Characterization of Activated Carbon from Eggshell Membranes Prepared Using Sodium Acetate and Zinc Metal Activation

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Abstract: The eggshell membranes of ducks and hens were carbonized or activated with 4 wt% sodium acetate or zinc at 400-600°C. The carbonized or activated products were characterized by SEM-EDS, TEM, FTIR and XRD. It was found that the suitable activation temperature for eggshell membranes is 500°C with 30.03-35.26% yield. The activation performance of CH$_3$COONa for eggshell membrane activated carbon production was higher than that of Zn metal. The CO$_3^{2-}$, Ca-O, C=C, Na-O and C-O functional groups have been formed on the surface of eggshell membrane activated carbon materials during both CH$_3$COONa and Zn activation. Furthermore, CaO, MgO, Na$_2$O and ZnO have also accumulated on eggshell membrane activated carbon materials with high content and regular dispersion. It was shown that the particles on the duck eggshell membrane activated carbon formed with Zn had weaker attachment on the surface than for duck eggshell membrane activated carbon formed with CH$_3$COONa at same temperature. The XRD and TEM results revealed that the eggshell membrane activated carbons consist of an amorphous carbon matrix with some disordered graphite carbon matrix, spherical particles and nanofiber.

Keywords: Eggshell Membrane, Activated Carbon, Sodium Acetate, Zinc

Introduction

Large quantities of egg waste are discarded worldwide. They consist of egg shells and Eggshell Membranes (ESM) (Mittal et al., 2016). The ESM resides between the egg white and the inner surface of the eggshell (Tsai et al., 2006). The Hen Eggshell Membrane (HESM) consists of interwoven protein fibers and spherical masses (Tsai et al., 2008). The duck egg contains about 11% eggshell and ESM. It also consists of an inner and an outer membrane with entangled threads or randomly knitted net shapes. The diameter of ESM fiber is less than 0.2 µm (Kaewmanee et al., 2009). Furthermore, ESM also consists of yolk spherocrystal with diameter of about 30 µm (Tong et al., 2008). The ESM possess a porous and fibril structure, with a very high surface area and special functional groups such as hydroxyl (-OH), thiol (-SH), carboxyl (-COOH), amino (-NH$_2$), amide (-CONH$_2$) etc., which strongly interact with various chemical species (Mittal et al., 2016). The protein fibers of ESM are arranged to form a semi-permeable membrane which possesses an intricate lattice of hierarchically ordered macroporous network of stable and water-insoluble fibers, which also has high surface area (Tsai et al., 2006). It has a high decomposition temperature (>220 °C), enough mechanical strength and low water uptake and swelling properties (<10%) (Yu et al., 2012) resulting its use in various applications such as adsorbents (Tsai et al., 2006). The ESM has also been used for adsorption of chlorinated phenols, Direct Red 80 and Acid Blue 25, from aqueous solutions (Guru and Dash, 2014). Since ESM is a highly cross-linked protein structure with excellent permeability to substrates and products (Tembe et al., 2008), it has been used as the substrate and template to immobilize the layered double hydroxide formed by hydrothermal crystallization method and used as adsorbent for Cr(VI) adsorption (Guo et al., 2011). It has been activated by glutaraldehyde for the immobilization of the enzyme tyrosinase achieved with high effectiveness (Tembe et al., 2008). In general, porous carbon composites containing different metals such as Fe, Co, Pt, Ag, Ni, Sn, Mn, etc. and their species have been synthesized to be used in electrochemical, catalytic, adsorption and other applications.
applications. Metals and metal oxides in these composites can strongly affect the structural, textural and other characteristics of the materials (Gun’ko et al., 2014). For example, activated carbon from coconut shells has been modified with 10-15% sodium acetate and used in a fixed-bed column for copper ions removal. The authors have shown that the material could adsorb 33-45 mg of Cu with Cu(II): Na ratio of 3.85 mol: 7.54 mol (Mugisidi et al., 2007). Zinc acetate has been used as a catalyst for polycondensation and polymer carbonization of resorcinol-formaldehyde mixtures. The mixtures were carbonized at 780-800°C to form ZnO doped chars. The texture of the doped chars depends strongly on the content of ZnO. The chars can be purely nanoporous and composed of micro sized smooth globules with low ZnO content, or composed of nano-mesoporous particles of 20-100 nm in size with high ZnO content, or differently aggregated into secondary meso-macroporous structures (Gun’ko et al., 2014). ZnO micro/nano materials were also hydrothermally grown on activated carbon cloth and used as electrodes in a flow cell for brackish water desalination by capacitive deionization (Myint et al., 2014). In addition, the nano ZnO/activated carbon composite has been used for tributyltin removal from seawater (Ayanda et al., 2013).

This research studied the effect of activation agents (5wt% of sodium acetate or zinc metal) and pyrolysis temperature (400-600°C) on the preparation of carbonized and activated carbon products from duck and hen eggshell membranes. The products were characterized by FTIR, XRD, SEM-EDS and TEM. The percent yields of carbonized products and activated carbons are also calculated.

Materials and Methods

The eggshell wastes of hen and duck were obtained from local households and were washed with deionized water. The ESMs were then manually removed from outer eggshells and dried in oven (SL shellab, 1350 FX, USA) at 120°C for 3 h. The dried ESMs were then carbonized at 780-800°C to form ZnO doped chars. The texture of the doped chars depends strongly on the content of ZnO. The chars can be purely nanoporous and composed of micro sized smooth globules with low ZnO content, or composed of nano-mesoporous particles of 20-100 nm in size with high ZnO content, or differently aggregated into secondary meso-macroporous structures (Gun’ko et al., 2014). ZnO micro/nano materials were also hydrothermally grown on activated carbon cloth and used as electrodes in a flow cell for brackish water desalination by capacitive deionization (Myint et al., 2014). In addition, the nano ZnO/activated carbon composite has been used for tributyltin removal from seawater (Ayanda et al., 2013).

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Characterizations

The morphological structure and elemental composition of the dried ESMs, Carbonized Eggshell Membranes (CESMs) and Eggshell Membranes Activated Carbons (ESMACs) were observed and photographed by Scanning Electron Microscopy equipped with Energy Dispersive Spectrometer (SEM-EDS, LEO 1455 VP). The CESMs and ESMACs were also characterized by X-ray powder diffract meter (PW 3040/60, X’ Pert Pro MPD), FTIR (Spectrum GX, Perkin Elmer) and TEM (PHILPS, Tecnai 12).

Results and Discussion

Percent Yield

Data in Table 1 show that the percent yields of all products decrease with increase in carbonization or activation temperature. This indicates that the volatile matters such as proteins, carbohydrates and lipids (Ahmed et al., 2017), in ESMs were degraded to a higher extent at higher temperatures. Furthermore, it was seen that all products from Duck Eggshell Membrane (DESM) give higher percent yields than products made from Hen Eggshell Membrane (HESM) made at the same conditions. This may be attributed to CaCO₃ and other metal compounds, which show higher content in DESM which than in HESM. The egg shell membranes were decomposed into CaO and other metal oxides with high content of carbonized or activated products (Table 2). Another reason may be the protein content (80-85%) of HESM (Baláž, 2014), which is higher than that of DESM. Thus, the HESM undergoes more substantial thermal degradation than DESM. Furthermore, percent yield of all products decreased at a relatively low rate from 400 to 500°C, but a higher rate from 500 to 600°C for both ESMs. This is attributed to the thermal degradation of collagen and glycan chains in the ESMs with a slow rate in the temperature range between 250 and 450°C and then with a high mass loss rate at 500-600°C (Baláž, 2014; Yu et al., 2012). Additionally, it was found that the percent yields of activated products from both ESMs formed after mixing with 5wt% of CH₃COONa or Zn metal powder decreased more substantially than CESMs at all temperatures. This shows that both CH₃COONa and Zn metal result in higher rate of decomposition of ESMs by partial oxidation in comparison to the carbonization process. The percent yields of ESMACs formed in procedures using mixing with Zn metal are higher than those formed using mixing with CH₃COONa at same temperature. This result is attributed to poor solubilities of ZnO in the reaction mixtures (Simanjuntak et al., 2011) and high thermal degradation of CH₃COONa.
The FTIR spectra of the Carbonized Duck Eggshell Membrane (CDESM) and Duck Eggshell Membrane Activated Carbon (DESMAC) prepared at 400, 500, and 600°C are shown in Fig. 1. Figure 1a shows that the FTIR spectrum of CDESM prepared at 400°C contains peaks at 3367 cm⁻¹ (N-H bonds or C-O asymmetric stretching), 2919 cm⁻¹ (C-H bonds in = C-H and = CH₂ groups), 1760 cm⁻¹ (C=O stretching vibration in carboxylic groups), 1650 cm⁻¹ (amide C=O stretching), 1431 cm⁻¹ (CaO, C=C) and 712 cm⁻¹ (CO₁⁻ of calcite) (Mami et al., 2008; Baláž et al., 2016; Tan et al., 2015; Botomé et al., 2017; Zaki et al., 2006). It contains features that can be attributed to amines, amides, CaCO₃ = C-H and =CH₂, which remained in CDESM after preparation at 400°C. Especially, carboxylate CO₁⁻ of CaCO₃ is still not completely decomposed after preparation at 400°C, as demonstrated by FTIR peaks at 3367, 1431 and 712 cm⁻¹ of C-O asymmetric stretching and out of plane bending vibration modes (Tan et al., 2015). The peaks indicating the presence of amines and amides in the ESMs are also located at 3367 cm⁻¹ with an additional peak at 1650 cm⁻¹ (Tsai et al., 2006). Thus, the organic components of ESMs are not completely decomposed after the carbonization process carried out at 400°C. This result is in accord with the percent yields of CESMs at 400°C (Table 1), which are lower than those at 500-600°C. These FTIR peaks of DESM disappeared after carbonization at 500-600°C with the exception of the peak at 1431 cm⁻¹. This confirms that the functional groups on surface of the carbon material were burnt off to a large extent after the carbonization at these temperatures. This results in the decrease of the percent yield of carbonized products as well as the activated products (Table 1). The peak at 1431 cm⁻¹ is attributed to CaO (Zaki et al., 2006), as well as C=C stretching of aromatic rings (Nasrollahzadeh et al., 2016). A new peak is observed in CDESM after carbonization at 500-600 °C at 712 cm⁻¹ (very weak). This peak can be attributed to calcite, which is formed by heating at 500°C and is more crystalline than the initial calcium carbonates (López Granados et al., 2007). Materials prepared with CH₃COONa activation (CH₃COONa-DESMACs, Fig. 1d-f) show FTIR spectra with peaks similar to the CDESM, but intensity of these peaks tends to be lower than for CDESM. The intensity of the peaks also decreases with increasing temperature from 400 to 600°C. Especially, the spectrum of CH₃COONaDESMAC prepared at 600°C (Fig. 1f) shows peaks only at 1431 cm⁻¹ (strong) and 875 cm⁻¹ (very weak) which are due to CO₁⁻ species of calcite (Zaki et al., 2006). At 400-500°C, the FTIR spectra of CH₃COONaDESMACs also contain peaks at 1110 cm⁻¹, which are attributed to C-O and C-N (Baláž, 2014; Park et al., 2016). Analogously, FTIR spectra of Zn-DESMAC (Fig. 1g-i) contain peaks similar to CH₃COONa-DESMAC, with the exception of the spectrum of the material prepared at 400°C (Fig. 1g). The spectrum of Zn-DESMAC prepared at 400°C also contains peaks at 3367 cm⁻¹, 2919, 1700, 1600, 1431, 1350 cm⁻¹ (C-OH, Kashinath et al., 2016) and 1110 cm⁻¹. These peaks also disappeared after activation at 500 and 600°C (Fig. 1h-i) where the remaining of peaks are found at 1431, 875 and 720 cm⁻¹. These peaks remaining after activation at 600°C are also attributed to CO₁⁻ of calcite. It should be noted that calcite is usually completely decomposed into CaO above 700°C (Zaki et al., 2006). However, the peaks of C=C, Na-O and C-O stretching (Magdziarz et al., 2016) are also located at 1431 cm⁻¹, which has caused the peak at 1431 cm⁻¹ to remain with high intensity for all activated

<table>
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<th>Mg</th>
<th>Ca</th>
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FTIR Analysis

The FTIR spectra of the Carbonized Duck Eggshell Membrane (CDESM) and Duck Eggshell Membrane Activated Carbon (DESMAC) prepared at 400, 500, and 600°C are shown in Fig. 1. Figure 1a shows that the FTIR spectrum of CDESM prepared at 400°C contains peaks at 3367 cm⁻¹ (N-H bonds or C-O asymmetric stretching), 2919 cm⁻¹ (C-H bonds in = C-H and = CH₂ groups), 1760 cm⁻¹ (C=O stretching vibration in carboxylic groups), 1650 cm⁻¹ (amide C=O stretching), 1431 cm⁻¹ (CaO, C=C) and 712 cm⁻¹ (CO₁⁻ of calcite) (Mami et al., 2008; Baláž et al., 2016; Tan et al., 2015; Botomé et al., 2017; Zaki et al., 2006). It contains features that can be attributed to amines, amides, CaCO₃ = C-H and =CH₂, which remained in CDESM after preparation at 400°C. Especially, carboxylate CO₁⁻ of CaCO₃ is still not completely decomposed after preparation at 400°C, as demonstrated by FTIR peaks at 3367, 1431 and 712 cm⁻¹ of C-O asymmetric stretching and out of plane bending vibration modes (Tan et al., 2015). The peaks indicating the presence of amines and amides in the ESMs are also located at 3367 cm⁻¹ with an additional peak at 1650 cm⁻¹ (Tsai et al., 2006). Thus, the organic components of ESMs are not completely decomposed after the carbonization process carried out at 400°C. This result is in accord with the percent yields of CESMs at 400°C (Table 1), which are lower than those at 500-600°C. These FTIR peaks of DESM disappeared after carbonization at 500-600°C with the exception of the peak at 1431 cm⁻¹. This confirms that the functional groups on surface of the carbon material were burnt off to a large extent after the carbonization at these temperatures. This results in the decrease of the percent yield of carbonized products as well as the activated products (Table 1). The peak at 1431 cm⁻¹ is attributed to CaO (Zaki et al., 2006), as well as C=C stretching of aromatic rings (Nasrollahzadeh et al., 2016). A new peak is observed in CDESM after carbonization at 500-600 °C at 712 cm⁻¹ (very weak). This peak can be attributed to calcite, which is formed by heating at 500°C and is more crystalline than the initial calcium carbonates (López Granados et al., 2007). Materials prepared with CH₃COONa activation (CH₃COONa-DESMACs, Fig. 1d-f) show FTIR spectra with peaks similar to the CDESM, but intensity of these peaks tends to be lower than for CDESM. The intensity of the peaks also decreases with increasing temperature from 400 to 600°C. Especially, the spectrum of CH₃COONaDESMAC prepared at 600°C (Fig. 1f) shows peaks only at 1431 cm⁻¹ (strong) and 875 cm⁻¹ (very weak) which are due to CO₁⁻ species of calcite (Zaki et al., 2006). At 400-500°C, the FTIR spectra of CH₃COONaDESMACs also contain peaks at 1110 cm⁻¹, which are attributed to C-O and C-N (Baláž, 2014; Park et al., 2016). Analogously, FTIR spectra of Zn-DESMAC (Fig. 1g-i) contain peaks similar to CH₃COONa-DESMAC, with the exception of the spectrum of the material prepared at 400°C (Fig. 1g). The spectrum of Zn-DESMAC prepared at 400°C also contains peaks at 3367 cm⁻¹, 2919, 1700, 1600, 1431, 1350 cm⁻¹ (C-OH, Kashinath et al., 2016) and 1110 cm⁻¹. These peaks also disappeared after activation at 500 and 600°C (Fig. 1h-i) where the remaining of peaks are found at 1431, 875 and 720 cm⁻¹. These peaks remaining after activation at 600°C are also attributed to CO₁⁻ of calcite. It should be noted that calcite is usually completely decomposed into CaO above 700°C (Zaki et al., 2006). However, the peaks of C=C, Na-O and C-O stretching (Magdziarz et al., 2016) are also located at 1431 cm⁻¹, which has caused the peak at 1431 cm⁻¹ to remain with high intensity for all activated
The FTIR spectra of CHESMs (Fig. 2a-c), CH\textsubscript{3}COONa-HESMACs (Fig. 2d-f) and Zn-HESMACs (Fig. 2g-i) show similar trends to the FTIR spectra of corresponding DESM materials. The analysis of the FTIR spectra revealed that the CH\textsubscript{3}COONa and Zn activations have no effect on the type of functional groups found on activated carbon products made both from DESM and HESM, but they accelerated the decomposition or modification of functional groups on surface of ESMACs. Based on the FTIR results, it can be concluded that the suitable activation temperature for the preparation of ESMs lies in the range 500-600°C, which is in line with the report of Rath et al. (2014).

Elements Analysis by EDS

The elemental composition of CH\textsubscript{3}COONa-DESMAC, Zn-DESMAC, CH\textsubscript{3}COONa-HESMAC and Zn-HESMAC prepared at 600°C, was obtained using EDS analysis. The results are shown in Table 2 and they indicate high carbon content in all of the materials. These results confirm that the ESMs have been converted into carbon during the activation process. Moreover, it can be seen that the carbon content in HESMACs for both activation reagents is higher than that of the DESMACs. This is because HESM has higher content of organic compounds than DESM, which are converted to carbon during high temperature degradation under partial oxidation conditions. Furthermore, it can be seen that CH\textsubscript{3}COONa-DESMAC and Zn-DESMAC have higher metal content than CH\textsubscript{3}COONa-HESMAC and Zn-HESMAC which is in line with results of percent yield reported in Table 1. The oxygen content of all activated carbon materials is quite high, indicating high content of oxygen containing functional groups and metals oxides on surface of the activated carbon materials. Especially, oxygen content in CH\textsubscript{3}COONa-DESMAC is very high (27.26%), which could in part originate from the CH\textsubscript{3}COONa activating agent. Calcium shows higher content in activated carbon materials from DESM than those from HESM. These results are also in line with the FTIR results (Fig. 1 and 2). The content of Na in CH\textsubscript{3}COONa-DESMAc and CH\textsubscript{3}COONa-HESMAC and Zn in Zn-DESMAc and Zn-HESMAC are quite high. This is because of the CH\textsubscript{3}COONa and Zn that were added to the ESMs for activation, which contain Na and Zn that remain in the activated products. The Mg present in the final materials originated from starting ESMs.

XRD Analysis

The XRD patterns of carbonized and activated products made from DESM and HESM display a peak at 20 = 25.5°, which is assigned as the crystallographic planes of graphitic layers with disordered graphite carbon structure (Fig. 3a-f). In addition, a weak peak located at 44° is attributed to amorphous carbon (Pant et al., 2017). These results confirm that the organic materials originally present in the ESMs have been converted into carbon for all produced materials thus supporting the high carbon content of carbonized and activated products as shown in Table 2. Furthermore, the XRD patterns also show crystalline peaks of calcite, which remained in final products after carbonization or activation, at 20 = 23, 29.5, 34.2, 36, 39.5, 43.2, 48.5, 57.5, 60.5, 63, 64.5, 72 and 81.5° (Slimani et al., 2014).

Fig. 1. FTIR transmittance spectra of (a) CDESM prepared at 400°C, (b) CDESM prepared at 500°C, (c) CDESM prepared at 600°C, (d) CH\textsubscript{3}COONa-DESMAc prepared at 400°C, (e) CH\textsubscript{3}COONa-DESMAc prepared at 500°C, (f) CH\textsubscript{3}COONa-DESMAc prepared at 600°C, (g) Zn-DESMAc prepared at 400°C, (h) Zn-DESMAc prepared at 500°C and (i) Zn-DESMAc prepared at 600°C
Fig. 2. FTIR transmittance spectra of (a) CHESM prepared at 400°C, (b) CHESM prepared at 500°C, (c) CHESM prepared at 600°C, (d) CH$_3$COONa-HESMAC prepared at 400°C, (e) CH$_3$COONa-HESMAC prepared at 500°C, (f) CH$_3$COONa-HESMAC prepared at 600°C, (g) Zn-HESMAC prepared at 400°C, (h) Zn-HESMAC prepared at 500°C and (i) Zn-HESMAC prepared at 600°C.

Fig. 3. XRD patterns of (a) CDES, (b) CH$_3$COONa-DESMA, (c) Zn-DESMA, (d) CHESM, (e) CH$_3$COONa-HESMAC and (f) Zn-HESMAC prepared at 600°C.

The XRD peaks at 31.5, 40.5, 50.2, 54 and 57.5° are attributed to CaO (Mohammadi et al., 2014), which was formed from CaCO$_3$ by thermal degradation. XRD peaks of NaO, which formed from CH$_3$COONa by thermal degradation, are located at 32.1 and 47.4° (Magdziarz et al., 2016). The peaks present at 43, 49 and 75° are attributed to MgO, which originated from oxidation of Mg compounds found in the starting ESMs. Finally, the XRD diffraction peaks belonging to ZnO, which originated from oxidation of the Zn metal powder in Zn-DESMA (Fig. 3c) and Zn-HESMAC (Fig. 3f), are located at 20 = 31.7, 34.4, 36.2, 47.5, 56.6, 62.8, 66.3, 67.9 and 69.1° (Kashinath et al., 2016). The intensities of XRD peaks of NaO and ZnO in the activated products are higher after CH$_3$COONa and Zn addition in comparison to products prepared without CH$_3$COONa and Zn additives carbonized. These XRD results correspond to FTIR and EDS data presented in Fig. 1 and 2 and Table 2.

**SEM Analysis**

The SEM images of the fresh DESM, CDESs, CH$_3$COONa-DESMAcs and Zn-DESMAcs are shown in Fig. 4. The fresh DESM (Fig. 4a) shows a hierarchically ordered macroporous network and some microporous structures on the surface. After carbonization, the CDESs show a network-like structure with an aggregation of particles on the surface (Fig. 4b-d). The surfaces of CDESs are quite smooth. The amount and size of particles on the surfaces of CDESs decrease as the carbonization temperature is increased.
Fig. 4. Morphologies of (a) fresh DESM, (b) CDESM prepared at 400°C, (c) CDESM prepared at 500°C, (d) CDESM prepared at 600°C, (e) CH$_3$COONa-DESMAC prepared at 400°C, (f) CH$_3$COONa-DESMAC prepared at 500°C, (g) CH$_3$COONa-DESMAC prepared at 600°C, (h) Zn-DESMAC prepared at 400°C, (i) Zn-DESMAC prepared at 500°C and (j) Zn-DESMAC prepared at 600°C.
The size of particles on the surface of CDESMs is 0.27-3.73, 0.09-1.18 and 0.05-1 μm for materials prepared at 400, 500 and 600 °C, respectively. This shows that the volatile compounds in DESM undergo a more extensive thermal degradation as higher carbonization temperatures. The activated products exhibit a more extensive thermal degradation than the CDESMs at same temperature (Fig. 4e-j). The CH₃COONa-DESMACs (Fig. 4e-g) show more open, porous and rough surfaces with spherical particles for activation at 500-600°C. The spherical particles with a diameter of about 90.9 nm are due to sodium oxide. However, the surface of CH₃COONa-DESMAC obtained with activation at 400°C does not show open porous structures. This indicates that the CH₃COONa-DESMAC prepared with activation at 400°C show small extent of degradation and partial oxidation. Furthermore, it was seen that the spherical particles on the surfaces CH₃COONa-DESMAC are firmly attached. This might be due to the fact that CH₃COONa can incorporate with proteins present in the ESMs fibers (Camaratta et al., 2015). The amount of spherical particles and particles with uncertain shape increases as the activation temperature is increased, with especially high content at 600°C. This is because of volatile matters being degraded while Na₂O, CaO and some other metal oxides dominate the surface. Likewise, Zn-DESMACs (Fig. 4h-j) show high thermal degradation in comparison to CDESMs prepared at the same temperature. This result is related to the percent yield data in Table 1. At the activation temperature of 400°C, the smooth and quite clear surface containing only some particles is observed for Zn-DESMAC. However, Zn-DESMACs prepared at 500-600°C show surfaces with higher amounts of particles of various sizes in comparison to the material prepared at 400°C. It can be seen that the particles on Zn-DESMACs surface are attached more weakly than those on the surface of CH₃COONa-DESMACs prepared at the same temperature. This is attributed to low solubility of Zn metal in the reaction mixtures (Simanjuntak et al., 2011). After activation at 600°C the Zn-DESMAC surface shows some disordered graphite carbon matrix (Fig. 5f). Furthermore, it was seen that particles with differing sizes (0.05-4.82 μm) and shapes have accumulated on CH₃COONa-HESMAC at 400°C (Fig. 5e) to a greater extent than to which they formed on the surfaces of CHESMs. As the activation temperature is increased (from 500 to 600°C) a substantial amount of regularly dispersed small sized particles are formed on the surface of the HESMACs (Fig. 5f-g). A small amount of large spherical particles also form on these products. It has been seen that the particles on HESMAC prepared at 600°C (Fig. 5f) became spherical in shape and larger in size (214.9-574.1 nm) in comparison to HESMAC prepared at 500°C (90.9-272 nm in diameter size) (Fig. 5g). However, quite clear and smooth surface with some rough character and particles was observed for Zn-HESMAC prepared at 400°C. Similarly, the high amount of differently sized particles (0.05-1.91 μm) were formed on Zn-HESMAC surface for the material prepared at 500°C (Fig. 5i). Furthermore, the high amount of spherical particles (about 45 nm diameter) with some large particles (0.182-2.091 μm diameter) was also observed on Zn-HESMAC surface for the material prepared at 600°C (Fig. 5j). These results indicated that Na₂O and ZnO accumulated on the surface of HESMACs after activation.

**TEM Analysis**

The TEM images shown in Fig. 6a and e reveal that the CDESM and CHESM prepared at 500°C consist of an amorphous carbon matrix. For material prepared with activation by CH₃COONa (at 500-600°C) and Zn (at 500°C), the TEM images of the activated products show some disordered graphite carbon matrix (Fig. 6b-d and f). Furthermore, it was seen that CH₃COONa-HESMAC prepared at 600°C (Fig. 6g) and Zn-HESMAC prepared at 500°C (Fig. 6h) show an amorphous carbon matrix with spherical particles (diameter of 68-578 nm) and nanofiber (diameter range of 13.51-43.24 nm), respectively. These results are consistent with XRD and SEM results.
Fig. 5. Morphologies of (a) fresh HESM, (b) CHESM prepared at 400°C, (c) CHESM prepared at 500°C, (d) CHESM prepared at 600°C, (e) CH$_3$COONa-HESMAC prepared at 400°C, (f) CH$_3$COONa-HESMAC prepared at 500°C, (g) CH$_3$COONa-HESMAC prepared at 600°C, (h) Zn-HESMAC prepared at 400°C, (i) Zn-HESMAC prepared at 500°C and (j) Zn-HESMAC prepared at 600°C.
Conclusion

It was concluded, based on the experimental results, that the percent yields of all carbonized and activated products have decreased with increasing carbonization or activation temperature. The results also show that all products prepared from DESM have percent yields higher than products prepared from HESM at the same conditions. There was a small relative decrease in the yield between 400 and 500°C followed by a high yield decrease between 500 and 600°C. The percent yields of ESMACs prepared using mixing with Zn metal were higher than those prepared using mixing with CH$_3$COONa at same temperature. The results have shown that some organic functionalities such as amines, amides, CO$_2^-$, = C-H and = CH$_2$ groups still remain in CDESM after preparation at 400°C. It was shown that carboxylate of CaCO$_3$ is still incompletely decomposed after treatment at all activation temperatures. The C=O, Na-O and C-O functional groups were also observed in ESMACs. Furthermore, it was shown that the CH$_3$COONa and Zn activation modes have no effect on the type of functional groups formed on the activated carbon products from both DESM and HESM. However, the additives have accelerated the decomposition or modification of functional groups on the surfaces of ESMACs. EDS analysis has shown that the HESMAC materials are mainly composed of carbon for both activation reagents and that their carbon content is higher than of the corresponding DESMACs. In addition, all activated carbon materials have quite high oxygen content, which is exhibited in high content of oxygen containing functional groups and metals oxide compound on the surfaces of the activated carbon materials. The XRD and TEM results of carbonized and activated products made from DESM and HESM displayed disordered graphite carbon structures and amorphous carbon. XRD patterns of ESMACs also showed crystalline calcite, CaO, MgO, ZnO.
and Na₂O. The TEM images of CH₃COONa-HESMAC prepared at 600°C and Zn-HESMAC prepared at 500°C also show spherical particles (68-578 nm diameter) and nanofibers (13.51-43.24 nm diameter). The SEM morphologies of CDESMs are quite smooth but containing some particles. The amount and size of particles on the surfaces of CDESMs decrease as the carbonization temperature is increased. After activation at 500-600°C, ESMACs showed more open, porous and rough surface with spherical particles of sodium oxide or ZnO. It was seen that the particles on Zn-DESMACs are less firmly attached on the surface than those on CH₃COONa-DESMACs formed at the same activation temperature. Finally, it was also shown that the activation activity of CH₃COONa is stronger than that of Zn metal for ESMACs preparation. The characteristics of ESMACs observed in this study show that ESMACs can be considered for use as adsorbents for the removal the pollutants from water and other applications to achieve low-cost and also reduction of costs for waste disposal.

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Sumrit Mopoung: Designed the research plan, organized the study and wrote of all paragraphs.
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Ethics
This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues are involved.

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