

Article

Removal of Yellow20 dye from Aqueous Solution using Organo-rice Straw: Characteristic, Kinetic and Equilibrium Studies

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Abstract. The adsorbent of tetradecyltrimethyl ammonium bromide by an adsorbent termed ‘organo-rice straw’ was developed in this research to enhance the decolorization behavior of yellow20 in aqueous solutions. The organo-rice straw was characterized by elemental analysis, Brunauer-Emmett-Teller (BET) method, Fourier transform infrared spectroscopy (FTIR) technique, and scanning electron microscopy (SEM) images. Batch studies were researched to address various experimental parameters such as contact time, the initial pH solution, and initial dye concentration. Results showed that the major contents of yellow20 and organo-rice straw were carbon and hydrogen indicating their hydrophobic natures. The percentage of yellow20 that was removed by the organo-rice straw was 96.01%, higher than the 36.44% removed by the precursor. The equilibrium adsorption was reached within 3.0 h and the amount of yellow20 adsorbed was independent of the pH_0 . The kinetic data were fitted to pseudo-first order, pseudo-second order, and intra-particle diffusion models. Results implied that adsorption of yellow20 by this adsorbent followed the second order kinetic model and the maximum adsorption capacity was found to be 166.55 $mg.g^{-1}$. Equilibrium isotherms were analyzed by the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevitch isotherms. The Freundlich isotherm described the isotherm data with high-correlation coefficients. The results of the study indicate that organo-rice straw is a potential and active bio-sorbent for the removal of yellow20.

Keywords: Yellow20, organo-rice straw, adsorbent, hydrophobic-hydrophobic interaction.

ENGINEERING JOURNAL Volume 19 Issue 2

Received 7 July 2014

Accepted 4 December 2014

Published 30 April 2015

Online at <http://www.engj.org/>

DOI:10.4186/ej.2015.19.2.59

1. Introduction

There are many household-scale textile industries in UbonRatchathani province, Thailand, and many synthetic and natural dyes are used to color the products. However, synthetic dyes produced by several Thai factories are preferred because they are very cheap and locally available. These synthetic dyes are organic dyes as their major contents are carbon and hydrogen [1]. The natural threads subjected to these synthetic dyes are colorful and resistant to fading when exposed to heat, light, water, and chemicals. However, the pigmentation process also releases colored aqueous effluents that are highly visible, undesirable, and have the potential to inhibit photosynthesis [2]. Discharge of untreated water from this process causes damage to aquatic life and is severely harmful to humans [3]. Therefore, it is very important to treat the discharged water.

Various physical, chemical, and biological methods have been used in the treatment of these textile effluents. Although these methods are highly efficient, they have certain drawbacks, such as high capital and operational costs and secondary sludge disposal problems [4, 5]. Adsorption is a physico-chemical method of treating wastewater in which activated carbon is widely used as an adsorbent for the removal of dye from colored waters due to its excellent adsorption ability, but its expense limits its usage [6]. Therefore, bio-sorbents derived from agricultural residues, such as corn stalk, fruit peel, rice husk, and sugarcane bagasse, are currently used for the removal of these dye effluents [7–10].

The agricultural waste products are lignocellulosic materials which contain mainly cellulose, hemicelluloses, and lignin, and these provide specific functional groups, such as hydroxyl, aldehyde, aliphatic acid, amide, aromatic nitro, and silicate, which are considered to be beneficial to adsorption [11]. It has been documented that the adsorption capacity of agricultural waste is high in cationic molecules and low in anionic molecules, due to the fact that the surface of the plant residue is usually negatively charged in natural water bodies. Hence, the surface of the natural plant waste can be easily modified by organic cations such as quaternary ammonium compounds by electrostatic attraction and ion exchange reaction, known as 'adsolubilization.' This process involves the adsorption of the surfactant molecules on the external surface of the agricultural residue forming admicelle layers in a manner that alters their surface properties from hydrophilicity to organophilicity [12]. Recently, some natural plant waste was modified by cationic surfactant for the removal of organic dyes and satisfactory adsorption capacities were obtained [13–15].

Thailand has abundant lignocellulosic agricultural resources, especially rice straw. Rice straw is readily available, is an easily renewable resource, and it has been reported recently as a good bio-sorbent for the removal of a cationic dye, malachite green, from aqueous solutions [16]. However, the authors of this paper conducted a preliminary test using rice straw for anion dye adsorption and found that it had almost no effect on anion dye adsorption. Therefore, the high adsorption capacity of surfactant cations on the external surface of the rice straw could be expected. To increase the range of application of rice straw adsorbent in the treatment of different types of organic dye wastewater, the surface of the rice straw was adsolubilized by a cationic surfactant, tetradecyltrimethylammonium bromide (TDMA-Br), in the present work.

The main objectives of this research were: (i) to study the physical and chemical characteristics of the yellow20, rice straw, and organo-rice straw; (ii) to study the feasibility of using surfactant modified rice straw as an adsorbent for the removal of an organic dye, yellow20; (iii) to determine the various affecting parameters for the sorption, such as contact time, initial solution pH, and initial dye concentration; (v) to determine kinetic parameters and explain the nature of adsorption; and (iv) to determine the applicability of various isotherm models (such as Langmuir, Freundlich, Dubinin, and Radushkevich) to find out the best-fit isotherm equation.

2. Materials and Methods

2.1. Preparation of Bio-Sorbents

Rice straw was purchased from a local market near UbonRatchathani University, Thailand and was repeatedly washed with distilled water 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. To ensure uniform adsolubilization and reproducible results, the rice straw was crushed and shredded in a blender for about 15 min and sieved to obtain a particle size below 300 µm, designated as raw rice straw. 1.0 g of the raw rice

straw was treated with 100 mL of 1000 mg/L tetradecyltrimethyl ammonium bromide surfactant ($C_{17}H_{38}NBr$) purchased from the Merck Chemical Company (Germany). Mixing took place at 200 rpm for 15 min at room temperature using an orbital shaker. Afterwards, the organo-rice 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. To obtain more reproducible data, the organo-rice straw particles were sieved (50 mesh) before its use for adsorption studies. Furthermore, all adsorbents were packed in plastic bags and stored in desiccators for further use. The percentages of yellow20 removal of the precursor and the organo-rice straw were 16.19% and 97.31% so that only the organo-rice straw was used as bio-sorbent for further experiments.

2.2. Adsorbent Characterization

The elemental contents of the yellow20, the raw rice straw, and the organo-rice straw were analyzed by CHNS analyzer. 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 adsorbate. Fourier transform infrared (FTIR) spectroscopic analysis was used to determine the active functional groups of rice straw and organo-rice straw. The morphological features and surface characteristics of the bio-sorbents were obtained by the use of scanning electron microscopy (SEM).

2.3. Procedure of Adsorption Studies

Batch adsorption tests were conducted in 250 mL Erlenmeyer flasks which contained 100 mL of the yellow20 purchased from a local market near UbonRatchathani University, Thailand. Firstly, the percentages of dye removed by the raw rice straw and organo-rice straw were investigated. 100 mL of dye solutions which had initial concentration of 200 mg/L were mixed with 0.5 g of the precursor or organo-rice straw and then shaken at 200 rpm for 24 hr. Secondly, the effect of contact time on the dye sorption was investigated. A series of 250 mL Erlenmeyer flasks containing 100 ml of dye solutions was mixed with 0.1 g of the organo-rice straw. 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. Thirdly, the effect of initial dye concentration was studied. 0.1 g of the organo-rice 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 3 hours). All samples were measured at equilibrium condition. Finally, the effect of the initial solution pH on the sorption was investigated. 100 ml solution of the yellow20 of 200 mg/L and 0.1 g of the modified adsorbent were placed in a 200 ml Erlenmeyer flask. The initial solution pH was adjusted between 2.0 to 10.0 by 0.01N NaOH and/or 0.01N HCl and then horizontally shaken at 200 rpm for 24 hours.

2.4. Analytical Method

All subjected samples of the batch experiments were filtrated through GF/C filter (Whatman, UK) to harvest the adsorbent. Then, the free adsorbent solution was analyzed by a UV-Vis Spectrophotometer to determine the remaining dye concentration. The maximum absorption wavelength of yellow20 was 476 nm.

2.5. Calculation

The equilibrium adsorption capacity (q_e : mg/g) was calculated from the relationship in Eq. (1).

$$q_e = V(C_0 - C_e)/m \quad (1)$$

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. Adsorbent Characterization

The percentages of yellow20 removed by the precursor and the organo-rice straw were 36.44% and 96.01% respectively. These results were in accordance with those reported in the literature [12, 16–18].

The chemical compositions of the yellow20, the precursor, and the organo-rice straw are shown in Table 1 [19]. The major constituents of the organic dye, the raw rice straw, and the organo-rice straw were carbon. The higher carbon content of organo-rice straw is due to the cationic surfactant existing in the modified adsorbent indicating its more organophilic nature. Therefore, a hydrophobic-hydrophobic interaction was taken into account as an interaction between the yellow20 and organo-rice straw. Increases in the dye sorption capacity as the carbon content of the modified adsorbents increased have been reported in the literature [12, 16–18].

Table 1. Element content of organic dye and bio-sorbents studied [16].

Sample	Element content (%)		
	C	H	N
Yellow20 dye	12.73	0.38	0.92
Raw rice straw	38.86	6.66	0.54
Organo-rice straw	40.71	7.05	0.88

Figure 1 shows N_2 adsorption isotherm of raw rice straw and organo-rice straw. The isotherms were typical type II, showing the non-porous structure of the two bio-sorbents. The specific surface areas, analyzed by the Brunauer-Emmett-Teller (BET) method, of raw rice straw and the organo-rice straw were 4.85 and 4.53 m^2/g respectively. It was observed that the specific surface areas of both bio-sorbents were not significantly different. The slightly lower BET surface area comes from the loss of small amounts of internal and external surface areas of rice straw during adsorbent modification. It is well documented that the coating of surfactant on the surface of adsorbent generates a lower specific surface area of the modified bio-sorbent [20]. Consideration of BET surface area as the only affecting factor on the adsorption capacity of yellow20 by organo-rice straw is not sufficient but consideration of a hydrophobic-hydrophobic interaction as a major interaction is a more possible explanation. Furthermore, the pore volumes of the precursor and the organo-rice straw were 7.00×10^{-6} and 3.35×10^{-4} mL/g respectively. It was observed that the pore volume of the modified rice straw were slightly higher. The increase of pore volume was attributed to the presence of a porous structure of admicelle coating. The results suggested that the textural properties may not play an important role in adsorption.

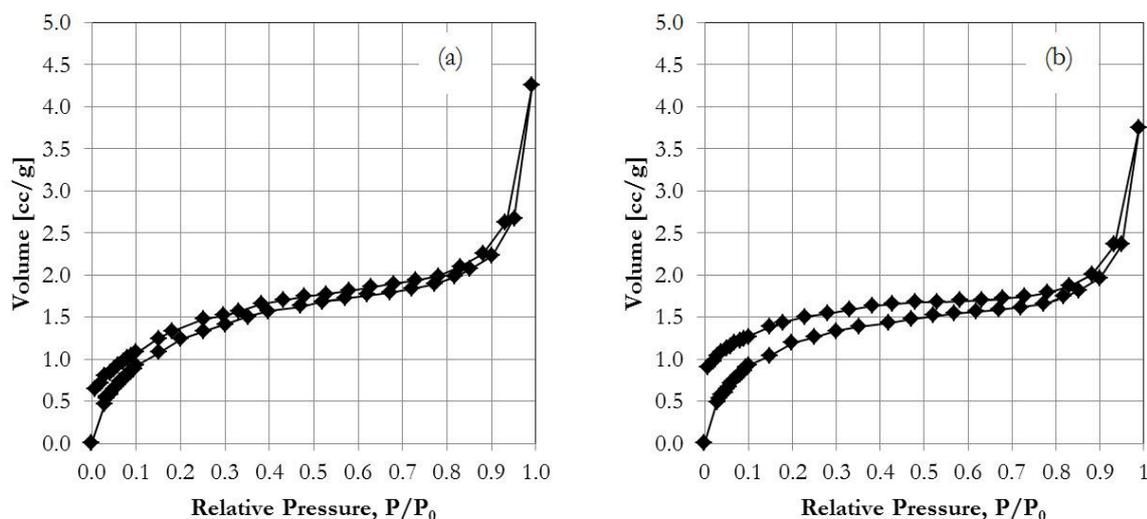


Fig. 1. N_2 adsorption-desorption isotherms measured on the raw rice straw (a) and the organo-rice straw (b).

Figure 2(a) shows the FTIR spectrum of the raw rice straw. After surfactant modification a new small peak was observed on the IR-spectra of the organo-rice straw at $3,590\text{cm}^{-1}$ [see Fig. 2(b)], referred to as the N-H stretching group [21]. This peak indicated that an additional amount of functional groups containing N-H bonds, a major constitution of TDMA-Br, were loaded on the surface of the bio-sorbent. This

revealed that the surface properties of the bio-sorbent could be altered from hydrophilicity to organophilicity.

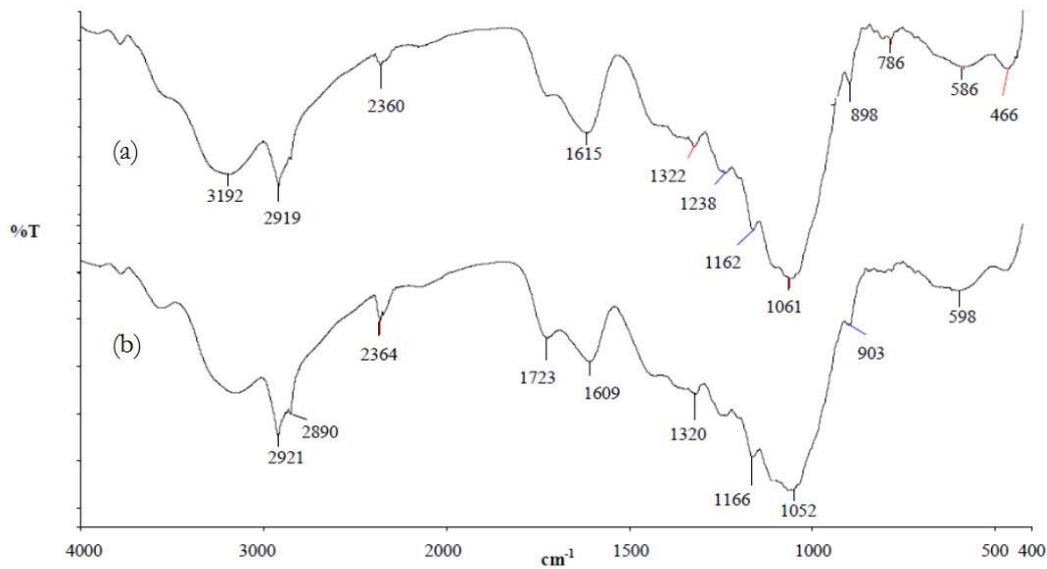


Fig. 2. IR-spectra of the rice straw (a) and the organo-rice straw (b).

Figure 3(a) shows the morphology of the raw rice straw and Fig. 3(b) indicates the morphology changes of the organo-rice straw. The external surface of the raw rice straw [Fig. 3(a)] has a ridged profile which has several small warts. On the other hand, the surface of the organo-rice straw [see Fig. 3(b)] is coated with a thin smooth layer of the cationic surfactant. The ridged profile on the surface of the raw rice straw cannot be observed. The differences in the morphologies of the raw rice straw and the modified one confirm the adherence of the cationic surfactant molecules on the external surface of the raw rice straw.

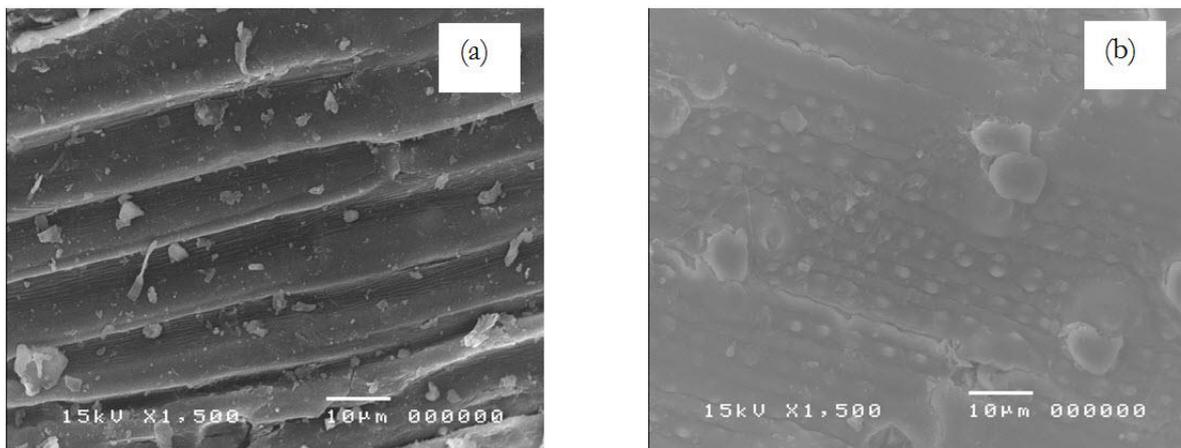


Fig. 3. SEM image of the raw rice straw (a) and the organo-rice straw (b).

3.2. Effect of Contact Time

Figure 4 shows that the percentage of dye removed by the organo-rice straw instantly increases in the first 5 min and then gradually increases with time until reaching a constant. The rapid adsorption rate observed at the initial stage was probably due to the abundant availability of active sites on the external surface of the organo-rice straw particles and the gradual increase in the later stage was due to the limited availability of active sites and diffusion of the organic dye molecules into the interior of the organo-bio-sorbent. The

equilibrium time required for the adsorption of the yellow20 was approximately 3.0 hours. To ensure the equilibrium, the mixing duration in the later adsorption experiments was 24 hours.

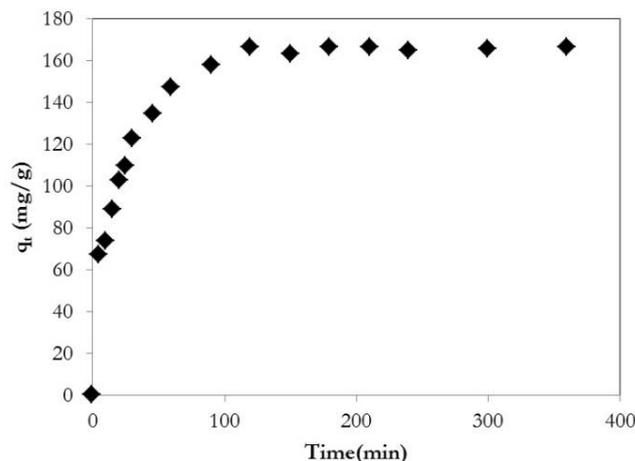


Fig.4. Effect of contact time on the percentage of dye removed by the organo-rice straw.

3.3. Effect of Initial Solution pH

The yellow20 uptake was quite independent of the pH of the initial solution as depicted in Fig.5. The adsorption capacity of the organo-rice straw was probably attributed to the fact that the main interaction between the organic yellow20 dye and the admicelle on the organo-rice straw surface was hydrophobic-hydrophobic interaction. Therefore, the change of proton and hydroxyl ions amounts in the solution did not affect the adsorption ability. Hence, it can be mentioned that the adsorption between the yellow20 and the organo-rice straw was pH independent.

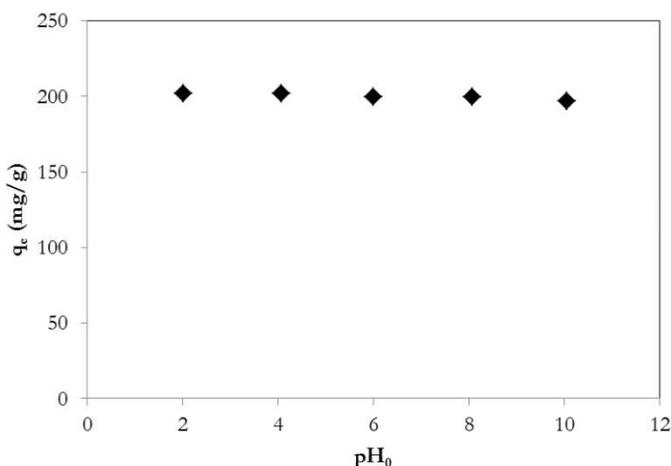


Fig.5. Effect of initial solution pH on the dye uptake by the organo-rice straw.

3.4. Kinetic Models

To predict the sorption mechanisms, the kinetic data are usually fitted by kinetic models such as pseudo-first order and pseudo-second order models. The pseudo-first order model, proposed by Lagergren [22] was 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 a time t , respectively, and k_1 is the rate constant for pseudo-first order adsorption (1/min).

The pseudo second order equation proposed by Ho [23] can be written in linear form as:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (3)$$

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

The intra-particle diffusion equation [24] 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 Eq. (2) revealing that the external mass transfer through a boundary layer was the rate of limiting step. The best fit of kinetic data to Eq. (3) indicating that the forming of interaction between adsorbate and adsorbent on the external surface of adsorbent was the rate of limiting step. The best fit of kinetic data to Eq. (4) showing that the diffusion of adsorbate into the interior of adsorbent was the rate of limiting step.

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

Model	Parameter	value
Pseudo-first order model	q_e (exp) (mg/g)	166.55
	k_1 (1/min)	3.24×10^{-2}
	q_e (cal) (mg/g)	157.10
	r^2	0.8849
Pseudo-second order model	k_2 (g/(mg.min))	4.38×10^{-4}
	q_e (cal) (mg/g)	188.68
	r^2	0.9980
Intra-particle diffusion model	k_i (mg/(g.min ^{1/2}))	8.10
	C (mg/g)	62.19
	r^2	0.7789

The parameters of the kinetic models and the correlation coefficients are given in Table 2. Poor correlations of the equilibrium data with the pseudo-first order kinetic and intra-particle diffusion model were observed. Normally, the pseudo-first order equation was well fitted for the data obtained at the beginning of the batch experiment. On the other hand, the kinetic data were well described by the pseudo-second order ($r^2=0.9980$) indicating chemical sorption which took place on the surface of the organo-rice straw was the rate of limiting step. The chemical sorption could be involved the adsorption process.

3.5. Adsorption Isotherms

The adsorption isotherm of yellow20 which is a relationship between q_e and C_e was plotted in Fig. 6. The adsorption capacity initially increased and then tended to be constant.

The adsorption isotherms developed by Langmuir and Freundlich [25] were commonly used to fit the equilibrium data. The Langmuir isotherm is related to the sorption taking place 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 the Langmuir isotherm in Eq. (5) and the Freundlich isotherm in Eq. (7) are shown below:

$$C_e/q_e = C_e/q_m + 1/(K_L q_m) \quad (5)$$

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 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 [26]. The R_L is defined as:

$$R_L = 1/(1+K_L C_0) \quad (6)$$

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-rice straw was favorable.

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (7)$$

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

The Temkin isotherm model [27] 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:

$$q_e = (RT/b)\ln K_T + (RT/b)\ln C_e \quad (8)$$

where b is the Temkin constant related to the heat of sorption (J/ mol), R is Universal gas constant, 8.314 J/mol.K, T is the temperature (K) and K_T is the Temkin isotherm constant (L/g) [23].

The Dubinin-Radushkevich (D-R) [28] 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:

$$\varepsilon = RT \ln[1 + 1/C_e] \quad (10)$$

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

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

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 correlation coefficients, r^2 , value of Freundlich isotherm model was the highest.

Poor correlation of the Langmuir isotherm model was observed ($r^2=0.7346$). The maximum monolayer coverage (q_{max}) was determined to be 416.67mg/g which is different from maximum adsorption capacity (q_i) of 166.67mg/g due to the poor correlation. The separation factor (R_L) was greater than 0 but less than 1.0 indicating highly favorable sorption for the dye yellow20 by the studied organo-bio-sorbent. The Freundlich isotherm described the isotherm data with high-correlation coefficients ($r^2=0.9780$). This suggested that the multilayer coverage on the adsorbent surface had taken place. The constant n value was greater than unity, meaning that the forces between the adsorbed molecules were repulsive. This implied that the interaction between the adsorbate and adsorbent was stronger than the adsorbate/adsorbate repulsion. Furthermore, the linear plot for the Temkin adsorption isotherm, which considers chemisorption of an adsorbate onto the adsorbent [29], fitted quite well with a correlation coefficient of 0.8824 (Table 3). This further supported the findings that the adsorption of the yellow20 by the organo-rice straw 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 the Temkin isotherm model (Table 3). This suggested that the yellow20 adsorption by the organo-rice straw particles involved both chemical and physical processes.

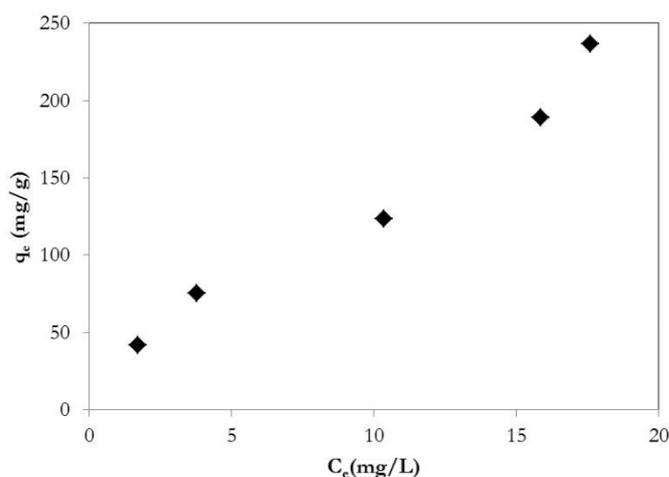


Fig.6. Adsorption isotherm of the dye sorption by the organo-rice straw.

Table 3. Isotherm constants and correlation coefficients.

Model	Parameter	Value
Langmuir isotherm	$q_m(\text{mg/g})$	416.67
	$K_L(\text{L/g})$	23.20
	R_L	1.72×10^{-4}
	r^2	0.7346
Freundlich isotherm	$K_F(\text{mg}^{1-1/n} \cdot \text{L}^{1/n}/\text{g})$	28.36
	n	1.44
	r^2	0.9780
Temkin isotherm	$K_T(\text{L/g})$	0.646
	$b(\text{kJ/mol})$	0.0331
	r^2	0.8824
Dubinin-Radushkevich isotherm	$q_s(\text{mg/g})$	116.17
	$E(\text{kJ/mol})$	0.655
	r^2	0.8060

3.6. Adsolubilization Process

The adsorption of cationic surfactant on oppositely charged rice straw surface is highly dependent on the surfactant concentration [30]. At low concentrations, surfactant is adsorbed as monomers due to electrostatic attraction between the charged head groups of cationic surfactant and those of the oppositely charged rice straw surface. At higher concentrations, the surfactant begins to form a bi-layer on the adsorbent surface due to the electrostatic attraction between the cations, the charged adsorbent surface, and interaction between the hydrocarbon chains. Micelle-like aggregates are formed on the adsorbent surface. The mono-layered structure is called hemimicelle and the bi-layered structure is called admicelle. Admicelles are generally formed above a critical micelle concentration surfactant of $10^{-3} - 10^{-2}$ M. In the present research, the surfactant concentration was 2.98×10^{-3} M. Thus, the admicelles had the ability to solubilize organic dye molecules within their structures. This process is called 'adsolubilization.' The yellow20 solubilized on the surface of organo-rice straw is schematically represented in Fig. 7.

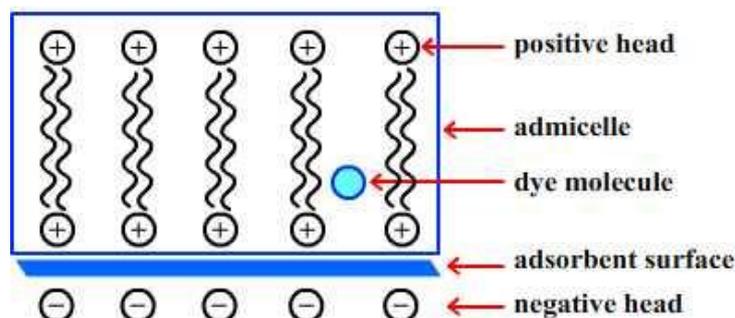


Fig. 7. Schematic representation of organo-rice straw surface after adsolubilization.

4. Conclusions

The modification of rice straw with a cationic surfactant enhanced the sorption efficiency for yellow20 from 36.44% of the dye being removed before modification to 96.01% after and the surface property of the adsorbent altered from hydrophilic to hydrophobic. Furthermore, the modification caused a decrease of BET surface area, an addition of amine and the alkyl groups, and a change of morphology in the modified adsorbent. The adsorption of the yellow20 reached equilibrium within 180 min. The kinetic data conformed to the pseudo-second order equation and the formation of adsorbate/adsorbent interaction was the rate of limiting step. The sorption of yellow20 by the organo-rice straw was independent of the solution's pH. The adsorption isotherm followed the Freundlich, Temkin, and D-R isotherm equations showing that yellow20 molecules formed a multilayer on the adsorbent surface. The above results suggest that organo-rice straw was an effective adsorbent for the removal of yellow20 from synthetic effluents.

Acknowledgements

The research was financially supported by the National Research Council of Thailand in 2013. The authors express his sincere gratitude to Mr. Boonsong Jutarat for research assistance and to Bob Tremayne, from the Office of International Relations at Ubon Ratchathani University, for assistance with English.

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