AJChE 2018, Vol. 18, No. 2, 31 – 40

Anionic Dye Adsorption from Aqueous Solutions by Chitosan Coated Luffa Fibers

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Chitosan (CS) is biopolymer derived from deacetylation of chitin which can be found mainly in crustacean shells such as shrimp, crab, lobster etc. CS powder has been used to remove dye in many research. However, it was difficult to separate CS powder from aqueous solution. Considering the three-dimensional sponge natural structure of luffa fiber. it may address this issue by coating CS onto the surface of luffa fiber. This adsorbent was called chitosan coated luffa fiber (CS-LF). The aim of this studied is to investigate the potential of CS-LF to remove the anionic dye. Congo red is representative of anionic dye. Adsorption of anionic dye from aqueous solution using CS-LF was studied in a batch system. The effect of chitosan concentration coated on luffa fiber and initial anionic dye concentrations had been investigated on adsorption equilibrium and adsorption kinetic. An adsorption isotherm data were regularly analyzed using Langmuir and Freundlich isotherm models. While, adsorption kinetic were basically evaluated by pseudo-first-order, pseudo-second-order and intraparticle diffusion equation. The results showed that the adsorption isotherm fitted well by Langmuir isotherm model with maximum adsorption capacity 20.37 mg/g. The anionic dye adsorption kinetic of CS-LF were greatest described by pseudo-second-order equation and rate-controlling step of anionic dye adsorption process may be chemical reaction. Therefore, CS-LF is potential adsorbent as low-cost adsorbent to remove anionic dye from aqueous solution and could be simply separated from aqueous solutions after used. Finally, our study is firstly report in anionic dye adsorption using chitosan coated luffa fiber.

Keywords: Adsorption, Chitosan, Luffa Fibers, Congo Red, Anionic Dye

INTRODUCTION

Dyes are directly applied in many industries such as textile, paper and printing production which can significantly generated a large amount of wastewater which contained suspended solid, colloids and high concentration of dissolved inorganic and organic compounds from dyeing process [1]. The dye wastewater can produces negative impacts on the ecosystem and human health when them expose to our environment [2]. Therefore, the dye wastewater needs to be treated before discharge to environment. Even though, the conventional method of wastewater treatment processes which are primary and secondary treatment is high efficiency to remove those contaminants. But some of the inorganic and organic compound from dying processes may still remain in treated water and over the limitation of wastewater disposal standard. Therefore, it essentially requires to proceed the treated wastewater to tertiary treatment process in order to remove those contaminants to meet the wastewater disposal standard.

Tertiary wastewater treatment has several techniques to eliminate dye residue from secondary wastewater such as adsorption, precipitation, ion exchange, membrane filtration, and electrochemical techniques. However, Among the above-mentioned techniques, adsorption is more attractive technique because it is inexpensive, simplicity and efficiency [3]. The adsorption technique usually used activated carbon as adsorbent. However, activated carbon has the disadvantage of being very expensive. Thus, low-cost adsorbents as natural adsorbents increase a wide attention and extensively studied in dye removal from aqueous solution due to they are inexpensive, available in large quantities, easy to regenerate for reuse and eco-friendly [4].

Chitosan(CS) is biopolymer derived from deacetylation of chitin which can be found mainly in crustacean shells such as shrimp, crab, lobster etc [5]. CS powder has been used to remove dye in many research. However, it was difficult to separate CS powder from aqueous solution. To address this issue, CS may need to coat on a material that can be easily separated from the adsorption process. Luffa fiber has been carefully considered to be used as supporting material due to it is natural fiber structure, cheap, large amount available and being easy to separate from adsorption process.

Therefore, the main objective of this study is to investigate the dye adsorption potential of chitosan coated on luffa fiber. The adsorption kinetics and isotherms were also studied in order to obtain maximum adsorption capacity and understanding adsorption mechanism of dye onto chitosan coated on luffa fiber. The adsorption isotherm and kinetic model equations were mathematically fitted and discussed with adsorption data.

THEORY

Adsorption Isotherm Equations

Adsorption isotherms are the relationship between equilibrium adsorption (q_e) and adsorbate concentration in the aqueous solution at equilibrium (C_e). The most common isotherms equations were normally described by Langmuir and Freundlich equations in order to obtain maximum adsorption capacity and describe distribution of adsorbate ion/molecule between solid and liquid phase [6],[7].

Langmuir Isotherm

The Langmuir isotherm model is mostly used to describe adsorption behavior by assuming that (1) active site on adsorbent surface are identical, (2) each of active sites on adsorbent surface use equivalent adsorption energy for adsorbing ion/molecule, (3) there are no interactions between adsorbed ion/molecule on the adsorbent surface, and (4) there are monolayer adsorption on the adsorbent surface [8],[9]. The Langmuir isotherm model is given by

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{1}$$

where K_L (L/g) = $q_m \cdot a_L$, q_m (mg/g) is maximum adsorption capacity, q_e (mg/g) is equilibrium adsorption capacity and a_L (L/mg) is Langmuir isotherm constant.

Langmuir isotherm constants, K_L and a_L, can be estimated by linearized Eq. (1) to linear form (Eq. (2)) and then plotting C_e/q_e versus C_e

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{2}$$

Therefore, slope is a_L/K_L and intercept is $1/K_L$, can be used to estimate maximum adsorption capacity (q_m, mg/g) and Langmuir isotherm constant (a_L, L/mg). Moreover, Langmuir isotherm equation can be expressed in terms of dimensionless equilibrium parameter (R_L) which was defined by Weber and Chakravorti [10] as:

$$R_L = \frac{1}{1 + a_L C_o} \tag{3}$$

Values of R_L can be used to show either unfavorable or favorable of adsorption process as following. $R_L > 1$ present unfavorable adsorption process, $R_L = 1$ indicates linear adsorption process, $0 < R_L < 1$ indicates that favorable adsorption process and $R_L = 0$ indicates irreversible adsorption process.

Freundlich Isotherm

Freundlich isotherm model is used to describe non-ideal adsorption behavior by assuming that (1) ions or molecules could be adsorbed more than one layer on the adsorbent surface, (2) the adsorbent surface is heterogeneous. The Freundlich is given by

$$q_e = K_f C_e^{1/n} \tag{4}$$

where K_f (mg/g) is adsorption capacity and n is the adsorption intensity. K_f and n can be estimated by linearized the Eq. (4) to Eq. (5) and then plotting log q_e versus log C_e

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \tag{5}$$

the slope is $1/n$ and an intercept is log K_f, can be used to calculate K_f and n values. The magnitude of exponent n indicates either unfavorable or favorable of adsorption process. value of $n > 1$ shows favorable adsorption [6].

Adsorption Kinetic Equations

In order to gain insight the adsorption mechanism, pseudo first-order equation, pseudo second-order equation and intraparticle diffusion model were essential applied to analyse the experiment data [11].

The pseudo-first order equation [3].

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \tag{6}$$

The pseudo-second-order equation [3].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

where q_t (mg/g) is the amount of adsorbed at any time and k_1(min^{-1}) is the equilibrium rate constant of pseudo-first-order adsorption. k_2 (g/mg·min) is the rate constant of pseudo-second order adsorption.

The intraparticle diffusion model was defined as following [12]

$$q_t = k_p t^{1/2} + C \qquad (8)$$

where k_p (mg/g· $min^{1/2}$) is the intraparticle diffusion rate constant, t (min) is time and C is the thickness of the boundary layer.

MATERIALS AND METHODS

Luffah Fiber Preparation

Luffa fibers were acquired from northern Thailand. The luffa fibers were approximately cut into 1x1 cm square and cleaned with distilled water. After that, the luffa fiber was heated at 80 ˚C and stirred 30-minute with 0.2 %w/v lauryl sulphate in order to remove grease. Then the luffa fiber pretreated with 3 %w/v NaOH solution in order to remove lignin out of the fibers. Finally, the luffa fibers were cleaned with distilled water until reach to neutral pH. After that the luffa fibers were dried 80 ˚C in the oven overnight. The luffa fibers were stored for the further use and mark as LF.

Chitosan Stock Solution Preparation

The 0.5 %w/v chitosan solution was simply prepared by slowly dissolving 5 g of chitosan powder (85%DD) from biological laboratory, department of chemical engineering, Burapha University, into 250 mL acetic acid (1%v/v). Then, chitosan solution was adjusted to 1000 mL by acetic acid. The chitosan homogeneous mixture was shaken overnight. The chitosan solution was stored at room temperature for the further use and mark as CS.

Congo Red Solution Preparation

500 ppm Congo red stock solution was prepared by dissolving 0.5 g of congo red in distilled water and adjust to 1000 mL in volumetric flask. the distilled water was used to dilute congo red to desire concentration.

Chitosan Coated on Luffa Fiber

Chitosan had simply coated on luffa fiber by dip method at different chitosan concentration. Firstly, the chitosan solution was diluted with acetic acid solution (1%v/v) to 0.1, 0.25 and 0.5 %w/v, respectively. The luffa fiber was dipped into the solutions for 10 minutes, then dried in oven at 105 ˚C for 2 hr. The dried chitosan coated on luffa fiber were directly cleaned with distilled water until reach to neutral pH. The chitosan coated on luffa fiber dried in oven at 105 ˚C for 2 hr and mark as CS-LF for the further use.

Kinetic Study

Adsorption kinetic was basically investigated by batch studies. Congo red was used in this study as representative of anionic dye. The adsorption kinetics of CS-LF was studied by shaking a mixture of 0.035 g of 0.5%w/v CS-LF and 40 mL of

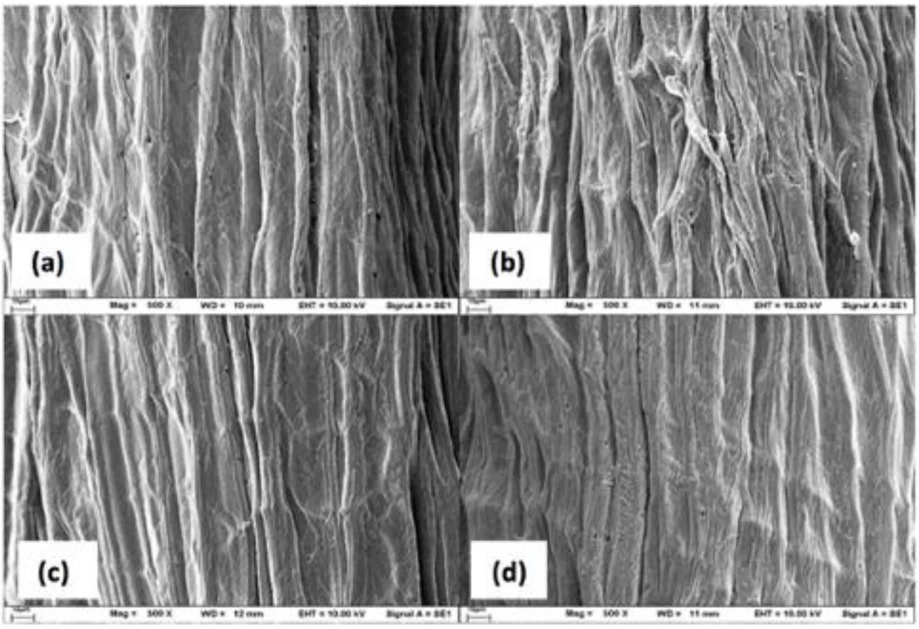


Fig. 1: SEM micrographs of LF and CS-LF at 500x; (a). LF, (b) 0.1 %w/v CS-LF, (c) 0.25 %w/v CS-LF and d) 0.5%w/v CS-LF

Congo red solution at neutral pH in a 45-mL tube. The initial congo red concentrations were 20 ppm, 60 ppm and 120 ppm. Each of initial congo red concentration was prepared seven (7) tubes for 3, 6, 12, 24, 48, 72 and 96 hr. The sample was taken at different time intervals. The remain of Congo red concentration was determined by spectrophotometry. The kinetic study has been done by triplicate.

Isotherm Study

Adsorption isotherm of CS-LF was also investigated by batch studies in order to obtain maximum adsorption capacity and isotherm constant for design purposes. The 45 mL tubes were employed and each tube was added with 40 mL of Congo red solution in various concentrations from 20 to 120 ppm at neutral pH. The 0.035 g of CS-LF was added to each tube and shaken at 170 rpm continuously at room temperatures for 96 hr. The equilibrium adsorption capacities were calculated using Eq. (9). The adsorption isotherm was plotted and analysed with adsorption isotherms model.

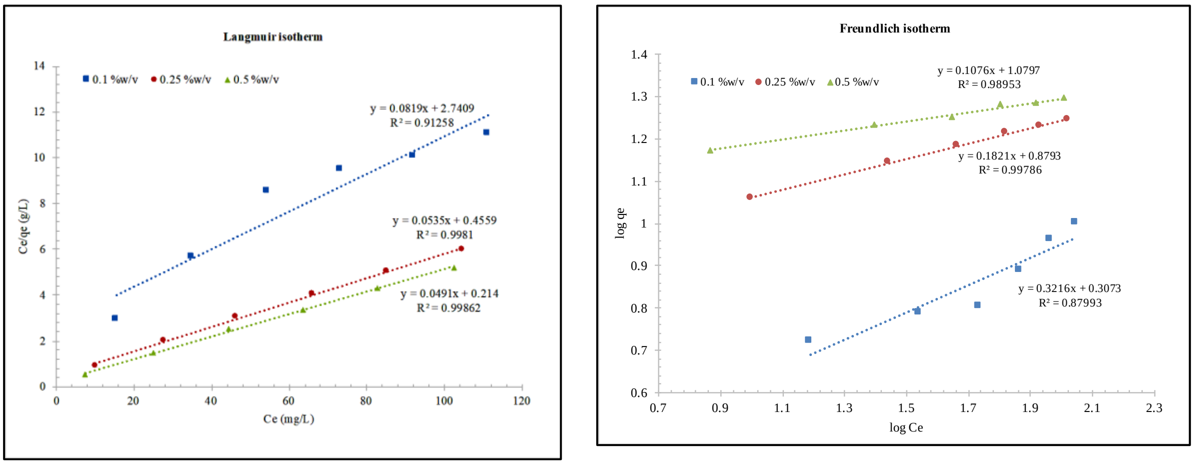
$$q_e = \frac{(C_0 - C_e)V}{m} \tag{9}$$

where q_e (mg/g) is adsorption capacity at equilibrium, C_0 (mg/L) is initial Congo red concentration, C_e (mg/L) is equilibrium congo red concentration, V (L) is volume of Congo red solution, and m (g) is the mass of CS-LF.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

The surface of LF and CS-LF with difference chitosan concentration was characterized by scanning electron microscopy (SEM) image. The SEM used was a Philips, TECNAI 20. As shown in Fig. 1, the LF (a) are irregular in shape. However, when the luffa fiber was coated with



a. Langmuir isotherm b. Freundlich isotherm

Fig. 2: Adsorption isotherm of Congo red on CS-LF at different Chitosan concentration: a. Langmuir and b. Freundlich

chitosan, the surface of luffa fiber was smooth than non-coated luffa fiber and obtain smoother surface when increase chitosan concentration as shows in (b), (c) and (d), respectively. This implied that the luffa fibers were coated with chitosan and could be used as adsorbent to remove Congo red from aqueous solution.

Analysis of Isotherm Data

Adsorption isotherms of congo red onto CS-LF are presented in Fig.2 (a) and (b). The adsorption isotherms showed the relationship between the q_e of CS-LF and C_e. The adsorption isotherm data were analyzed by fitting with Langmuir and Freundlich isotherm model. The adsorption isotherm constants were estimated and presented in Table 1**.**

The q_m were 12.21 mg/g, 18.69 mg/g and 20.37 mg/g for 0.1 %w/v CS-LF, 0.25%w/v CS-LF and 0.5%w/v CS-LF, respectively. It shown that increasing of chitosan concentration will increased adsorption capacity. High correlation coefficient (r^2) suggested that the Langmuir model could fit very well for Congo red adsorption isotherms onto CS-LF. Additionally, the dimensionless constant separation factor, R_L based on Langmuir model have been also calculated at 120 ppm initial congo red concentration. It can be observed from Table. 1 that the calculated values of R_L of all adsorbent range between 0 and 1. It indicated that CS-LF were favorable congo red adsorption.

Table 1. the parameter of Langmuir and Freundlich models simulating the adsorption isotherm of Congo red on CS-LF

Parameters	**Chitosan concentration (%w/v)**		
	0.10	**0.25**	**0.50**
Langmuir			
K_L(L/g)	0.36	2.19	4.67
a_L(L/mg)	0.03	0.12	0.23
q_m(mg/g)	12.21	18.69	20.37
R_L	0.22	0.07	0.04
r^2	0.9126	0.9981	0.9986
Freundlich			
n	3.11	5.49	9.29
K_f (mg/g)	2.03	7.57	12.01
r^2	0.8799	0.9979	0.9895

In the Fig.2b, the adsorption isotherms were evaluated by plotting log qe versus C_e. It showed that the adsorption isotherms were satisfactory fitted with Freundlich isotherm model (Eq.5). The adsorption isotherm of 0.25%w/v CS-LF and 0.5%w/v CS-LF can be fitted well with great correlation coefficient (r^2) values as 0.9979 and 0.9895. But 0.1%w/v CS-LF obtain low correlation coefficient (r^2) comparing to 0.25%w/v CS-LF and 0.5%w/v CS-LF. It suggested 0.1%w/v CS-LF was not fit well with Freundlich model. The Freundlich constant were evaluated and listed in the Table.1. The K_f showed the congo red adsorption capacity of the adsorbent, which are 2.03 mg/g, 7.57 mg/g and 12.01 mg/g. Higher values of K_f suggest the highest adsorption capacity[2] The value of Freundlich constant n also gives a measure of favourability of adsorption. the n value of Freundlich constant indicating a favorable adsorption when n value is relied between 1 to 10 [13]. The n value of Freundlich constant shown 3.11, 5.49 and 9.29 for 0.1%w/v CS-LF, 0.25%w/v CS-LF and 0.5%w/v CS-LF, respectively. It indicated that all adsorbents were favorable congo red adsorption.

Since, it has clearly seen that for 0.1%w/v CS-LF can not fit the adsorption isotherm data for either Langmuir isotherm or Freundlich isotherm model. This may suggested that the use of low chitosan concentration coat onto LF may not appropriate.

Therefore, Langmuir isotherm and Freundlich isotherm models are suitable to be used to describe the congo red adsorption isotherm onto CS-LF where coated with chitosan at least 0.25 %w/v chitosan. The maximum adsorption capacity obtained from Langmuir isotherm model were in better agreement with the experimental data than those obtained from the Freundlich isotherm equation. This implied that Langmuir isotherm model may be the greatest isotherm model to describe congo red adsorption isotherm onto CS-LF. In addition, it also indicated that adsorption on CS-LF was a monolayer adsorption and homogeneous surface adsorbents with a limited number of same binding sites, this means all active sites were energetically identical.

Analysis of Kinetic Data

Congo red adsorption kinetic onto CS-LF was examined by batch studies. The adsorption kinetic were typically performed at different initial concentration of congo red (20, 60 and 120 ppm) over time (0 to 96 hr) and the result were shown in Fig.3.

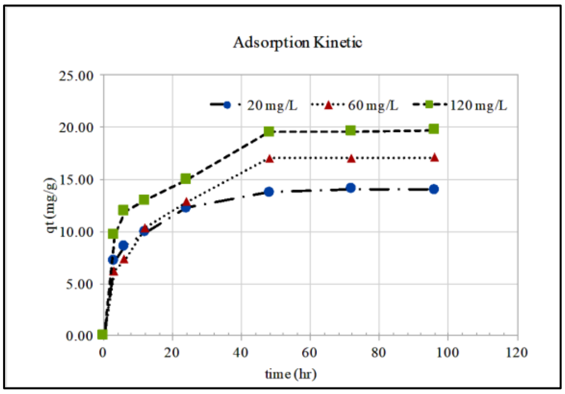
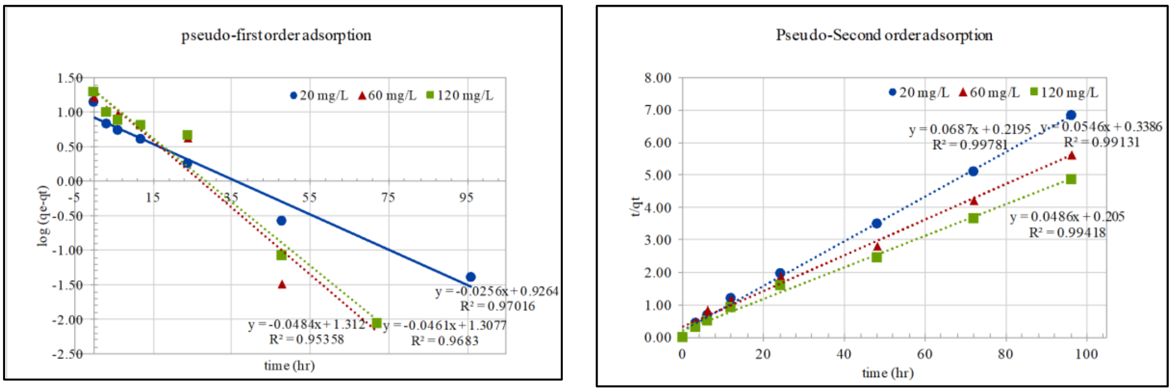


Fig. 3: The effect of contact time on the adsorption capacity of congo red by CS-LF at different initial concentration of congo red

As shown in Fig.3, it found that the congo red has been adsorbed onto 0.5%w/v CS-LF. the adsorption of Congo red was sharply fast at the beginning of



a. Pseudo-first order b. Pseudo-secondorder

Fig. 4: Plot of kinetic model for the adsorption of congo red on CS-LF: a. Pseudo-first order and b. Pseudo-second order

adsorption reaction and slightly decease speed of the adsorption reaction over time and finally reach to equilibrium adsorption in all initial concentration of Congo red. This was due to the fact that higher initial concentration of adsorbate provided more driving force of adsorption of congo red onto adsorbents surfaces, which made the adsorbate easier be adsorbed the ion or molecules [11]. The adsorption kinetic was almost used 48 hr to reached the adsorption equilibrium. However, at 20 ppm of congo red slightly reached to the adsorption equilibrium before 60 ppm and 120 ppm, respectively.

In order to comprehend the adsorption mechanism, adsorption kinetics data gained from kinetic experiment essentially need to be fitted by pseudo first-order (Eq.6), pseudo second-order (Eq.7) and intraparticle diffusion model (Eq.8). The Fig.4 was shown the linearization of kinetic adsorption data were plotted log (q_e − q_t) versus t for pseudo-first-order equation (Fig.4a) and t/q_t versus t for pseudo-second-order equation (Fig.4b) at different initial concentration of congo red. The kinetic adsorption data were fitted with the kinetic adsorption model. The value of k_1, q_e and r^2 for pseudo-first order and the value of k_2, q_e and r^2 for pseudo-second-order were estimated and list in Table 2.

Table 2. Kinetic model parameters for the adsorption of Cu(II) onto luffa fibers.

Parameters	**Initial Congo red concentration (ppm)**		
	20	**60**	**120**
q_e, exp (mg/g)	14.08	17.07	19.65
Pseudo-first-order			
k_1 (hr^{-1})	0.059	0.111	0.106
q_e (mg/g)	8.44	20.51	20.31
r^2	0.9702	0.9536	0.9702
Pseudo-second-order			
k_2 (hr^{-1})	0.022	0.009	0.012
q_e (mg/g)	14.56	18.32	20.58
r^2	0.9978	0.9913	0.9941

From the Table 2, It shows noticeably that correlation coefficient (r^2) from the pseudo-second-order model are definitely higher than correlation coefficient (r^2) from the pseudo-first-order model. Moreover, the values of the q_e obtained from the pseudo-second-order model were in better agreement with the experimental kinetic data than those obtained from the pseudo-first order model. Therefore, the pseudo-second-order model could be perfectly used to fit and explain the Congo red adsorption kinetic onto CS-LF.

To evaluate the rate-controlling step of adsorption process, q_t versus $t^{1/2}$ were plotted and fitted the kinetic adsorption data from adsorption kinetic experiment using intraparticle diffusion model (Eq.8). The values of k_p, C and r^2 were estimates and shown in the Table 3.

Table 3. Parameters of Intraparticle diffusion

Parameters	**Initial Congo red concentration (ppm)**		
	20	**60**	**120**
k_p (mg/g. hr^{-1})	1.25	1.72	1.78
C	4.11	2.87	5.16
r^2	0.7957	0.9063	0.8360

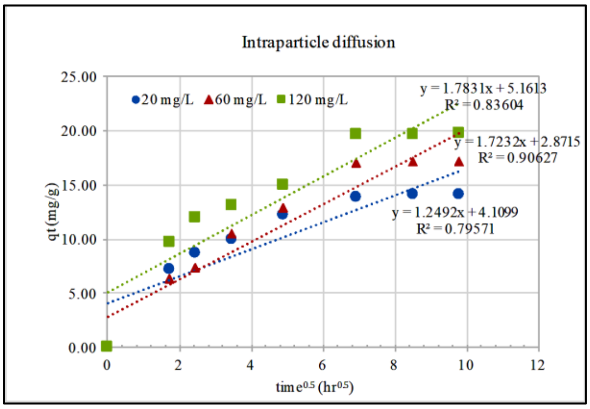


Fig. 5: Plot of intraparticle diffusion model for the adsorption of Congo red at different initial concentration onto CS-LF

The Fig.5, It obviously shown that the plots of $t^{1/2}$ versus q_t were non-linear as show by correlation coefficient (r^2) less than 0.9063. It suggested that the intraparticle diffusion kinetic was not appropriate in adsorption process of congo red onto CS-LF. The plots can be identified as multi-linear. It means that there are two or more steps control adsorption process [12]. Thus, The rate-controlling step may be chemical reaction [11].

CONCLUSIONS

The adsorption of congo red as representative of anionic dye onto chitosan coated on luffa fibers (CS-LF) was investigated under ambient condition and neutral pH. The adsorption kinetic and isotherm of congo red was also determined. The adsorption kinetic by CS-LF with different initial dye concentrations were the greatest described by pseudo-second-order equation. As the concentration of the initial congo red increased, the adsorption rate constant also increased and the adsorption isotherm fitted well by Langmuir isotherm equation with maximum adsorption capacity 20.37 mg/g. rate-controlling step of adsorption process of congo red onto CS-LF may be chemical reaction and a monolayer adsorption, all active sites were energetically identical and favorable congo red adsorption. Therefore, CS-LF is potential adsorbent as low-cost adsorbent to remove anionic dye from aquouse solution and could be simply separated from aqueous solutions after used. Finally, our study is firstly report in anionic dye adsorption using chitosan coated luffa fiber.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial and laboratory support of Department of Chemical Engineering and Faculty of Engineering (grant no. 5/2559).

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