

## Preparation of Eggshell Powder/Low Density Polyethylene Composites and Their Acid Dye Removal Efficiency

Supitcha YAISUN and Tatiya TRONGSATITKUL\*

*School of Polymer Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand*

(\* Corresponding author's e-mail: tatiya@sut.ac.th)

*Presented at 41<sup>st</sup> Congress on Science and Technology of Thailand: November 6<sup>th</sup> - 8<sup>th</sup> 2015  
Full paper accepted: 2 March 2016*

### Abstract

This study focused on the preparation of eggshell powder (ESP)/low density polyethylene (LDPE) composites and the acid dye (Acid Yellow 137) removal efficiency of the prepared composites. ESP was prepared using a domestic coffee grinder and then sieved to determine the particle size distribution. The smallest particle size of ESP obtained was  $\leq 45 \mu\text{m}$  which was used in ESP/LDPE composite preparation. ESP (45  $\mu\text{m}$ ) concentrations of 30, 50 and 70 wt% were incorporated into LDPE using an internal mixer, then extruded and cut into pellet form using a twin screw extruder. Batch adsorption experiments were carried out as a function of contact time and adsorbent dosage. Dye removal efficiency was determined using UV-Vis spectrophotometry and found to be dependent on ESP concentration and adsorbent dosage. The highest removal efficiency was 18 % for the 70 wt% ESP/LDPE composite. Results from the Brunauer-Emmett-Teller (BET) technique showed that surface area increased with ESP content and was highest at  $0.71 \text{ m}^2 \cdot \text{g}^{-1}$  for the 70 wt% ESP/LDPE composite. SEM micrographs revealed that the large surface area of 70 wt% ESP/LDPE composite was due to a significant amount of ESP protruded from the pellet surface. The process kinetics of ESP and its composites were found to follow the pseudo-second order rate equation. Although, the maximum dye removal efficiency of the composite was 2.6 times lower than that of 45  $\mu\text{m}$  ESP at the same adsorbent dosage, the ease of adsorbent recovery after utilization of the composite was significantly improved over that of ESP.

**Keywords:** Eggshell powder, composite, acid dye, adsorption kinetics, waste water treatment

### Introduction

Silk production is one of the main small scale industries in Nakhon Ratchasima province, Thailand. Acid dyes are used in the silk dyeing process. Large volumes of water are needed in this process including dyeing, fixing, and washing. Large volumes of waste water containing acid dye is, therefore, generated as a consequence of the process. This waste water must be properly treated before discharging into the environment. Dye chemicals must be removed from the water not only because of its carcinogenicity, but also because dye stained water can hinder light penetration and disturb the life processes of living organisms in water [1,2].

Several waste water treatment technologies are available nowadays. Each technology presents unique advantages and drawbacks. These waste water treatments can be categorized as physical process, for example filtration, adsorption, and dialysis; chemical process such as flocculation and coagulation, and biological process such as the use of microalgae and activated sludge. Among these treatments, adsorption processes have attracted much attention in recent years. This is because the adsorption process is a simple, economical, and effective method that can provide high removal efficiency. Activated carbon is the most utilized adsorbent for dye removal. However, because of the high cost of activated carbon and

the difficulty in the regeneration, the adsorption process of this adsorbent still remains an expensive process. For this reason, alternative adsorbents are needed. Biomass and food wastes [3-6] such as fruit peel [1,2,7], leaf powder [3], fly ash, eggshell [8,9], and rice husk have gained significant interest for use as alternative adsorbents. These adsorbents are low in cost and to use this biomass waste and food wastes are also beneficial as a bio-resource recycling [5,9].

Eggshell is one of food processing by-products that has attracted substantial interest as an alternative, low-cost adsorbent in recent years [8-10]. This is for 3 main reasons. Firstly, eggshell possesses a high surface area due to its porous nature. It was estimated that an egg could have about 7,000 - 17,000 holes on its shell [11]. Secondly, around 96 % of eggshell is calcium carbonate ( $\text{CaCO}_3$ ). When it comes into contact with water, calcium carbonate will partially dissolve and yield  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  ions [12]. These ions could provide a mechanism for removing ions of contaminants from water, such as heavy metals and dyestuffs via ionic interaction. Thirdly, eggshell is an abundant food processing by-product. In Thailand, egg production in 2014 was approximately 11,700 eggs. The egg production has also reportedly increased at least 2 - 5 % every year [13]. Therefore, eggshell as a by-product will increase. In short, the porosity, the ions affinity, and the availability of eggshell make eggshell an attractive candidate as an alternative option for adsorbent.

Surface area is one of the most crucial parameters for an effective adsorption. Grinding the eggshell into fine powder to increase its surface area has also been shown to improve the adsorption efficacy [10]. However, fine particles can also be problematic during the preparation and utilization processes. Specifically, fine eggshell powder (ESP) can be easily blown off and is difficult to collect during the preparation and after utilization. An improvement in the ease of use is desired in order to utilize fine eggshell powder for its full potential as an alternative, low cost adsorbent.

In this study, fine ESP was prepared using a domestic coffee grinder. This grinding technique consumes considerable less amount time (minutes) than the conventional ball milling technique (days). The prepared ESP were then sieved to classify and investigate the particle size distribution. ESP with 2 different particle sizes of 45 and 300  $\mu\text{m}$  were selected as representatives for adsorption properties. The 45  $\mu\text{m}$  ESP was selected to be used in ESP/composites as it possessed a better dye removal efficiency than the larger particle size of 300  $\mu\text{m}$  ESP. The composites of 45  $\mu\text{m}$  ESP/low density polyethylene (LDPE) at different ESP concentrations (30, 50 and 70 wt%) were prepared using a 2-step melt mixing method. Their acid yellow 137 dye removal efficiencies were studied and compared with their individual components (LDPE and ESP) using a batch adsorption process. The parameters affecting adsorption efficiency i.e. contact time, ESP concentration in the composites, and adsorbent dosage were examined. The dye removal efficiency of the ESP/LDPE composite may be compromised as compared to ESP alone, however improvements in the ease of use and handling are expected.

## Materials and methods

### Materials

LDPE InnoPlus LD2426K, was supplied by PTT Chemicals Thailand, and used as a matrix binding ESP together. ESP was prepared from chicken eggshell waste collected from restaurants around Suranaree University of Technology campus area (Nakhon Ratchasima, Thailand). Acid yellow 137 (CAS No. 72827-84-0), the structural formula is not known.

### Sample preparation and characterization

ESP preparation: the eggshell waste was first washed with distilled water several times to remove egg residue and other contaminants. The cleaned eggshells were then dried in a hot air oven at 80 °C for 12 h before grinding. A domestic coffee grinder was used in this study because it was readily available and easy to use with minimal time consumption. The pulsating grinding method was carried out with 20 s grinding and 10 s intervals, 4 times. The size distribution of ESP was then classified using a British Standard (BS) sieve.

ESP/LDPE composite preparation: a 2-step melt mixing method was used to prepare the highly loaded ESP/LDPE composites. LDPE was used as a matrix to bind the ESP together. ESP/LDPE

composites with various ESP (45  $\mu\text{m}$ ) concentrations; i.e. 30, 50 and 70 wt% were first compounded using an internal mixer (HAAKE™ 3000P, Germany) equipped with a roller rotor at 190 °C, 60 rpm for total mixing time of 10 min. The compounds were then extruded and cut into pellet form using a co-rotating twin screw extruder (Brabender DSE35/17D, Germany). The temperature profile from hopper to die was 170, 175, 185 and 190 °C, respectively, and the screw speed was kept constant at 20 rpm.

#### Characterizations of adsorbents

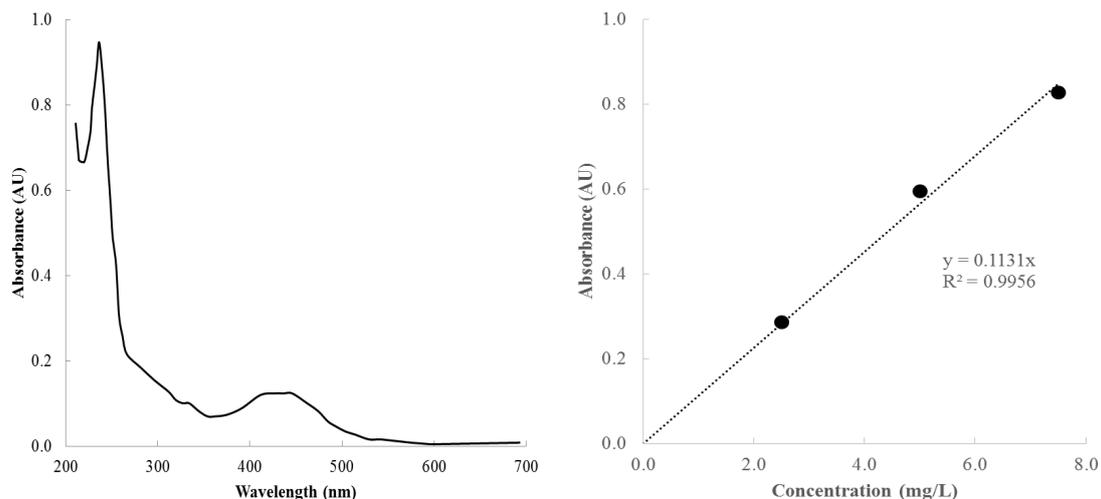
ESP, LDPE pellets, and ESP/LDPE composites containing ESP of 30, 50 and 70 wt% were characterized for their features and morphologies using scanning electron microscope (SEM), (Model: Auriga, Carl Zeiss, Germany). All samples were coated with gold and were fixed onto aluminum stubs using carbon tape. The Brunauer-Emmett-Teller (BET) surface area and total pore volume of the samples were determined using a BELSORP-miniII surface analyzer (Bel Japan Inc., Japan).

#### Adsorption experiments

Batch adsorption experiments were carried out in an incubator shaker New Brunswick Innova® 42 (Eppendorf, Canada) under a temperature-controlled environment at 40 °C and a shaking speed of 200 rpm. In general, 5.0 g of adsorbent sample was dispersed in 250 mL of 10  $\text{mg.L}^{-1}$  acid yellow 137 aqueous solution without adjusting the pH value. Seven mL-Aliquots were collected from the dispersion at a pre-determined time (usually 30 min intervals) and then centrifuged at 5,000 rpm for 5 to 20 min, depending on the ease of separation, until clear aliquots were achieved. The remaining dye concentrations in the clear aliquots were determined using a UV-Vis spectrophotometer (Carry300 Agilent, Agilent technology, USA). The characteristic absorption peaks of acid yellow 137 were observed at 227 and 433 nm (**Figure 1** (Left)). The stronger peak of maximum absorption at 227 nm was used for dye removal efficiency study. A linear relationship between the dye concentration and the adsorption intensity at maximum absorption wavelength of 227 nm was obtained as shown in **Figure 1** (Right). The quantity of dye adsorbed on an adsorbent was derived from the change in concentration of the dye solution as shown in Eq. (1).

$$\text{Dye Removal Efficiency (\%)} = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

where  $C_i$  is the initial dye concentration and  $C_t$  is the dye concentration at time  $t$



**Figure 1** Adsorption spectrum of acid yellow 137 aqueous solution (Left) and its standard curve (Right) showing a linear relationship between the dye concentration and the adsorption intensity at a maximum absorption wavelength of 227 nm.

### Kinetic study

The adsorption kinetics study was carried out to compare the performance of ESP/LDPE composite and ESP as adsorbents for acid yellow 137 at different loading. In this study, only the pseudo-second-order equation showed a good fit with the experimental data and was therefore used. The pseudo-second-order equation is shown below in Eq. (2).

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

where  $q_e$  and  $q_t$  are the amounts of dye adsorbed ( $\text{mg.g}^{-1}$ ) on the adsorbent at equilibrium and at time  $t$ , respectively. The parameter  $k_2$  is the rate constant of the pseudo-second-order adsorption ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ). For the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of Eq. (2) becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (3)$$

Eq. (3) can be rearranged and a linear form equation can be obtained as shown in Eq. (4). As such,  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot, respectively.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

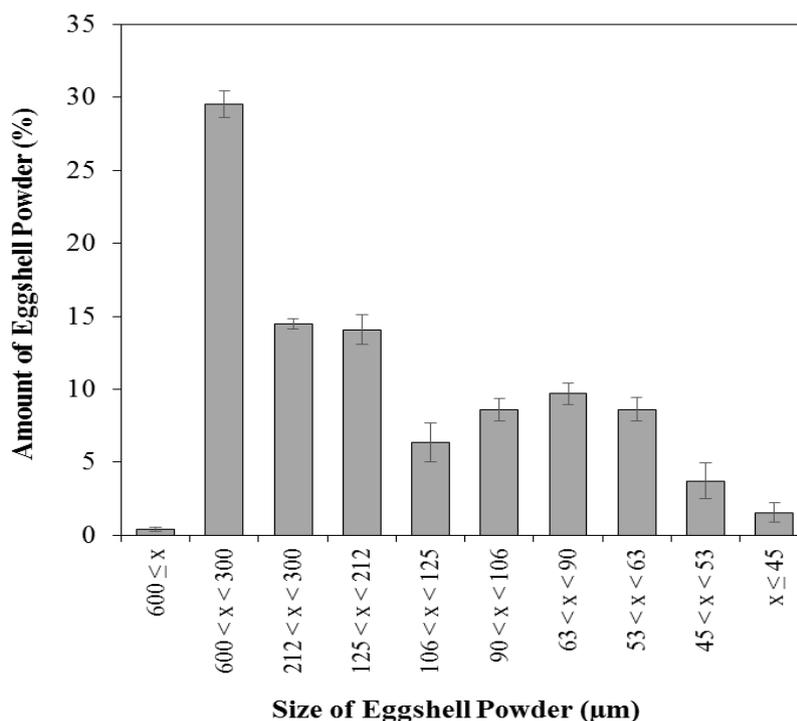
## Results and discussion

### Characteristics of adsorbents

The particle size distribution of ESP prepared using a domestic coffee grinder is shown in **Figure 2**. The particle size of ESP obtained from this method did not show a normal distribution. The highest amount (~30 wt %) obtained was ESP with a particle size between 300 and 600  $\mu\text{m}$  (referred to as 300  $\mu\text{m}$  ESP for short). The lowest amount of ESP had a particle size of > 600  $\mu\text{m}$ . The smallest size of ESP was < 45  $\mu\text{m}$  (referred as 45  $\mu\text{m}$  ESP for short) obtained at ~2 wt%. The ESP with particle sizes of 300

and 45  $\mu\text{m}$  were selected for further investigation to determine their adsorption properties. These 2 particle sizes of ESP were of particular interest. The highest amount of 300  $\mu\text{m}$  ESP yielded from the preparation bearing the benefit of minimum effort and energy used. The 45  $\mu\text{m}$  ESP was selected as it was expected to possess the highest surface area, and thus more suitable to be used as an absorbent. The adsorption study, reported in the next section, showed that 45  $\mu\text{m}$  ESP possessed a better dye removal efficiency than that of the 300  $\mu\text{m}$  ESP. Thus, 45  $\mu\text{m}$  ESP was selected to be used in the ESP/LDPE composite. For this reason, it was necessary to increase the yield of 45  $\mu\text{m}$  ESP. A longer grinding time of 10 to 15 min was later used and the amount of 45  $\mu\text{m}$  ESP increased to 20 - 30 wt%. The SEM micrograph of 45  $\mu\text{m}$  ESP is presented in **Figures 3a** and **3b**. Particles with irregular shape and uniform size were observed. The SEM micrograph at a high magnification of 5,000 $\times$  revealed the presence of uniform round pores with diameter of approximately 0.2  $\mu\text{m}$  distributed evenly throughout the eggshell particles. The observed structure was believed to be an inherent porous characteristic of an eggshell [10].

Composites of ESP/LDPE with ESP in pellet form were produced in order to improve the ease of utilization of ESP. The ESP/LDPE composite pellets containing 30, 50, and 70 wt% ESP are shown in **Figures 4a** and **4b**. ESP particles were uniformly distributed throughout the pellets. Voids between the particles and matrix indicated poor adhesion between the 2 phases which, in this case, were beneficial as they increased the overall surface area and consequently exposed more surface area of ESP to the adsorbate (Acid Yellow 137 dye) in the solution. It was also found that as the ESP content was increased, the ESP/LDPE pellets became more porous with a higher number of ESP particles protruding from the surface of the composite pellet. Inset images at high magnification of 5,000 $\times$  illustrated the characteristic porous structure of ESP, similar to that of observed in **Figure 3b**, that remained even after processing through the 2-step melt mixing method.



**Figure 2** Particle size (x) distribution of ESP prepared using domestic coffee grinder.

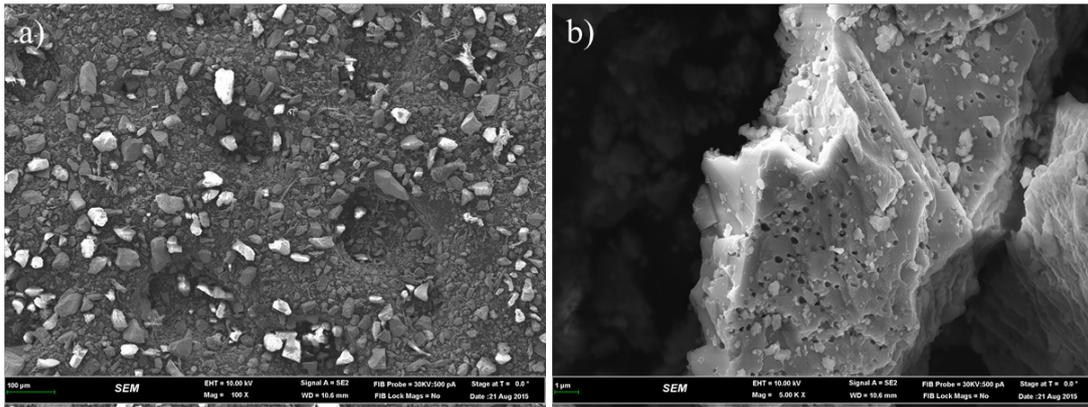
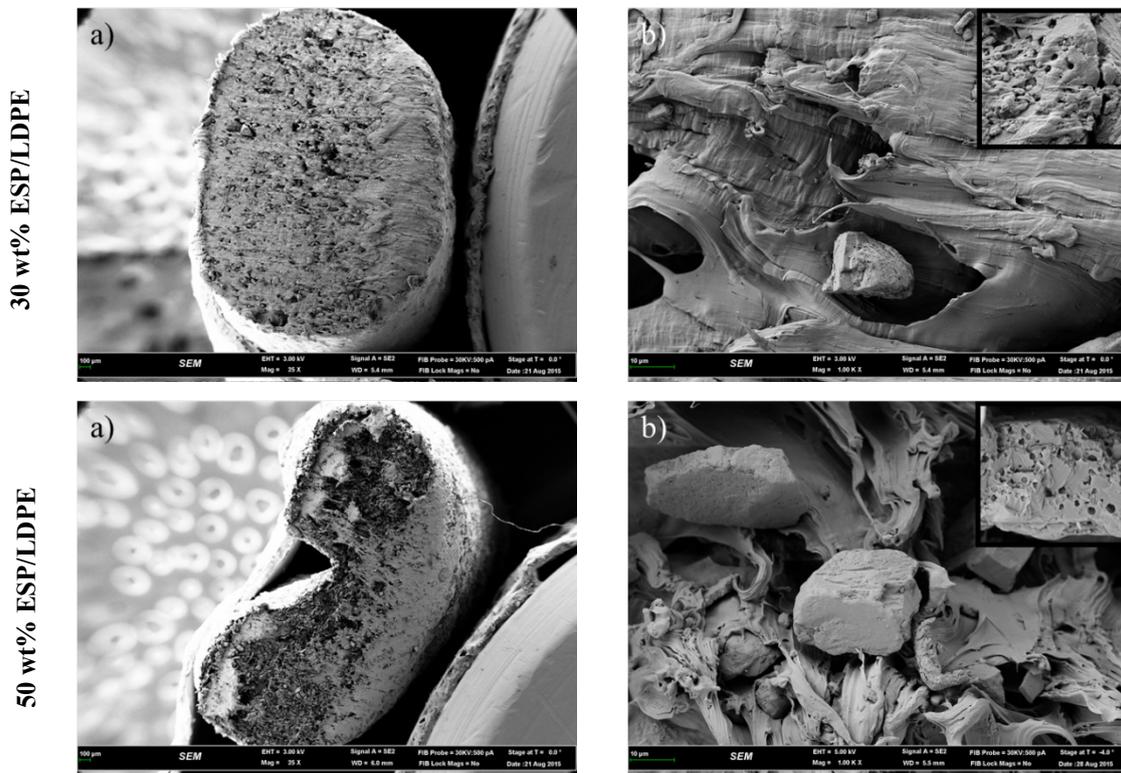
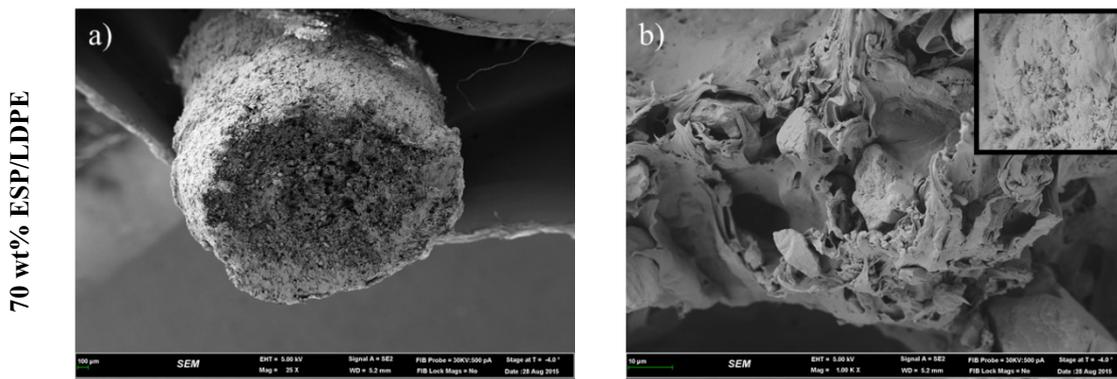


Figure 3 SEM micrographs of 45 μm ESP at magnifications of a) 100x and b) 5,000x.





**Figure 4** SEM micrographs of ESP/LDPE composites containing 45  $\mu\text{m}$  ESP with concentrations of 30, 50, and 70 wt% (from top to bottom, respectively) at magnifications of a) 25 $\times$ , b) 1,000 $\times$ , and 5,000 $\times$  for the insets.

**Specific surface area, pore size, and pore volume**

The specific surface area, pore size, and pore volume of 45  $\mu\text{m}$  ESP and its composites are shown in **Table 1**. It was clear that the specific surface area of 45  $\mu\text{m}$  ESP was significantly greater than its composites. The large specific surface area (2.32  $\text{m}^2\cdot\text{g}^{-1}$ ) of 45  $\mu\text{m}$  ESP was attributed to its small pore diameter (22.89 nm) as well as the large pore volume ( $13.27\times 10^{-3} \text{ cm}^3\cdot\text{g}^{-1}$ ). The composites of 45  $\mu\text{m}$  ESP and LDPE, however, possessed significantly smaller specific area and pore volume. These were expected due to the fact that firstly, the use of LDPE, a non-porous material, as a binder would unenviably cover the surface area of the ESP and secondly, when comparing adsorbents at the same amount, the ESP/LDPE composite containing less porous ESP and more non-porous LDPE unsurprisingly possessed lower specific area and pore volume as compared to ESP. This finding agrees well with the morphology observation using SEM, reported in the previous section. As the ESP content increased, the specific surface area and pore volume increased. The maximum specific area of 0.71  $\text{m}^2\cdot\text{g}^{-1}$  was obtained in 70 wt% ESP/LDPE which was approximately 3 times smaller than that of 45  $\mu\text{m}$  ESP. The pore sizes of the composites were significantly larger than that of 45  $\mu\text{m}$  ESP. The larger pore sizes of the composites were accounted for the size of the natural pores of eggshell but more importantly the size of the voids between the ESP and LDPE matrix. The pore sizes of the composites could be classified as macropores ( $d > 50 \text{ nm}$ ) whereas the pore size of 45  $\mu\text{m}$  ESP could be classified as mesopores ( $2 \text{ nm} < d < 50 \text{ nm}$ ) [14]. These pore sizes and characteristics could affect the flow of a liquid through a porous material.

**Table 1** Specific surface area and pore size of ESP and ESP/LDPE composite pellet.

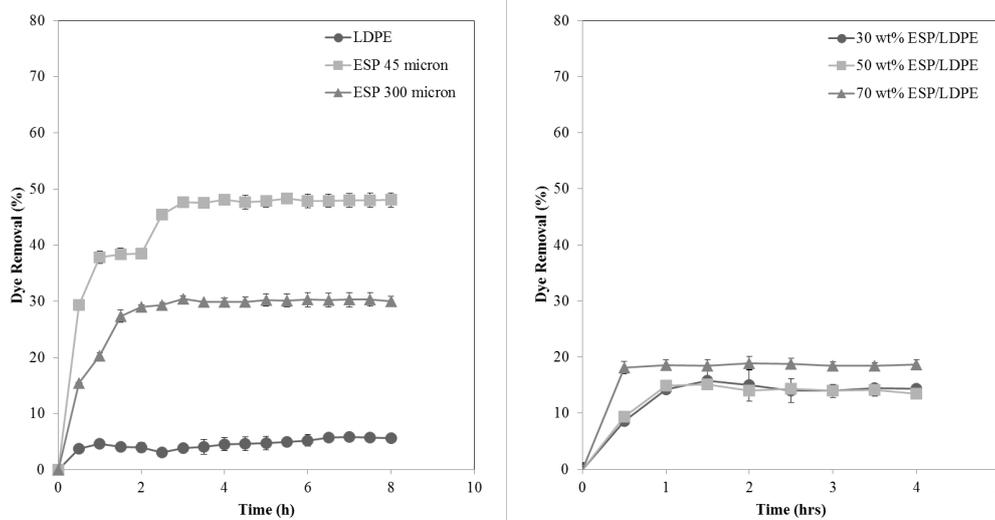
Adsorbent	Specific surface area ( $\text{m}^2\cdot\text{g}^{-1}$ )	Average pore diameter ( $d$ , nm)	Pore volume ( $\text{cm}^3\cdot\text{g}^{-1}$ )
100 ESP (45 $\mu\text{m}$ )	2.32	22.89	$13.27\times 10^{-3}$
70:30 ESP/LDPE	0.71	51.08	$9.01\times 10^{-3}$
50:50 ESP/LDPE	0.66	54.93	$9.12\times 10^{-3}$
30:70 ESP/LDPE	0.42	76.48	$7.96\times 10^{-3}$

### Adsorption studies

#### Effect of contact time and ESP content of the ESP/LDPE composites

Neat LDPE, ESP with 2 different particles sizes i.e. 45 and 300  $\mu\text{m}$  were investigated for their dye removal efficiency over a period of 8 h. The adsorbent dose was 1 g to 50 mL of 10  $\text{mg.L}^{-1}$  acid yellow 137 dye solution. The results are depicted in **Figure 5** (Left). It was found that the dye removal efficiency increased as a function of contact time. For ESP, both 45 and 300  $\mu\text{m}$ , a rapid dye adsorption took place in the first hour and then the adsorption rate decreased gradually in the second and the third hour. The adsorption process which finally reached equilibrium within 4 h when no change in removal efficiency was observed. Similar changes in adsorption rate over time of ESP has been reported by others [3,8,9]. The fast adsorption in the early stage of ESP as compared to LDPE indicated a strong adsorption interaction between the positive charge on the surface of ESP and the acid (anionic) dye compound [9]. The higher dye removal at equilibrium of 45  $\mu\text{m}$  ESP (50 %) as compared to that of 300  $\mu\text{m}$  ESP (30 %) was plausibly due to the larger surface area of the smaller particle size of ESP [15]. LDPE showed the lowest dye removal efficiency of 6 % at equilibrium. This was due to the fact that LDPE is an inert and non-porous material. Since 45  $\mu\text{m}$  ESP possessed greater dye removal efficiency, it was selected to be used as a component in the ESP/LDPE composite for the rest of the study.

Effect of contact time on dye removal efficiency of ESP/LDPE composites is illustrated in **Figure 5** (Right). Again, the dye removal increased as a function of contact time. A rapid adsorption in the early stage of adsorption process was also observed which was most pronounced in the case of 70 wt% ESP/LDPE. The maximum dye removal (18 %) was found in the ESP/LDPE composite containing 70 wt% of 45  $\mu\text{m}$  ESP, clearly lower than that of 45  $\mu\text{m}$  ESP. This was due to the fact that 1) the LDPE matrix, a poor dye adsorbent, presenting in the composite hindered the contact between the ESP surface and the dye in solution and 2) the ESP content, the main adsorbent, was lower in the ESP/LDPE composite.



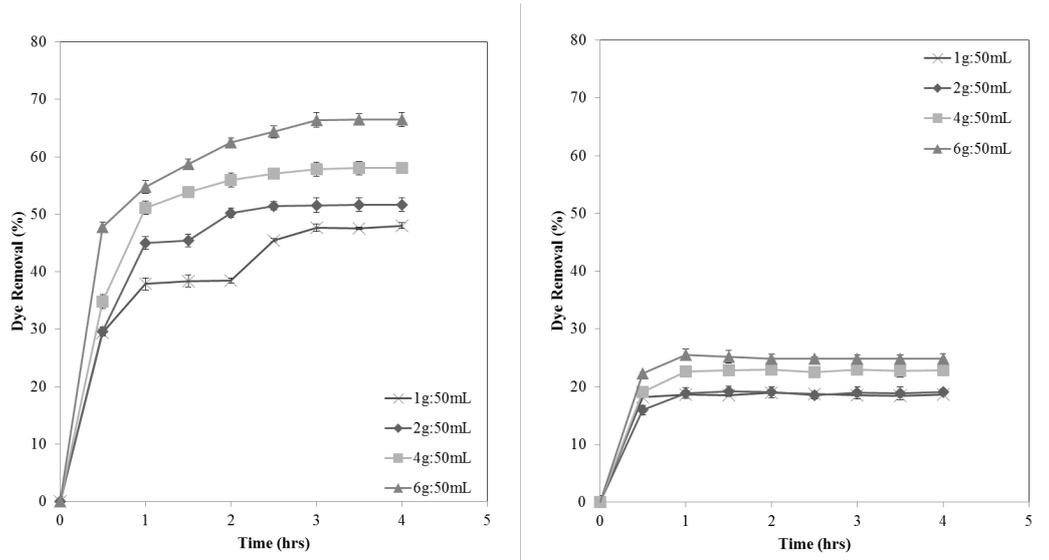
**Figure 5** Effect of contact time of (Left) neat LDPE, 45  $\mu\text{m}$  ESP, and 300  $\mu\text{m}$  ESP and (Right) ESP content in ESP/LDPE composites on acid yellow 137 removal (adsorbent dose 1.0 g in 50 mL of 10  $\text{mg.L}^{-1}$  acid yellow 137 aqueous solution).

### Effect of adsorbent dosage

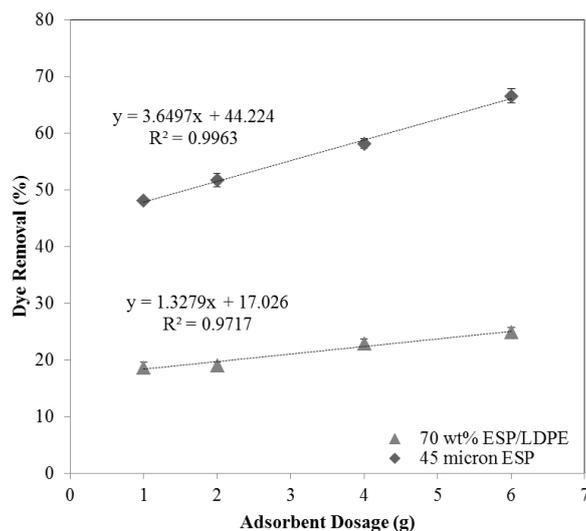
Various doses, ranging from 1.0 to 6.0 g, of 45  $\mu\text{m}$  ESP and 70 wt% ESP/LDPE composite were investigated for the effect of adsorbent dosage on the dye removal efficiency. The acid yellow 137 dye solution with a constant concentration of 10  $\text{mg}\cdot\text{L}^{-1}$  used. An initial rapid adsorption was found in all dosage of all adsorbent as shown in **Figure 6**. The dye removal increased as a function of contact time. The higher dose showed greater removal due to the greater availability of the surface area and adsorption sites [6]. It should be noted that as ESP dosage increased, it became more difficult to separate the fine particles from the dye solution. The centrifugation time was increased from 5 to 20 min to ensure that a clear aliquot was obtained. This was not an issue for the composite sample. The ESP/LDPE composite pellets usually settled at the bottom of the test tube and were very easy to separate from the dye solution. The ease of separation can imply that the composite in pellet form may beneficially improve adsorbent recovery after utilization in an actual waste water treatment process.

**Figure 7** shows the comparison of dye removal efficiency at equilibrium of ESP and 70 wt% ESP/LDPE composite at different adsorbent doses. The dye removal efficiency of ESP was approximately 2.6 times greater than that of 70 wt% ESP/LDPE at all dosages. Simply increasing the dose of 70 wt% ESP/LDPE composite to match the ESP dose does not yield the same dye removal efficiency. To be specific, 6.0 g of 70 wt% ESP/LDPE composite containing approximately 4 g of ESP showed a removal efficiency of 25 %, which was far lower than that of 4 g of 45  $\mu\text{m}$  ESP at 67 %. This was plausibly due to the lower specific surface area of the composite attributed from LDPE coverage over ESP. An increase in surface area of ESP/LDPE composite may help improve its adsorption efficiency. Foams of ESP/LDPE composites have been produced to increase the surface area of the composite and their dye adsorption efficiencies are currently under investigation.

**Figures 6** and **7** showed that dye removal efficiency increased as a function of adsorbent dosage. It can be safely assumed that the dye removal can be efficiently improved by increasing the adsorbent dosage. It should also be noted that the composite at all dosages took a shorter time to reach adsorption equilibrium as compared to the ESP. This could imply that adsorption sites on the composite might have reached its limit, in other words, all the adsorption sites on the composite were occupied by the adsorbed dye molecules and no further adsorption could take place. The adsorbent dosage is a critical parameter which must be carefully optimized so that the maximum removal efficiency can be achieved. In the case of ESP/LDPE composite to become efficient, the dose may need to be increased at least 10 times higher than the dose used in the study.



**Figure 6** Effect of adsorbent dosage of (Left) 45 µm ESP and (Right) 70 wt% ESP/LDPE composite on acid yellow 137 removal (adsorbent dose varied from 1.0 - 6.0 g in 50 mL of 10 mg.L<sup>-1</sup> acid yellow 137 aqueous solution).



**Figure 7** Effect of adsorbent dosage of 45 µm ESP and 70 wt% ESP/LDPE composite on acid yellow 137 removal at equilibrium (adsorbent dose 1.0 g in 50 mL of 10 mg.L<sup>-1</sup> acid yellow 137 aqueous solution, contact time of 4 h).

**Effect of adsorbent dosage on adsorption kinetics**

The effect of the adsorbent loading on the process kinetics was investigated. **Table 2** summarizes the parameters obtained from fitting the experimental data with a pseudo-second-order equation. The high correlation coefficients ( $R^2$ ) ranging from 0.9943 - 0.9986 show the applicability of pseudo-second-order equation for interpretation of the experimental data. In the case of ESP, the pseudo-second-order rate

constant  $k_2$  and theoretical adsorption capacity  $q_e$  increased with an increase in adsorbent loading used. The trends indicated that a greater surface area i.e. the available adsorption sites increased as the amount of ESP increased. The results also implied that the adsorbent loadings (2.0 to 6.0 g) were deficient for the amount of dye used (50 mL of 10 mg.L<sup>-1</sup>). In the case of 70 wt% ESP/LDPE composite, the pseudo-second-order rate constant  $k_2$  also increased with adsorbent loading used. The even greater rate constants of the composite than that of ESP may imply an even greater deficiency of adsorbent in the system as the amount of the effective adsorbent material ESP was lower in the composite. As the composite loading increased, the theoretical adsorption capacity  $q_e$ , decreased and was significantly lower than that of ESP. This trend agrees well with the results from the adsorption study and confirmed our hypothesis of the decrease of adsorbing area due to the LDPE coverage in the previous section.

**Table 2** Effect of adsorbent type and loading on kinetic parameters for the acid yellow 137 removal.

Adsorbent loading (g)	ESP			70 wt% ESP/LDPE composite		
	$k_2$ (g.mg <sup>-1</sup> .min <sup>-1</sup> )	$q_e$ (mg.g <sup>-1</sup> )	$R^2$	$k_2$ (g.mg <sup>-1</sup> .min <sup>-1</sup> )	$q_e$ (mg.g <sup>-1</sup> )	$R^2$
2	0.0067	5.6948	0.9943	0.5235	0.1982	0.9981
4	0.0077	6.1463	0.9965	0.9262	0.1186	0.9976
6	0.0081	6.7385	0.9986	2.3005	0.0834	0.9970

### Conclusions

Fine ESP was efficiently prepared using a domestic coffee grinder. The smallest ESP was 45 μm that showed a significantly greater dye removal efficiency than that of 300 μm, which was the highest yield particle size of ESP from the grinding process. Various high loading (45 μm) ESP/low density polyethylene composites were successfully prepared using a 2-step melt mixing method and the highest loading was 70 wt% ESP. The acid yellow 137 dye removal efficiency of the 30, 50 and 70 wt % ESP/LDPE composites were investigated and compared to neat LDPE and ESP. Batch adsorption experiments were performed to study the effects of contact time, type of adsorbent and adsorbent dosage. The equilibrium time of dye adsorption was 4 h. The 70 wt% ESP/LDPE composite showed the highest dye removal efficiency of 25 % when the highest dose was used (6.0 g in 50 mL dye solution). The process kinetics of both ESP and its composite were found to follow a pseudo-second order rate equation. The dye removal efficiency of the 45 μm ESP was higher than that of its composite; however it was difficult to separate from the dye solution. The pellet form of the composite adsorbent was preferable because of the ease of use and handling.

### Acknowledgements

The authors would like to thank School of Polymer Engineering and The Center for Scientific and Technological Equipment at Suranaree University of Technology for technical supports.

## References

- [1] MR Fathi, A Asfaram, A Hadipour and M Roosta. Kinetics and thermodynamic studies for removal of acid blue 129 from aqueous solution by almond shell. *J. Environ. Health Sci. Eng.* 2014; **12**, 1-7.
- [2] M Arami, NY Limaee, NM Mahmoodi and NS Tabrizi. Removal of dyes from colored textile wastewater by orange peel adsorbent: Equilibrium and kinetic studies. *J. Colloid Interface Sci.* 2005; **288**, 371-6.
- [3] M Arami, NY Limaee and NM Mahmoodi. Evaluation of the adsorption kinetics and equilibrium for the potential removal of acid dyes using a biosorbent. *Chem. Eng. J.* 2008; **139**, 2-10.
- [4] M Ahmaruzzaman. Adsorption of phenolic compounds on low-cost adsorbents: A review. *Adv. J. Colloid Interface Sci.* 2008; **143**, 48-67.
- [5] SJT Pollard, GD Fowler, CJ Sollars and R Perry. Low-cost adsorbents for waste and wastewater treatment: A review. *Sci. Total Environ.* 1992; **116**, 31-5.
- [6] M Ahmaruzzaman and SL Gayatri. Batch adsorption of 4-nitrophenol by acid activated jute stick char: Equilibrium, kinetic and thermodynamic studies. *Chem. Eng. J.* 2010; **158**, 173-18.
- [7] R Sivaraj, C Namasivayam and K Kadirvelu. Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions. *Waste Manag.* 2001; **21**, 105-10.
- [8] IA Oke, NO Olarinoye and SRA Adewusi. Adsorption kinetics for arsenic removal from aqueous solutions by untreated powdered eggshell. *Adsorption* 2008; **14**, 73-83.
- [9] WT Tsai, KJ Hsien, HC Hsu, CM Lin, KY Lin and CH Chiu. Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution. *Bioresource Technol.* 2008; **99**, 1623-9.
- [10] WT Tsai, JM Yang, CW Lai, YH Cheng, CC Lin and CW Yeh. Characterization and adsorption properties of eggshells and eggshell membrane. *Bioresource Technol.* 2006; **97**, 488-93.
- [11] SE Kuh and DS Kim. Removal characteristics of cadmium ion by waste eggshell. *Environ. Tech.* 2000; **21**, 883-90.
- [12] MA Zulfikar, ED Mariske and SD Djajanti. Adsorption of lignosulfonate compounds using powdered eggshell. *Songklanakar J. Sci. Tech.* 2012; **34**, 309-16.
- [13] Agricultural Statistics of Thailand 2014. *The Office of Agricultural Economics*. Thailand Ministry of Agriculture and Cooperatives, 2015.
- [14] J Rouquerol, D Avnir, CW Fairbridge, DH Everett, JM Haynes, N Pernicone, JDF Ramsay, KSW Sing and KK Unger. Recommendations for the characterization of porous solids. *Pure Appl. Chem.* 1994; **66**, 1739-58.
- [15] M Arami, NY Limaee and NM Mahmoodi. Investigation on the adsorption capability of egg shell membrane towards model textile dyes. *Chemosphere* 2006; **65**, 1999-2008.