Solid fly ash waste from the sugar industry was treated by HCl and then carbonized under N₂ at 900 °C for 1 h. The resulting carbon was used as an adsorbent for the removal of colored dyes from wastewater generated in the silk dying process. The untreated fly ash and commercial activated carbon were also used as adsorbents for comparison. Porous properties of all adsorbents were characterized by nitrogen adsorption/desorption at 77 K. The kinetics and equilibrium data were obtained from batch experiments with varying adsorption times (1–12 h) and initial concentrations (50–1,000 mg/L) of conventional commercial dye in wastewater, Dark Red 34. The adsorption isotherms and kinetics were studied for all three samples. The adsorption kinetics were analyzed using pseudo-first order, pseudo-second order and intra-particles diffusion models. The adsorption equilibrium data was analyzed by using Langmuir and Freundlich models. Results showed that the surface area of the treated fly ash increased from 26 to 239 m²/g after acid and carbonization treatments. Equilibrium adsorption was reached in 4 h for all samples. The experimental data indicated that the adsorption kinetics were well described by the pseudo-second order model. While isotherms fitted well with the Langmuir equation. The maximum adsorption capacities for the dye removal were 1258, 1156 and 666 mg/g for treated fly ash, activated carbon and untreated fly ash, respectively. Therefore, treated fly ash from the sugar industry shows its high potential as an adsorbent for the color removal of wastewater from silk dying process.

Key Words
Fly ash, Sugar industry, Dye for silk, Adsorption

1. Introduction
Thai silk is a famous product in the world due to its high quality. Thai silk producers can be found both within the household as a village industry and in an industrial context. One of the many steps in the making of Thai silk is the dying process. In the past, traditional dyes made from plants were used, however the commercial silk production of today uses synthetic dyes to achieve colors that are more difficult to make from natural dyes. Consequently, the discharge of colored wastewater is causing a serious environmental concern due to their poor biodegradability and toxicity. Various methods have been proposed to remove the color of dyes from wastewater including coagulation, chemical oxidation, membrane separation, electrochemical treatment, reverse osmosis, etc. Accordingly, the economical process should be considered. One of the powerful and convenient treatment processes is adsorption. Regarding the selection of adsorbent, many literatures reveal that activated carbon has been used for the treatment of textile wastewater. However, various low-cost adsorbents should be investigated as an alternative to activated carbon.

Fly ash is a solid waste material that arises in high volume from many industries. It will generate dust and pollute the atmosphere if placed in the open field without proper disposal. Various researchers have utilized fly ash for the removal of the most widely used synthetic
dye in industry such as methylene blue, malachite green, rhodamine B, orange-G or methyl violet but there is no information for the removal of synthetic dye used in household industry. The raw fly ash has a low adsorption capacity; however, its capacity is being increased by physical and chemical modification. The main physical method includes hammer mill, ball mill, jet mill, etc. As regards the chemical modification method, fly ash can be treated with acid.

Thus, the main objective of this study is to study the feasibility of using fly ash from the sugar industry as an adsorbent for the removal of commercial dye for silk dyeing process used in household industrial in Khon Kaen province, Thailand. The fly ash was treated using HCl and carbonized under nitrogen atmosphere. Batch adsorption studies were carried out to investigate the effects of adsorption time and initial dye concentration. The kinetic and equilibrium data of the adsorption were then studied to understand the adsorption mechanism. The untreated fly ash and commercial activated carbon have been used for comparison.

2. Experiments

Bagasse fly ash was obtained from a local sugar industry. Then the fly ash was treated with 1 mol/L HCl solution at room temperature for 24 h. The second sample was carbonized at 900 °C for 1 h under N₂ atmosphere. The third sample was treated with 1 M HCl for 24 h and then carbonized at 900 °C for 1 h under N₂ atmosphere. Powdered activated carbon commercial grade manufactured by the company located at Nakhon Ratchasima province and untreated fly ash were also used for comparison of adsorptive characteristics with treated fly ash. This activated carbon had properties as follows: moisture 8.5%, ash content 5.4%, pH value 10.5, apparent density 0.51 g/cm³, iodine adsorption 981.5 mg/g and particle size distribution over 325 mesh 5.6% and pass 325 mesh 94.4%.

Bulk density of bagasse fly ash was determined following the method published by Ahmedna et al. (1997). A 10 cm³ glass cylinder was filled with fly ash and the bulk density was calculated from weight of sample divided by and cylinder volume.

Proximate analysis of bagasse fly ash was carried out according to standard methods. The moisture content was determined following ASTM D2867 at 150 °C for 3 h. The sample was heated at 950 °C for 30 min according to ASTM D5832-98 method to find volatile matter. The ash content found at 800 °C for 2 h in a muffle furnace and the fixed carbon content was calculated by 100% – moisture (%) – volatile matter (%) – ash (%).

Pore structures of all adsorbents relating to surface area and pore volume were characterized by a Micromeritics ASAP 2460 porosity of N₂ adsorption at -196 °C. Brunauer–Emmet–Teller (BET) method was used for surface area measurement. Total pore volume (VT) was evaluated from the adsorbed volume of nitrogen at relative pressure or P/Po near 1.0. Micropore volume (Vmic) was calculated by the Dubinin–Radushkevich (DR) method. The mesopore volume (Vmeso) was obtained by deducting the micropore volume from the total pore volume. The average pore size (DP) of the sample was calculated using the Barrett–Joyner–Halenda (BJH) equation.

Dark Red 34 (Lion Dance Drumming Brand, Phua Kiam Seen, Co., Ltd) was chosen as adsorbate due to the fact it is commonly used dye for silk dyeing process in household industry in Khon Kaen province. The series of batch experiments were carried out to determine kinetics and equilibrium of adsorption. The effect of adsorption time (1–12 h) and initial dye concentration (50–1,000 mg/L) were studied using 50 mL of dye solution. In all experiments, an adsorbent dose of 0.05 g was used. The concentration of dye in solution was estimated at wavelength of maximum absorbance λmax 521 nm by UV-vis spectrophotometer (G1103A, Agilent). The adsorption capacity (qt, mg/g) was calculated using the following equation:

\[ q_t = \frac{C_i - C_f}{m} V \]  

where \( C_i \) and \( C_f \) are initial and final concentration of dye (mg/L), \( V \) is the volume of solution and \( m \) is the mass of adsorbents. The experiment was repeated for three times to get more accurate result and mean values were used for calculation.

3. Results and Discussion

The bagasse fly ash used in this study had bulk density of 0.36 g/cm³. The literature reported the bulk density of bagasse fly ash as 0.133, 0.186 and 0.41–0.59 g/cm³. This may be due to the different source of raw bagasse fly ash. Bulk density is critical for the adsorption performance. If bulk density is too small, it is not preferred since the open pores of the adsorbent are low thus reducing the adsorption capacity.

The proximate analysis showed that bagasse fly ash consisted of 21.58 wt% for moisture content, 27.12 wt% for volatile matter, 42.46 wt% for ash content and 8.84 wt% for fixed carbon. This means that the fly ash composed of organic and inorganic substances.

Fig. 1 shows the adsorption-desorption isotherms...
of untreated fly ash, treated fly ash and commercial activated carbon. It can be concluded that the isotherms of untreated fly ash and fly ash treated with HCl exhibit the Type I according to the International Union of Pure and Applied Chemistry (IUPAC), which is related to microporous adsorbent. The isotherms display a small hysteresis loop, indicating the presence of small mesopore volume. The isotherms for fly ash treated by carbonization with N₂ and treated with acid HCl then carbonized with N₂ display mixing between Type I and Type IV, indicating a mixture of microporous and mesoporous materials. Both the adsorption-desorption isotherms completely overlapped at low relative pressure P/P₀ < 0.4, but showed a distinct hysteresis loop at relatively high pressure (P/P₀ > 0.4). The adsorption behavior has a sharp increase in the low relative range because of the micropore filling effect, then behaves like capillary condensation (mesopores) at higher pressure. For commercial activated carbon, the isotherms present Type IV which is classified as mainly a mesoporous structure. According to IUPAC classification of pores system, the pores ranges from < 2 nm size are considered as micropores; 2–50 nm considered as mesopores and >50 nm were emphasized as macropores. Moreover, the more N₂ adsorption capacity results in more developed porosity. The textural characteristics of adsorbents are determined from these N₂ isotherms which will be discussed below. The results of textural characteristics of the adsorbents used in this study are given in Table 1. It reveals that the acid treatment and carbonization enhance the surface area and pore volume of the fly ash. Moreover, treated fly ash with acid and then carbonized under N₂ give the adsorbent with highest surface area and pore volume, while decreases its average pore diameter. This may be due to the increase of the micropore content of the treated fly ash after the impurities and organics are removed by acid and high temperature treatment. Therefore, this study uses treated fly ash with acid and N₂ to adsorb dyes from wastewater compared with untreated fly ash and commercial activated carbon. It is noted that commercial activated carbon has significantly higher surface area and total pore volume than treated fly ash.

Table 2 compares the surface area and total pore volume of adsorbents with the literature. The raw bagasse fly ash has different surface areas depending on the source. The raw fly ash used in this study showed lowest surface area. The treatment of fly ash can use many types activating agents such as H₃PO₄, ZnCl₂, steam and CO₂. The moderate specific surface area adsorbent obtained from this study when compared with some literature may be due to the low surface area of raw fly ash, using low concentrations of chemicals or no activating agents.

The adsorption of dye onto untreated fly ash (UFA), treated fly ash (TFA) and commercial activated carbon (CAC) at different times is depicted in Fig. 2. The dye
adsorption capacities of these adsorbents are given by treated fly ash > commercial activated carbon > untreated fly ash. For all adsorbents, the adsorption of dye increased with time and attained equilibrium at 4 h. Therefore, based on these results, 4 h was taken as the equilibrium time for studying adsorption isotherms. The rapid increase of the adsorption rate at the early stage is due to all the adsorbent sites being initially vacant and the concentration gradient between wastewater and adsorbent surface being very high. Then, the lower adsorption rate occurring at the latter stage is due to a decrease in the number of vacant sites of adsorbent and the low concentration gradient between solute concentrations and adsorbent surface.

Three kinetic models, pseudo-first order, pseudo-second order and intra-particles diffusion model, are employed to describe the limiting step and mechanism of adsorption process. The equations of these model are given by 19)

Pseudo-first order model:  
\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  (2)

Pseudo-second order model:  
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  (3)

Intra-particles diffusion model:  
\[ q_t = k_3 t^{1/2} + C \]  (4)

where \( q_e \) and \( q_t \) refer to the amount of dye adsorbed (mg/g) at equilibrium and at any time, \( t \) (min), respectively, \( k_1 \) (min\(^{-1}\)), \( k_2 \) (g/mg min) and \( k_3 \) (mg/g min\(^{1/2}\)) are the rate constant of pseudo-first order, pseudo-second order and intra-particles diffusion models, respectively, and \( C \) (mg/g) is a constant related to the thickness of the boundary layer.

Fig. 3 shows plots of the pseudo-first order, pseudo-second order and intra-particles diffusion models for adsorbing dye onto all three adsorbents. The kinetic constants and correlation coefficients of all models are presented in Table 3. It is clearly shown that the pseudo-second order is the better model to describe the kinetics of dye adsorption than pseudo-first order with \( R^2 \) equals to 0.999. This indicated that the rate limiting step of dye adsorption onto these adsorbents is chemical adsorption. Furthermore, the theoretical equilibrium capacities of dye \( (q_e) \) calculated by the pseudo-second order kinetic model almost equals the experimental adsorption capacities \( (q_{exp}) \).

Adsorption isotherms are undertaken to understand the behavior of the adsorbent at equilibrium conditions. Two famous isotherm equations, namely the Langmuir and Freundlich, are applied to fit the experimental data of dye adsorption on adsorbents. These equations can be written as 19):

Langmuir isotherm:  
\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  (5)

Freundlich isotherm:  
\[ q_e = K_F C_e^{1/n} \]  (6)

where \( q_m \) (mg/g) is the Langmuir maximum adsorption capacity, \( K_L \) (L/mg) is the Langmuir constant related to rate of adsorption and \( K_F \) ((mg/g)L/(mg)\(^{1/n}\)) and \( n \) are the Freundlich constants which give a measurement of adsorption capacity and adsorption intensity, respectively.
Table 3  Kinetics parameters for dye adsorption on different adsorbents

| Adsorbent | $q_{exp}$ (mg/g) | $q_e$ (mg/g) | $k_1$ (min$^{-1}$) | $R^2$ |
|-----------|------------------|--------------|-------------------|-------|
| TFA       | 83.412           | 38.784       | 0.0069            | 0.826 |
| UFA       | 51.243           | 11.534       | 0.0054            | 0.845 |
| CAC       | 58.664           | 23.812       | 0.0067            | 0.952 |

| Adsorbent | $q_{exp}$ (mg/g) | $q_e$ (mg/g) | $k_2$ (g/mg min) | $R^2$ |
|-----------|------------------|--------------|------------------|-------|
| TFA       | 83.412           | 86.956       | 3.703 × 10$^{-4}$| 0.999 |
| UFA       | 51.243           | 52.632       | 8.896 × 10$^{-4}$| 0.999 |
| CAC       | 58.664           | 61.728       | 4.813 × 10$^{-4}$| 0.999 |

| Adsorbent | $q_{exp}$ (mg/g) | $C$ (mg/g) | $k_{in}$ (mg/g min$^{1/2}$) | $R^2$ |
|-----------|------------------|------------|---------------------------|-------|
| TFA       | 83.412           | 68.765     | 0.5669                    | 0.923 |
| UFA       | 51.243           | 40.684     | 0.4837                    | 0.906 |
| CAC       | 58.664           | 37.97      | 1.0140                    | 0.964 |

Fig. 3  Plots of (a) pseudo-first order, (b) pseudo-second order and (c) intra-particles diffusion models for dye adsorption on different adsorbent.

Fig. 4  Plots the amount of dye adsorbed against the equilibrium concentrations and then fitted with Langmuir and Freundlich isotherms for all three adsorbents. The calculated constants of the two isotherm equations along with $R^2$ value are presented in Table 4. For all three adsorbents, the Langmuir isotherm gives a better fit to the experimental data with higher $R^2$ values than that of the Freundlich isotherm. The maximum adsorption capacities.
of dye, as indicated by \( q_{\text{max}} \) in Langmuir isotherm, are 1,258 mg/g for treated fly ash, 666 mg/g for untreated fly ash and 1,156 mg/g for commercial activated carbon. It implies that the maximum adsorption capacity of treated fly ash is about 1.89 and 1.09 times higher than those of untreated fly ash and commercial activated carbon, respectively. These results indicate that acid and carbonization treatment of fly ash enhanced the adsorption capacity. Moreover, although the commercial activated carbon had higher surface area and total pore volume than treated fly ash, it demonstrated marginally lower adsorption capacity. This indicates that it is not only surface area and pore volume that affect the adsorption behavior, the surface characteristic also the main factor. Therefore, the surface properties such as surface functional group and pH at the point of zero charge (pH_{pzc}) of adsorbent should be studied in future. In addition, the average pore size of treated fly ash is 2.37 nm while commercial activated carbon is 3.72 nm. It is generally believed that micropores are the major provider of adsorptive sites in aqueous solutions, whereas, in mesopores only weaker adsorption is observed. Thus, the adsorption would proceed through a sequence of diffusion steps from the bulk phase into the mesopores and then to the micropores, which contain adsorptive sites with higher adsorption energies 22).

### 4. Conclusions

This study has demonstrated the possibility of developing treated fly ash from the sugar industry and its potential as an effective adsorbent for the color removal of dye from wastewater of the silk dyeing process. Results showed that treatment with HCl and then carbonized under N\(_2\) at 900 °C produced an adsorbent with a surface area of 239 m\(^2\)/g and a total pore volume of 0.142 cm\(^3\)/g. This adsorbent was employed for the adsorption of the main color used in silk dyeing process, namely Dark Red 34, in batch process. Kinetic and isotherm data of the adsorption by treated fly ash were compared with untreated fly ash and commercial activated carbon. The adsorption process revealed that the initial adsorption capacity was rapid, and equilibrium was attained in around 4 h. Equilibrium adsorption data of dye onto all three adsorbents were well represented by Langmuir model with \( R^2 \) value of about 0.99. The maximum adsorption capacity for treated fly ash was 1,258 mg/g that about 1.89 and 1.09 times higher than untreated fly ash and commercial activated carbon, respectively. The adsorption kinetic data were well described by the pseudo-second order model, indicating that the adsorption mechanisms involve chemical adsorption with the intra-particle diffusion. Thus, treated fly ash prepared from solid waste of the sugar industry would be useful for the treatment of wastewater containing dye.
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