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Research Article
Potassium Permanganate Loaded Activated Carbon Production from Pineapple Leaf at Low Pyrolysis Temperature for Water Hardness Removal

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Abstract

Background and Objective: Generally, the high activation temperature was used for preparation of activated carbon from biomass which results in high energy costs. So in this study, $KMnO_4$ modified carbon material from pineapple leaf by single stage was studied for finding the lowest suitable pyrolysis temperature. **Materials and Methods:** The effects of 0.0-5.0 wt% $KMnO_4$ and pyrolysis temperature of 200-500°C were studied by SEM-EDS, XRD, FT-IR and BET analyzer. The pyrolyzed $KMnO_4$ modified pineapple leaf was used for Ca^{2+} and Mg^{2+} removal from aqueous solution. The Ca^{2+} and Mg^{2+} ions adsorption efficiency by pyrolyzed $KMnO_4$ modified product were evaluated. The Langmuir isotherm and Freundlich isotherm were also used for evaluation of Ca^{2+} and Mg^{2+} adsorption by the pyrolyzed pineapple leaf modified with 3.0 wt% $KMnO_4$. **Results:** The results show that MnO_2 deposited on the surface of $KMnO_4$ modified pineapple leaf with some heterogeneity. The OH, C=O, C-O and MnO groups are major functional groups on the surface of $KMnO_4$ modified product. The BET surface area and total pore volume of $KMnO_4$ modified pineapple leaf is decreases, while the average pore size is increases with increasing of $KMnO_4$ concentration. The Ca^{2+} and Mg^{2+} adsorption capacities on pyrolyzed modified products are in the range of 4.17-23.04 and 1.04-8.56 mg g^{-1}, respectively, based on fitting to the Freundlich isotherm model. **Conclusion:** This study indicated the possibility to reduce the pyrolysis temperature to 300°C for single stage pyrolyzed $KMnO_4$ modified pineapple leaf production, which could reduce energy costs of activated carbon production.

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Carbon rich agricultural wastes, which are available in large amounts and at low cost have been used as precursors for activated carbon[1]. The characteristics of agricultural wastes are biodegradability, non toxicity, durability, availability, thermal and mechanical stability etc.[2]. Therefore, these materials are suitable for the production of green activated carbon. In general, there are two steps in the production of activated carbon: Carbonization and activation[3]. During the activation step, physical activation and/or chemical activation are the two activation processes used for the development of the pores and surface area[4]. Practically, the activation temperature of lignocellulosic materials such as plants is ranging from 800-1000°C for physical activation, while temperatures lower than 800°C are used for chemical activation[3]. It can be seen that both activation processes are still require relatively high temperatures. Even, biochars from biomass are produced at temperatures of 400-700°C. Low pyrolysis temperatures in the range 300-500°C have been used for biochar production from poultry litter. However, a pyrolysis temperature of 450°C is suitable for converting agricultural residues into biochar and bio oil with maximum yield and maximum carbon content in the biochar[5]. If low activation temperatures could be used for activated carbon production, it could reduce energy consumption and cost. It has been reported that the torrefaction, which is pyrolysis of the biomass between 200 and 300°C under an inert atmosphere, could remove the moisture contents and low molecular weight organic compounds from the biomass[2]. In this process, lignocellulose, hemicellulose, cellulose and lignin were degraded[5] at about 120, 200-260, 240-350 and 280-350°C, respectively. Another report outlines an interesting one-step activation, which due to its process simplicity and reduction in operating time, cost, energy consumption and human effort, is considered as a green technique[6] and is also interesting for activated carbon production together with torrefaction. Furthermore, modifications of activated carbon materials are gaining prominence for development of affinity to certain contaminants that would allow their removal from varying types of wastewater[7]. Especially, KMnO₄, which a strong oxidizing agent, is often used in surface modifications of activated carbons[1]. It also could be used to increase porecapacity, specific surface area, pore size distribution, introduce MnO_2 and produce more acidic and basic groups on the modified activated carbon[8,9]. Furthermore, it also could oxidize labile carbon atoms at lower pyrolysis temperatures[10] and introduced hydrophilic sites by creating functional groups

such as carboxylic acids on the hydrophobic surfaces of activated carbon materials. The carboxylic acid groups can create a negative surface charge for cation adsorption on the surface of activated carbon[11]. Moreover, MnO_2 precipitates on the surface of activated carbon, which, when retained on the activated carbon surface, has a large surface area with strong adsorptive capacity[12]. The KMnO₄ has been widely used as a practical approach for treatment of groundwater contamination such as hardness, nitrate, heavy metals, soluble iron and chlorinated solvents like trichloroethylene[13]. It owes its popularity to its ease of handling, chemical stability, relatively low cost, the fact that its by products are less hazardous than those of other oxidants and its ability to provide long-term controlling scheme for aqueous-phase plumes of contaminants[14]. The KMnO₄ has been also used for preoxidation of organic matter in water by breaking down carbon–carbon double bonds of macro-molecular organic matter to form substances of lower molecular weight[12]. Water with total hardness higher than 200 mg dm^{-3} can still be tolerated by consumers. However, values higher than 500 mg dm^{-3} are not acceptable for most of domestic purposes. Hardness in water refers to existing divalent ions, such as iron, manganese, calcium and magnesium. However, calcium and magnesium are dominant species for water hardening[15].

Therefore, in this study, potassium permanganate should be used to pyrolysis temperature reducing for cellulosic materials with high cation adsorption capacity.

This work has investigated the effects of 0.0-5.0 wt% KMnO₄ pre-treatment of pineapple leaf before one step pyrolysis process at low temperature (200-500°C) to obtain KMnO₄ modified activated carbon to be used for hardness water removal. Since the pineapple leaf pretreated by KMnO₄ is a soft material, it was expected that reduced activation temperature for production of KMnO₄ modified activated carbon could be used, which resulted in the high adsorption capacity of hardness ion species.

MATERIALS AND METHODS

Preparation of KMnO₄ modified pineapple leaf activated carbon: Fresh pineapple leaves, which derived from Nakhon Thai, Phitsanulok province, Thailand, were cut to a length of 5 mm and dried in an oven (SL 1375 SHEL LAB 1350 FX) at 110°C for 3 h. The dried pineapple leafs were then pretreated with KMnO₄ (Merck, Germany) at 0.0, 1.0, 3.0 and 5.0 wt% by impregnation for 1 day. After that the impregnated pretreated pineapple leaves were dried in oven at 110°C for 6 h. The dried impregnated pretreated pineapple leaves were then

pyrolyzed at 200, 300, 400 and 500°C with temperature increased at a rate of 10°C min^{-1} and 1.0 h soaking time in an electric furnace (Fisher Scientific Isotemp® Muffle Furnace) under partial oxygen atmosphere in closed crucibles. After pyrolysis, the final products were cooled to room temperature and stored in a desiccator. The yield (%) of pyrolyzed products was calculated. The pyrolyzed products were characterized by X-ray powder diffractometer (XRD, PW 3040/60, X' Pert Pro MPD) with a Cu tube anode, a Fourier transform infrared spectrometer (Spectrum GX, Perkin Elmer), scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS, LEO 1455 VP) and BET analyzer (Micromeritics TriStar II).

Calcium and magnesium adsorption experiments: Batch calcium and magnesium adsorption experiments were performed following the method of Pastrana-Martinez *et al.*[16]. Solutions for this experiment were prepared using distilled water with varied degrees of hardness. Total hardness was calculated Eq. 1:

$$\text{Total hardness as } CaCO_3 \text{ (mg dm}^{-3}) = 2.50[Ca^{2+}, \text{ mg dm}^{-3}]+4.12\ [Mg^{2+}, \text{ mg dm}^{-3}] \quad (1)$$

Solutions with hardness values of 40, 100 or 200 mg dm^{-3} CaCO$_3$ were prepared by using CaCl$_2$ and MgCl$_2$ (AR grade, Merck, Germany) dissolved in distilled water. Hardness values of 40, 100 and 200 mg dm^{-3} CaCO$_3$ correspond to soft, moderately hard and hard water, respectively. The pH of the model hardness solutions was between 8.0 and 8.7. Concentrations of Ca^{2+} and Mg^{2+} for the 40 mg dm^{-3} hardness are 56.2 and 9.7 mg dm^{-3}, respectively. The concentrations for the same species for 100 mg dm^{-3} hardness are 123.5 and 24.2, respectively. Finally, for 200 mg dm^{-3} hardness the concentrations are 247.0 and 48.0 mg dm^{-3}, respectively.

For Ca^{2+} and Mg^{2+} adsorption experiments, modified pyrolyzed products (0.05-1.5 g) were added to 25 cm^3 of Ca^{2+} and Mg^{2+} solution (40, 100 and 200 mg dm^{-3}) in a conical flask. The suspension was shaken continuously at 120 rpm and a temperature of 32±2°C. Following the adsorption, the aqueous phase was separated by centrifugation at 4000 rpm for 10 min. The Ca^{2+} and Mg^{2+} concentrations were determined by FAAS with air-acetylene and cathode on Ca- or Mg-hollow cathode lamp[17] with 427.7 and 285.2 nm, respectively.

Removal efficiency of Ca^{2+} and Mg^{2+} ions: Final concentrations (C$_f$) of Ca^{2+} or Mg^{2+} were measured for the calculation of Ca^{2+} and Mg^{2+} removal percentages as shown[18] in the Eq. 2:

$$\text{Removal (\%)} = \frac{C_o\text{-}C_f}{C_o} \times 100 \quad (2)$$

where, C$_o$ is the initial Ca^{2+} and Mg^{2+} ion concentration (mg dm^{-3}), C$_f$ is the final Ca^{2+} and Mg^{2+} ion concentration (mg dm^{-3}). The adsorption capacity (q$_t$, mg g^{-1}) at any time was calculated using a mass balance equation as shown[18] in the Eq. 3:

$$q_t = (C_o\text{-}C_f) \times (V/W) \quad (3)$$

where, V is the volume of the solution (dm^3), W is the mass of dry modified pineapple carbon used (g).

Adsorption isotherms: The Ca^{2+} and Mg^{2+} experimental adsorption data were fitted with the linear forms of Langmuir (Eq. 4) and Freundlich Equations (Eq. 5)[19] as follows.

The linear form of Langmuir equation is:

$$C_e/Q_e = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (4)$$

The q$_{max}$ and constants K$_L$ can be determined from the slope and intercept of plotting C$_e$/Q$_e$ against C$_e$, respectively. The linear form of Freundlich equation is:

$$\log Q_e = \frac{\log K_F + 1}{n \log C_e} \quad (5)$$

where, Q$_e$ and C$_e$ have the same definitions as those in the Langmuir equation cited above. The K$_F$ and n are Freundlich constants related to adsorption capacity and heterogeneity factor, respectively. The constants K$_F$ and n can be determined from the intercept and slope of plotting log C$_e$ against log Q$_e$, respectively.

RESULTS

Yield of pyrolyzed products: The yield (%) of pyrolyzed KMnO$_4$ modified products decreased with increasing pyrolysis temperature (Table 1). The yield (%) of pyrolyzed products also increased slightly with increasing KMnO$_4$ modification concentration from 1.0-5.0 wt%. Furthermore, it was seen that the yield (%) of pyrolyzed products rapidly decreased at the pyrolysis temperatures 400 and 500°C. However, the yields (%) of pyrolyzed products made at pyrolysis temperature of 200-300°C were considered high as they lie in the range of 42.78-74.03%.
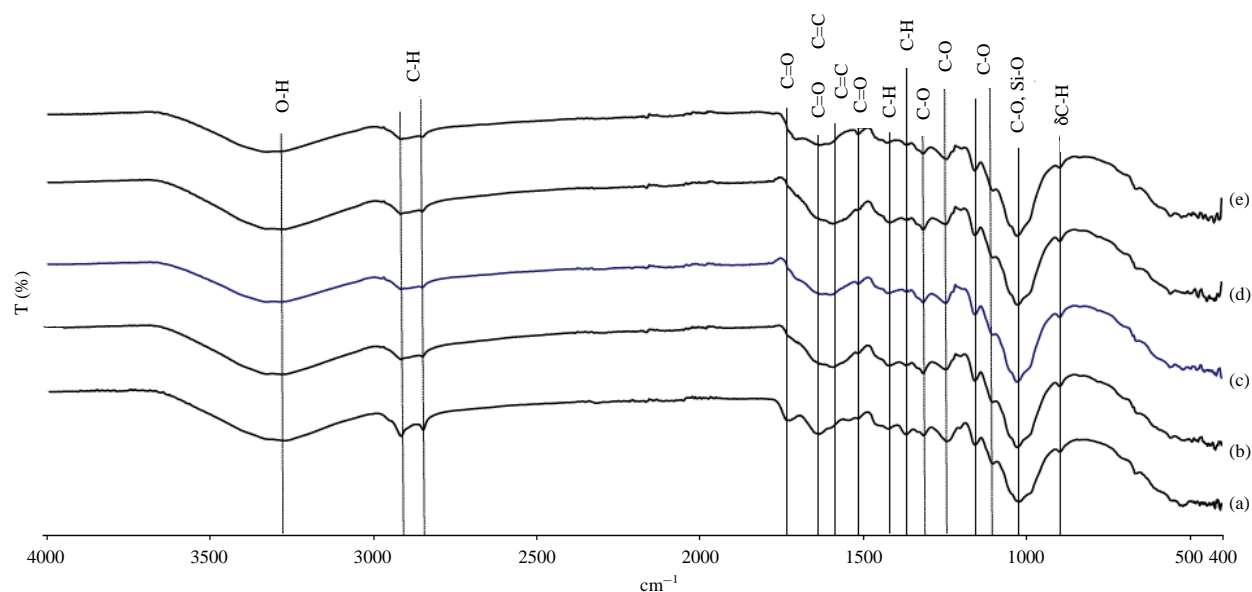
Fig. 1(a-e): FTIR spectrum of, (a) Dried pineapple leaf (b) Pyrolyzed pineapple leaf prepared at 200°C, (c) Pyrolyzed 1.0 wt% KMnO$_4$ modified pineapple leaf prepared at 200°C, (d) Pyrolyzed 3.0 wt% KMnO$_4$ modified pineapple leaf prepared at 200°C and (e) Pyrolyzed 5.0 wt% KMnO$_4$ modified pineapple leaf prepared at 200°C

Table 1: Yield of Pyrolyzed KMnO$_4$ modified products at 200-500°C

Temperature (°C)	Yield (%)			
	0.0% KMnO$_4$	1.0% KMnO$_4$	3.0% KMnO$_4$	5.0% KMnO$_4$
200	68.18	70.96	71.86	74.03
300	42.78	42.84	44.15	50.50
400	24.92	27.38	29.92	30.45
500	18.78	20.77	21.25	22.72

FTIR spectra of dried pineapple leaf and pyrolyzed products: It was seen that FTIR spectra for all samples were similar with slightly decreased intensities for materials modified by 1.0-5.0 wt% KMnO$_4$ and 200°C pyrolysis temperature (Fig. 1). The FTIR spectrum of dried pineapple leaf (Fig. 1a) showed peaks of lignin, cellulose, hemicellulose, C-O stretching vibration of carboxylic acids, alcohols, phenols, ethers and esters and asymmetric vibration of Si-O. In addition, C-H deformation ring vibrations was also found. When comparing the FTIR spectrum of dried pineapple leaf (Fig. 1a) to the FTIR spectra of pyrolyzed and activated products prepared at 200°C (Fig. 1b-e), it was seen that the peaks of organic compounds are still present. Furthermore, it can be seen that the double bond C=C vibrations and C-C vibrations in an aromatic system and the highly conjugated C=O stretching vibration of the functional group as a side chain of aromatic rings are occurred. This phenomenon is similar in all pyrolyzed modified products obtained at the same pyrolysis temperature of 300, 400 and 500°C. Therefore, the effects of

KMnO$_4$ concentration for all pyrolysis temperatures wasn't shown and rather focus on the effects of increasing the pyrolysis temperature from 200-500°C for materials prepared with 3.0 wt% KMnO$_4$. The FTIR spectra for corresponding modified pineapple leaf were shown in Fig. 2. It can be seen that all peaks in the FTIR spectrum of the pyrolyzed modified products decreased in intensity with increasing pyrolysis temperature between 300 and 500°C (Fig. 2b-d). The exception are the peaks of aromatic C=C vibration. However, a comparison of the pyrolyzed unmodified products to pyrolyzed KMnO$_4$ modified products indicates that this condensation in pyrolyzed KMnO$_4$ modified products occurs at lower pyrolysis temperature (300°C for modified products, while unmodified products pyrolyzed at 400°C are similar to those made at pyrolysis temperature of 200°C). In addition, the aromatic -C=O stretching vibrations with very weak band also appear. Furthermore, the Mn-O bond of the Mn oxide phase was also occurred. Furthermore, it can be seen that the peaks of the FTIR spectra for 3.0 wt% KMnO$_4$ modified at 300-500°C are similar, except for the disappearance of the O-H stretching vibration at 500°C as a result of extensive thermal degradation. These results have suggested that the 300°C pyrolysis temperature should be sufficient to provide stable KMnO$_4$ modified activated carbon from pineapple despite the fact that some functional groups from the original pineapple leaf remain on the surface.
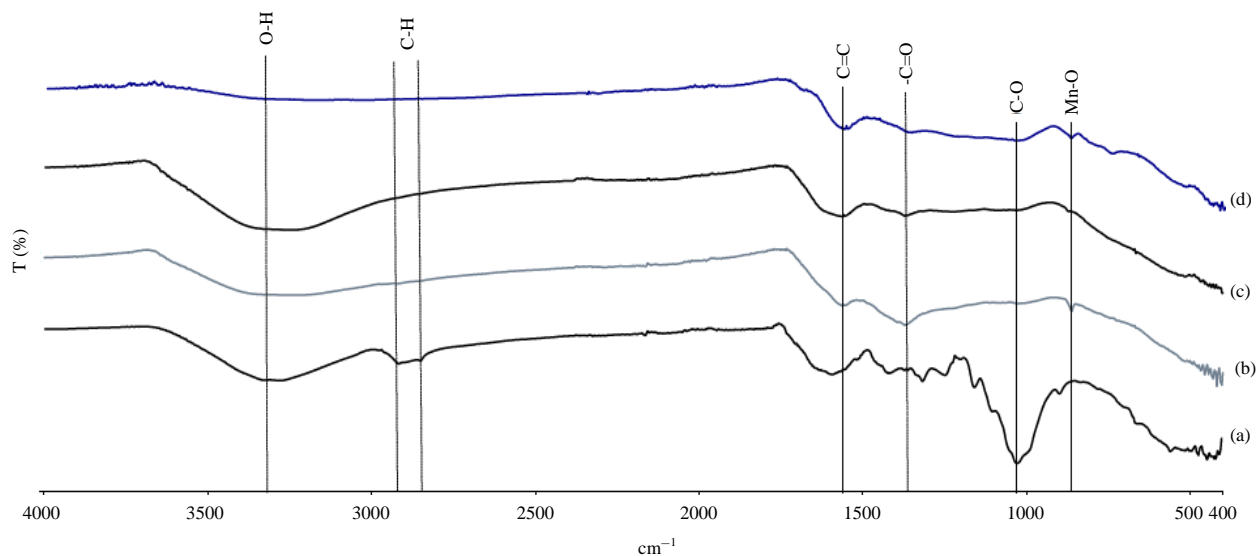
Fig. 2(a-d): FTIR spectrum of pyrolyzed 3.0 wt% $KMnO_4$ modified pineapple leaf prepared at (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C
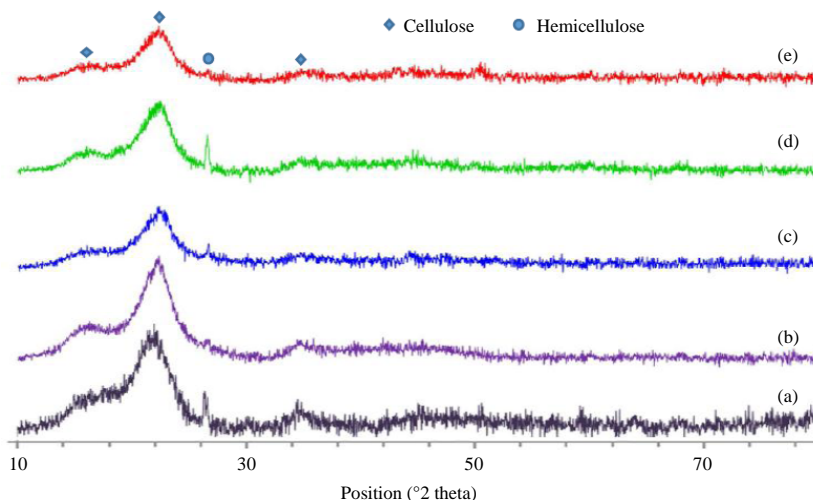

Fig. 3(a-e): XRD patterns of, (a) Dried pineapple leaf, (b) Pyrolyzed pineapple leaf prepared at 200°C, (c) Pyrolyzed 1.0 wt% $KMnO_4$ modified pineapple leaf prepared at 200°C, (d) Pyrolyzed 3.0 wt% $KMnO_4$ modified pineapple leaf prepared at 200°C and (e) Pyrolyzed 5.0 wt% $KMnO_4$ modified pineapple leaf prepared at 200°C

X-ray powder diffraction patterns of dried pineapple leaf and pyrolyzed products: The diffraction peaks of dried pineapple leaf showed cellulose I and hemicellulose composition (Fig. 3a), which were still a little present in materials made after modification with 1.0-5.0 wt% $KMnO_4$ and pyrolyzed at 200°C (Fig. 3b-e). However, potassium and manganese compounds have not clearly appeared even for modification with 5.0 wt% $KMnO_4$. The diffraction patterns of pyrolyzed $KMnO_4$ modified pineapple leafs prepared with pyrolysis at 300°C are different, except, a stable SiO_2 and

graphitic carbon (Fig. 4a-d). Furthermore, the results also showed that MnO_2 exists in the pyrolyzed modified products, which was formed by a redox reaction. These results corresponded to the results obtained from FTIR analysis. In addition, CaO and K_2O were also present.

SEM-EDS analysis of pyrolyzed products

EDS analysis: The result of EDS analysis indicated that the $KMnO_4$ modified products contained high amounts of K and Mn elements (Table 2). In this study, it was clearly seen that
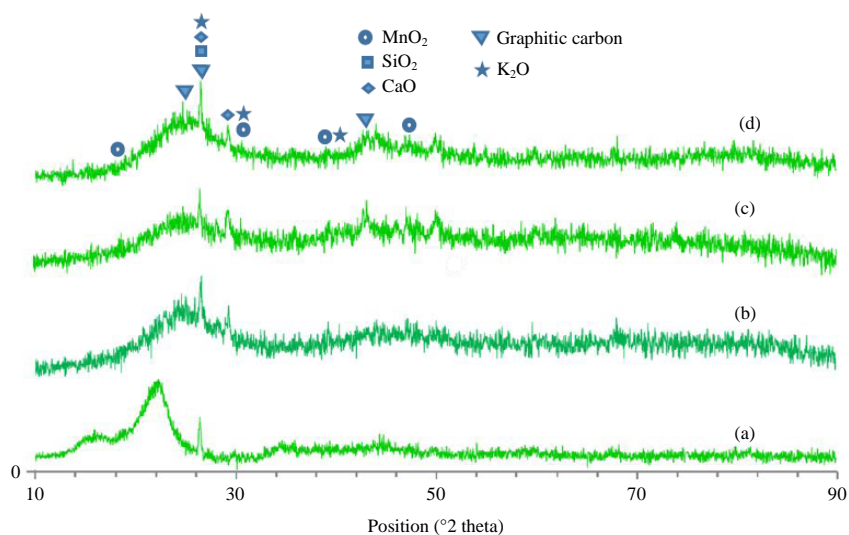
Fig. 4(a-d): XRD patterns of pyrolyzed pineapple leaf modified with 3.0 wt% $KMnO_4$ prepared at, (a) 200°C (b) 300°C (c) 400°C and (d) 500°C

Table 2: Elemental composition of pyrolyzed products prepared at 300°C determined with EDS analysis

Pyrolyzed sample	wt% of elements and ratio O/C						
	C	O	O/C	Si	K	Ca	Mn
Pyrolyzed pineapple leaf	75.67	19.26	0.25	2.24	0.17	2.05	-
Pyrolyzed 1.0 wt% $KMnO_4$ modified pineapple leaf	76.87	17.84	0.23	1.54	0.78	1.87	1.13
Pyrolyzed 3.0 wt% $KMnO_4$ modified pineapple leaf	77.98	15.98	0.20	1.42	1.51	1.34	1.46
Pyrolyzed 5.0 wt% $KMnO_4$ modified pineapple leaf	78.55	15.47	0.20	0.81	1.82	0.87	2.57

EDS: Energy dispersive spectrometer

Table 3: BET surface area, porous volume and average porous size of pyrolyzed pineapple leaf and pyrolyzed 1.0-5.0 wt% $KMnO_4$ modified pineapple leaf at 300°C

Pyrolysis samples	BET surface area ($m^2\ g^{-1}$)	Porous volume ($cm^3\ g^{-1}$)	Average porous size (nm)
Pyrolyzed pineapple leaf	3.2304	0.003234	2.9295
Pyrolyzed 1.0 wt% $KMnO_4$ modified pineapple leaf	2.5063	0.002932	3.0066
Pyrolyzed 3.0 wt% $KMnO_4$ modified pineapple leaf	1.9832	0.002353	3.0869
Pyrolyzed 5.0 wt% $KMnO_4$ modified pineapple leaf	1.7587	0.001963	3.1603

BET: Brunauer-emmett-teller

$KMnO_4$ could be converted into MnO_2 particles at 300°C. On the other hand Ca, Si and also some K were derived from raw materials. It can be seen that the pyrolyzed modified products had a high content of carbon with O/C ratios of 0.20-0.25 O/C.

SEM analysis: The pyrolyzed unmodified product showed a relatively uniform and smooth surface with some wrinkles (Fig. 5a). It can be seen that the surface morphology of the pyrolyzed products is more disrupted with increasing of $KMnO_4$ concentration (Fig. 5b-d). After modification with $KMnO_4$, the cell walls of the pyrolyzed modified products were more destroyed and covered with small particles on their surface. The small particles are assumed to be MnO_2 and other oxides. Furthermore, it was also shown that the surfaces of the pyrolyzed modified products were filled with numerous cavities and exhibited roughness. These features have increased with increasing $KMnO_4$ concentration. However, the content of small particles increased with increasing $KMnO_4$ concentration. As can be seen in Table 3, the results indicated that the BET surface areas and porous volume decrease with increasing $KMnO_4$ concentration, while the average porosity size exhibits a slight upward trend.

Hardness removal results: For adsorption experiments, only the pineapple leaf pyrolyzed and modified with 3.0 wt% $KMnO_4$ was investigated and compared to the leaf without $KMnO_4$ modification. The pyrolyzed pineapple leaf modified with 3.0 wt% $KMnO_4$ is stable enough for water treatment and was produced with minimum pyrolysis temperature. Therefore this sample was selected for harness removal experiments. It is note worthy that the pyrolyzed unmodified product is rather insoluble in hardness solution. This shows that the surface of the pyrolyzed unmodified product is quite hydrophobic.
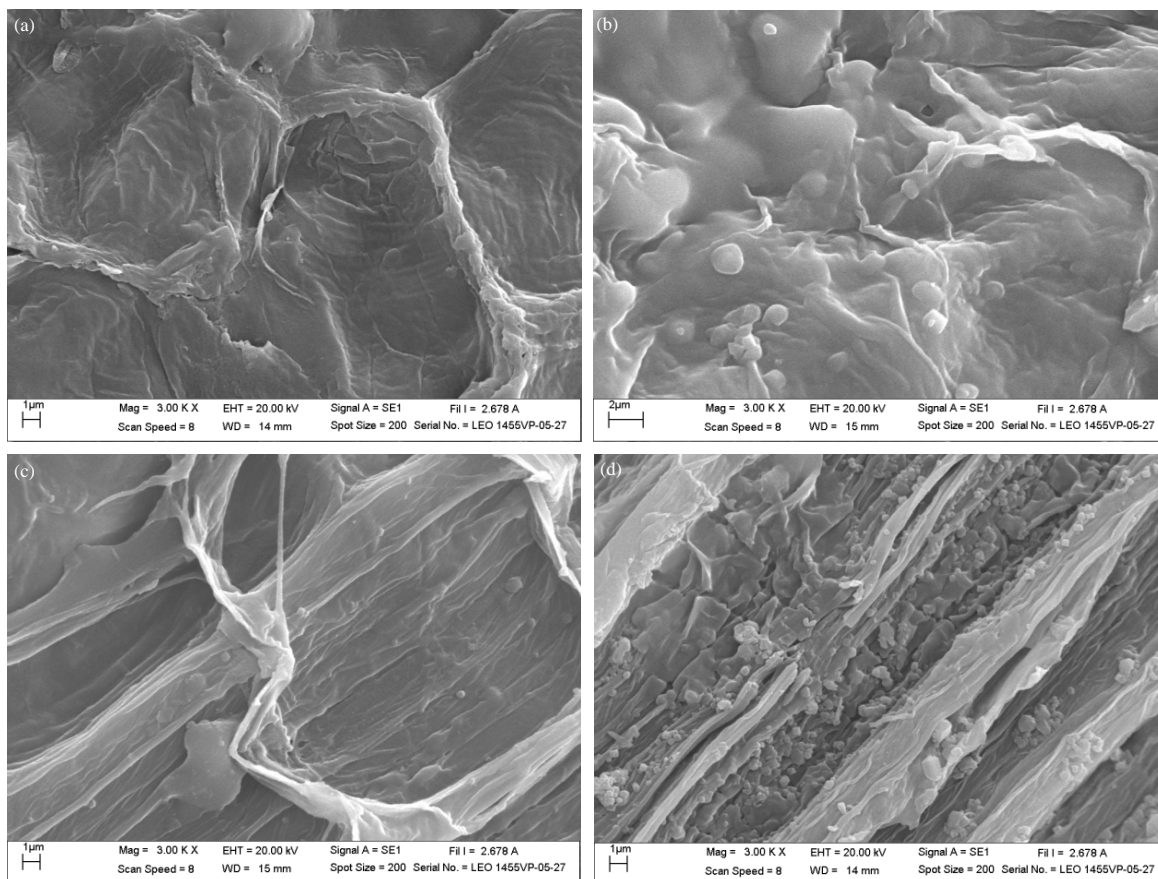
Fig. 5(a-d): SEM images of pyrolyzed products prepared at 300°C and modified with, (a) 0.0 wt%, (b) 1.0 wt%, (c) 3.0 wt% and (d) 5.0 wt% $KMnO_4$

Ca^{2+} and Mg^{2+} ions adsorption efficiencies: It can be seen that the adsorption efficiencies of Ca^{2+} and Mg^{2+} ions increased with increasing adsorbent dosage in solutions with the same hardness concentration and decreased with increasing hardness concentration for the same adsorbent dosage (Fig. 6). However, the adsorption capacity increased with increasing the initial concentrations of hardness. Furthermore, it was seen that the adsorption efficiencies of Ca^{2+} and Mg^{2+} ions on pyrolyzed pineapple leaf modified with 3.0 wt% $KMnO_4$ were higher compared to the values observed for pyrolyzed unmodified pineapple leaf at the same dosage and hardness concentration. Moreover, Ca^{2+} ion (Fig. 6a) showed higher adsorption efficiency when compared to Mg^{2+} ion (Fig. 6b) for same dosage and hardness concentration, which indicates a higher selectivity of the pyrolyzed products for Ca^{2+} ion.

Considering the Ca^{2+} ion and Mg^{2+} ion adsorption capacity values (mg g^{-1}) of pyrolyzed unmodified products and pyrolyzed products modified with 3.0% $KMnO_4$ (Table 4), it can be seen that adsorption capacity values have an inverse trend to adsorption efficiency. The metal ions adsorption capacities of both types of pyrolyzed products increased with increasing hardness concentration with the same pyrolyzed product dosage. While metals ions adsorption capacities of pyrolyzed products decreased with increasing dosage of pyrolyzed products at the same hardness concentration.

Ca^{2+} and Mg^{2+} ions adsorption isotherm: Both Ca^{2+} and Mg^{2+} ions adsorption isotherms (Langmuir isotherm model (Fig 7a, 8a) and Freundlich isotherm model (Fig. 7b, 8b) data provided a better fit to the Freundlich isotherm model more than the Langmuir isotherm model as can be seen from the R^2 values. Calculation from Eq. 5, the Freundlich factor (n) values of Ca^{2+} and Mg^{2+} ion on pyrolyzed $KMnO_4$ modified products are 3.182 and 1.961, respectively.

Table 4: Ca^{2+} and Mg^{2+} adsorption capacity (mg g^{-1}) for tests with different dosage of pyrolyzed unmodified pineapple leaf and pyrolyzed pineapple leaf modified with 3.0 wt% KMnO$_4$ at 40-200 mg dm^{-3} total hardness concentration

| Dosage adsorbent (g dm^{-3})	Ca^{2+} adsorption capacity (mg g^{-1}) at total hardness concentration (mg dm^{-3})			Mg^{2+} adsorption capacity (mg g^{-1}) at total hardness concentration (mg dm^{-3})		
	40	100	200	40	100	200
Unmodified						
2.0	4.067475	11.18647	23.04931	1.032772	3.714897	8.398925
4.0	2.031502	5.589386	11.52267	0.518100	1.858318	4.202478
20.0	0.407172	1.119030	2.305171	0.104177	0.372513	0.849480
40.0	0.203428	0.559419	1.152556	0.052092	0.186525	0.426299
60.0	0.135675	0.373299	0.768061	0.034729	0.124366	0.284442
Modified						
2.0	4.174364	11.20610	23.04404	1.043317	3.740120	8.560783
4.0	2.151086	5.615516	11.52883	0.524485	1.872902	4.280543
20.0	0.451432	1.148838	2.307905	0.105591	0.374836	0.856305
40.0	0.228774	0.586575	1.160241	0.052858	0.187595	0.428695
60.0	0.153915	0.396612	0.778987	0.035341	0.125689	0.286205
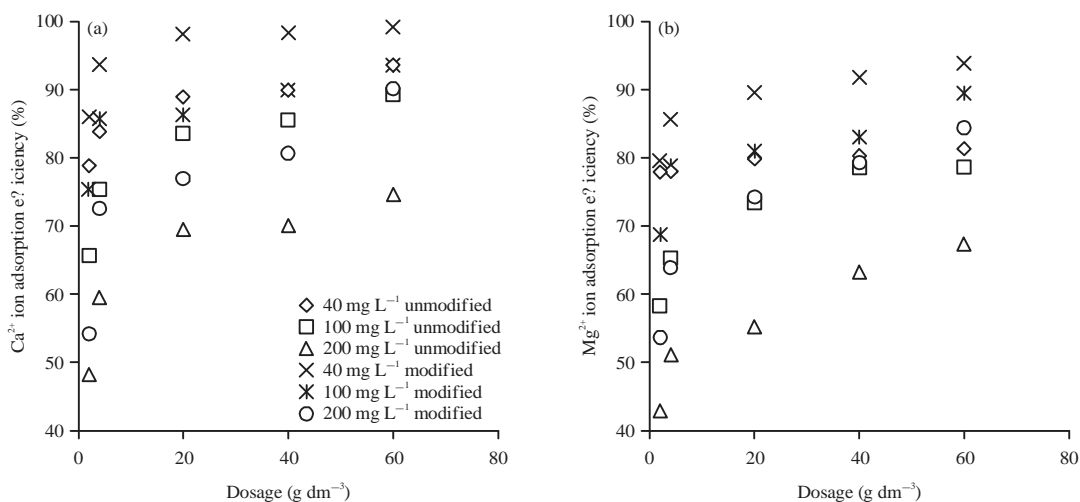
Fig. 6(a-b): (a) Ca^{2+} ion and (b) Mg^{2+} ion adsorption efficiencies of pyrolyzed unmodified product (unmodified) and pyrolyzed modified with 3.0% KMnO$_4$ at different dosage (2.0-60.0 g dm^{-3}) and hardness concentration (40-200 mg dm^{-3})
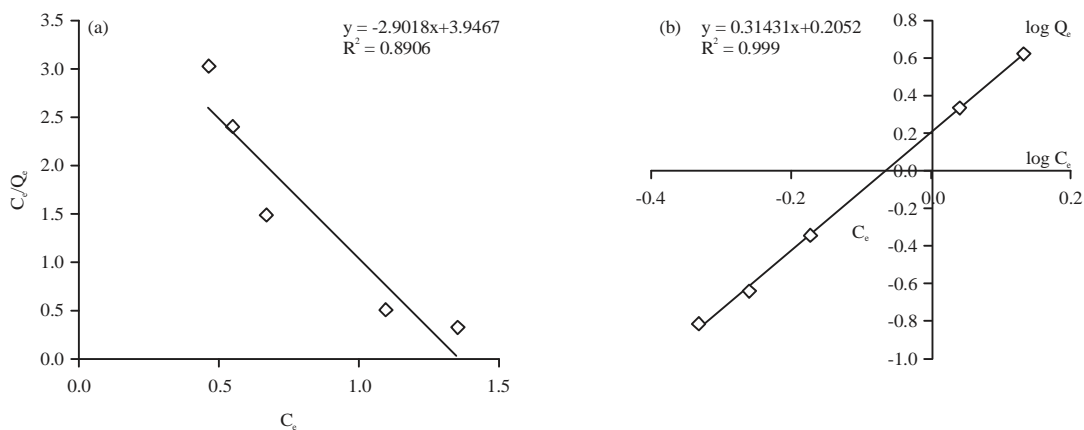

Fig. 7(a-b): (a) Langmuir isotherm of Ca^{2+} adsorption by pyrolyzed pineapple leaf modified with 3.0 wt% KMnO$_4$ prepared at 300°C and (b) Freundlich isotherm of Ca^{2+} adsorption by pyrolyzed pineapple leaf modified with 3.0 wt% KMnO$_4$ prepared at 300°C
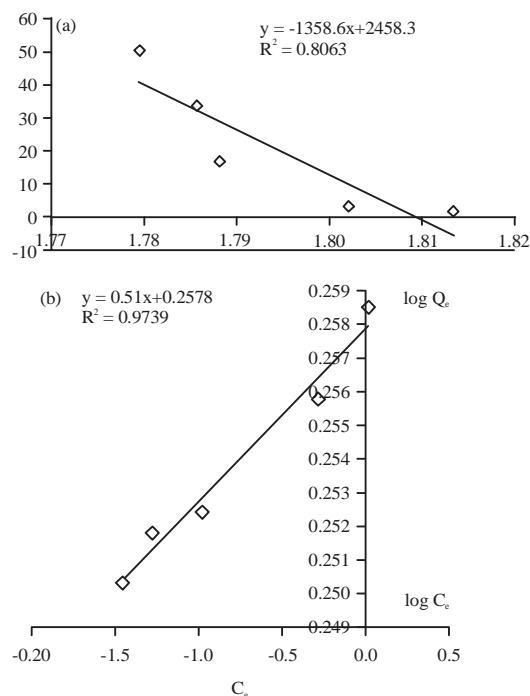
Fig. 8(a-b): (a) Langmuir isotherm of Mg^{2+} adsorption by pyrolyzed pineapple leaf modified with 3.0 wt% KMnO$_4$ prepared at 300°C and (b) Freundlich isotherm of Mg^{2+} adsorption by pyrolyzed pineapple leaf modified with 3.0 wt% KMnO$_4$ prepared at 300°C

DISCUSSION

The low yield (%) of pyrolyzed products at higher temperatures was attributed to higher extent of gasifying reaction between partial oxygen and carbon[20]. However, yield (%) increased slightly with increasing KMnO$_4$ modification concentration with oxides of K and Mn. This shows that the content of remaining K and Mn oxides was higher than the loss due to thermal degradation of oxidized substances. It should be noted that during pyrolysis, carbon based support can act as reducing agent and substrate for heterogeneous nucleation and precipitation of K doped manganese dioxides[21].

Form the results of FTIR spectra, it was indicated that the pyrolysis at 200°C is not sufficient for preparation of KMnO$_4$ modified activated carbon from pineapple leaf even with the 5.0 wt% concentration of KMnO$_4$, which is still present of some organic compounds. But, aromatic structures and polymerization are starting growth with removal of some volatile matter[5]. This phenomenon results in increasing single bond character of -C=O groups, the double bond C=C vibrations and C-C vibrations which are conjugated to aromatic rings[4,8]. This is the result of both thermal degradation and KMnO$_4$ oxidation with higher cyclization degree and increased conjugation character. This has effects on the condensation of the aromatic functional units in pyrolyzed modified products observed with increasing pyrolysis temperature. In addition, volatile organic substances were more readily oxidized by KMnO$_4$ at lower pyrolysis temperatures which is attributed to the breakdown of macro-molecular organic matter to form substances of lower molecular weights by KMnO$_4$ promoted oxidation[12]. These low molecular weight substances of oxidized products have lower thermal stability, which decreases with their molecular weights[22]. Moreover, Mn-O bond of the Mn oxide phase is also occurred. This confirms the presence of manganese oxide on the surface of pyrolyzed KMnO$_4$ modified products after 300°C formed by the reduction of KMnO$_4$ with organic matter[23]. These results from FTIR spectra have suggested that the 300°C pyrolysis temperature should be sufficient to provide stable KMnO$_4$ modified activated carbon from pineapple despite the fact that some functional groups from the original pineapple leaf remain on the surface. Generally, the acidic functional groups or volatile organic matter cannot be easily lost at pyrolysis temperatures lower[10] than 400°C. These results are similar to those of the X-ray powder diffraction result which showed some cellulose I and hemicellulose composition of pyrolyzed products with1.0-5.0 wt% KMnO$_4$ and pyrolyzed at 200°C. Likewise, it showed that the pyrolyzed modified products prepared by pyrolysis at 300°C are rather stable carbon materials with some SiO$_2$ and MnO$_2$. The EDS result also showed that O/C ratios of pyrolyzed modified products are range of 0.20-0.25 O/C, which is the more stable fraction of carbon. It was reported that pyrolyzed products with an O/C ratios of less than 0.2 are stable carbonaceous materials[10]. Therefore, it could be concluded that the pyrolyzed pineapple leaves modified with 3.0-5.0 wt% KMnO$_4$ prepared at 300°C are sufficiently are stable and have charcoal characteristics. Moreover, when viewing the results of SEM, the cell walls of the pyrolyzed modified products were more destroyed and covered with small particles on their surface after modification with KMnO$_4$. These morphology changes are due to the disruption of pineapple leaf structure by KMnO$_4$ and pyrolysis. The pore walls the modified pineapple leaf are corroded as a result of higher potassium permanganate concentration. Additionally, original micropores are continuously expanded and the walls of neighboring micropores are totally burned up, resulting in the formation of mesopores and macropores. These phenomena have the effect of reducing both pore capacity and specific surface area of modified products. It can be seen that the average porosity is almost that of a micropore (pore diameters less than 3 nm are considered as

micropores)[1]. In addition, the results confirmed that $KMnO_4$ has reacted with organic substances in pineapple leaf during pyrolysis process followed by the precipitation of MnO_2. The precipitated MnO_2 has then blocked the pores on the surface of the pyrolyzed modified products and also reduced the surface area and pore volume of modified products[24]. Although, the surface area and porous volume of pyrolyzed $KMnO_4$ modified pineapple leaf product is rather low. However, the $KMnO_4$ modified pyrolyzed product was expected to exhibit enhanced hardness removal from water as a result of surface functional groups.

For the result of hardness removal, the increasing capacity of Ca^{2+} and Mg^{2+} ions with increasing dosage at the same hardness concentration and with increasing the initial concentrations of hardness with the same dosage are relate to surface increasing area, increasing availability of more sorption sites and a driving force to overcome the resistance of mass transfer between the metals ions and the pyrolyzed modified products[25], respectively. On the other hand the decreasing adsorption efficiencies of metals ion in solutions with increasing hardness concentration results from the limited number of binding sites of pyrolyzed products[26]. These results indicated that the pyrolyzed $KMnO_4$ modified product showed much stronger binding affinity to Ca^{2+} and Mg^{2+} ions than the pyrolyzed unmodified products. This can be explained by the fact that the adsorption experiments were conducted with pH between 8.0 and 8.7 at which both MnO_2 and pyrolyzed products surfaces are negatively charged and adsorption would be hindered by electric repulsive force[27]. Both the functional groups and the MnO_2 particles could serve as the main adsorption sites for Ca^{2+} and Mg^{2+} ions in aqueous solutions. The surface of the pyrolyzed unmodified product is quite hydrophobic. The results showed that $KMnO_4$ promoted hydrophilic appearance on the pyrolyzed $KMnO_4$ modified products surface.

However, these pyrolyzed modified products have a relatively high Ca^{2+} ion capacity (11.21 mg g^{-1}), especially when compared to pineapple leaf modified with 3.0 wt% $KMnO_4$ and carbonized[28] at 500°C, which could adsorb Ca^{2+} ion in range of 4.37-8.95 mg g^{-1} for 100 mg dm^{-3} total hardness with 2.0 g dm^{-3} dosage. This may be attributed to the high content of surface functional acid groups, which remained on the product at low pyrolysis temperature. The results from adsorption isotherm. It showed that the Ca^{2+} and Mg^{2+} ions adsorptions are multilayer adsorption events, with non-uniform distribution of heat of adsorption over the heterogeneous adsorbent surface[2]. It was also indicated that the Freundlich isotherm is favorable for both metals ions. Because of the n values are in the range[15] 1-10. Furthermore, It can be seen that the n value of Mg^{2+} adsorption is lower than that of Ca^{2+} adsorption, which is consistent with the results of adsorption efficiency. This shows that Mg^{2+} ion adsorption is less favorable than Ca^{2+} ion adsorption by the pyrolyzed $KMnO_4$ modified product.

CONCLUSION

It was found that $KMnO_4$ could result in condensation of pyrolyzed modified products at only 300°C pyrolysis temperature when compared to pyrolyzed unmodified products. It was shown that Ca^{2+} and Mg^{2+} adsorption capacity of pyrolyzed product modified with 3.0 wt% $KMnO_4$ lies in the range of 4.17-23.04 and 1.04-8.56 mg g^{-1}, respectively, which fitted to Freundlich isotherm model.

SIGNIFICANCE STATEMENTS

This study found that $KMnO_4$ could be reduced pyrolyzed temperature of pineapple leaf to only 300°C for $KMnO_4$ modified activated carbon by single stage. It could reduce energy costs of activated carbon production from biomass with a high yield, which is possible to using for green industrial production. The $KMnO_4$ modified activated carbon with low pyrolysis temperature could be removal the actions with high capacity.

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