration & Biodegradation*, Vol. 76, (2013), 41-48.
- Ip, A.W., Barford, J.P. and McKay, G., "A comparative study on the kinetics and mechanisms of removal of reactive black 5 by adsorption onto activated carbons and bone char", *Chemical Engineering Journal*, Vol. 157, No. 2, (2010), 434-442.
- Mattaraj, S., Siripattanakul, S. and Viriyasenkul, V., "Adsorption performance of calcium and magnesium on cation exchange resin", *Journal of Science & Technology Ubon Ratchathani University*, Vol. 7, No. 2, (2003), 37-46.
- Jagdish, S. and Gagandeep, K., "Freundlich, langmuir adsorption isotherms and kinetics for the removal of malachite green from aqueous solutions using agricultural waste rice straw", *International Journal of Environmental Science*, Vol. 4, No. 3, (2013), 250-258.
- Ibrahim, S., Ang, H.-M. and Wang, S., "Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw", *Bioresource Technology*, Vol. 100, No. 23, (2009), 5744-5749.
- Zhang, Z., O'Hara, I.M., Kent, G.A. and Doherty, W.O., "Comparative study on adsorption of two cationic dyes by milled sugarcane bagasse", *Industrial Crops and Products*, Vol. 42, (2013), 41-49.
- Hegazi, H.A., "Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents", *HBRC Journal*, Vol. 9, No. 3, (2013), 276-282.
- Namasivayam, C. and Sureshkumar, M., "Modelling thiocyanate adsorption onto surfactant-modified coir pith, an agricultural solid 'waste'", *Process Safety and Environmental Protection*, Vol. 85, No. 6, (2007), 521-525.
- Rangabhashiyam, S., Anu, N. and Selvaraju, N., "Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents", *Journal of Environmental Chemical Engineering*, Vol. 1, No. 4, (2013), 629-641.
- Salleh, M.A.M., Mahmoud, D.K., Karim, W.A.W.A. and Idris, A., "Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review", *Desalination*, Vol. 280, No. 1, (2011), 1-13.
- Umpuch, C. and Jutarat, B., "Adsorption of organic dyes from aqueous solution by surfactant modified corn straw", *International Journal of Chemical engineering and applications*, Vol. 4, No. 3, (2013), 35-42.
- Wibulswas, R., "Batch and fixed bed sorption of methylene blue on precursor and qacs modified montmorillonite", *Separation and Purification Technology*, Vol. 39, No. 1, (2004), 3-12.
- Hameed, B. and El-Khaiary, M., "Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk

- fibre: Equilibrium isotherms and kinetic studies", *Journal of Hazardous Materials*, Vol. 154, No. 1, (2008), 237-244.
25. Swarnakar, V., Agrawal, N. and Tomar, R., "Sorption of Cr (VI) & As (V) on hdtma-modified zeolites", *International Journal of Computational Science and Engineering*, Vol. 2, No. 5, (2011), 1-9.
 26. Yan, L.-G., Wang, J., Yu, H.-Q., Wei, Q., Du, B. and Shan, X.-Q., "Adsorption of benzoic acid by CTAB exchanged montmorillonite", *Applied Clay Science*, Vol. 37, No. 3, (2007), 226-230.
 27. Lagergren, S. and Svenska, B.K., "About the theory of so-called adsorption of soluble substrates", *Vatenskapsakad Handlingar*, Vol. 24, No. 4, (1888), 1-39.
 28. Ho, Y.-S. and McKay, G., "Sorption of dye from aqueous solution by peat", *Chemical Engineering Journal*, Vol. 70, No. 2, (1998), 115-124.
 29. Dada, A., Olalekan, A., Olatunya, A. and Dada, O., "Langmuir, freundlich, temkin and dubinin-radushkevich isotherms studies of equilibrium sorption of zn²⁺ unto phosphoric acid modified rice husk", *Journal of Applied Chemistry*, Vol. 3, No. 1, (2012), 38-45.
 30. Umpuch, C. and Songsak, S., "Removal of methyl orange from aqueous solutions by adsorption using chitosan intercalated montmorillonite", *Songklanakar Journal of Science Technology*, Vol. 35, No. 4, (2013), 451-459.
 31. Chen, H., Zhao, J., Wu, J. and Dai, G., "Isotherm, thermodynamic, kinetics and adsorption mechanism studies of methyl orange by surfactant modified silkworm exuviae", *Journal of hazardous materials*, Vol. 192, No. 1, (2011), 246-254.
 32. Johnson, R.D. and Arnold, F.H., "The temkin isotherm describes heterogeneous protein adsorption", *Biochimica et Biophysica Acta (BBA)-Protein Structure and Molecular Enzymology*, Vol. 1247, No. 2, (1995), 293-297.
 33. Kumar, P.S., Ramalingam, S., Senthamarai, C., Niranjana, M., Vijayalakshmi, P. and Sivanesan, S., "Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions", *Desalination*, Vol. 261, No. 1, (2010), 52-60.
 34. Boparai, H.K., Joseph, M. and O'Carroll, D.M., "Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles", *Journal of Hazardous Materials*, Vol. 186, No. 1, (2011), 458-465.
 35. Koner, S., Pal, A. and Adak, A., "Utilization of silica gel waste for adsorption of cationic surfactant and adsolubilization of organics from textile wastewater: A case study", *Desalination*, Vol. 276, No. 1, (2011), 142-147.
 36. Hameed, B. and El-Khaiary, M., "Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modeling", *Journal of Hazardous Materials*, Vol. 159, No. 2, (2008), 574-579.

Batch Adsorption of Organic Dyes by Organo-bagasse: Carbon Content, pH Influence, Kinetics and Isotherms

RESEARCH
NOTE

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فاکتورهای موثره از قبیل محتوی کربن، زمان، pH محیط و غلظت رنگ اولیه در پاسخ به جذب سطحی سه رنگ ارگانیک آبی-زرد-۲۰ و سبز-۴۰ با استفاده از organo-bagasse به عنوانه جاذب مورد بررسی قرار گرفت. organo-bagasse توسط روش حلال سازی با استفاده از تترا دسیل متیل آمونیوم پروماید تهیه گردید. مواد موجود توسط روش های BET، طیف سنجی مادون قرمز و میکروسکوپ الکترونی نگاره مورد آنالیز قرار گرفت. آنالیزهای گروهی و تکمیلی روی محتوی کربن، pH اولیه محیط و محتوی اولیه رنگ مورد بررسی قرار گرفت. نتایج بدست آمده گویای این است که میزان جذب سطحی در سبز-۴۰ بالاترین بوده؛ زرد-۲۰ و آبی-۲۱ به ترتیب رتبه های دوم و سوم را دارا می باشند. نتیجه آنالیزی نشان می دهد که میزان جذب سطحی رنگ های ارگانیک با افزایش میزان محتوی کربن افزایش می یابد (همبستگی مثبت). میزان جذب سطحی هر سه رنگ (آبی-۲۱ (۰.۱۳۰ میلی گرم/گرم)، زرد-۲۰ (۰.۱۶۶ میلی گرم/گرم)، سبز-۴۰ (۰.۱۷۴ میلی گرم/گرم)) بعد از سه ساعت به میزان تعادل رسید. بیشترین میزان جذب سطحی در pH = ۲ بدست آمد. مطالعه سنتتیک تابع مدل شبه درجه دوم بود که نشان داد که نرخ انجام واکنش روی سطح جاذب عامل کنترل کننده سرعت واکنش است. باتوجه به مطالب مطرح شده، organo-bagasse یک جاذب موثر برای جذب سطحی رنگ های عالی می باشد.

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