

Full Length Research Paper

## Performance of activated carbons in the catalytic wet peroxide oxidation (CWPO) of maleic acid

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Catalytic wet peroxide oxidation (CWPO) of maleic acid using palm fruit shell, peach stone and cashew nut shell as catalysts was investigated. Physical activation of pyrolysed char with carbon dioxide was done at 900°C, 30 min holding time and heating rate of 20°C/min under nitrogen flowrate of 150 cm<sup>3</sup>/min. The activated carbons had maximum Brunauer Emmett-Teller (BET) surface areas of 389, 428 and 692 m<sup>2</sup>/g for palm fruit shell, peach stone and cashew nut shell, respectively. The morphology structures of the samples were determined using a scanning electron microscopy (SEM), while thermal stabilities were determined using thermal gravimetric analysis (TGA). The CWPO reactions were performed in a stirred batch reactor at an atmospheric pressure in the presence of H<sub>2</sub>O<sub>2</sub> as an oxidant. The results showed that peach stone and palm fruit shell catalysts are more effective for liquid phase oxidation of maleic acid than cashew nut shell and can be applied for catalytic wastewater treatment systems.

**Key words:** Activated carbon, catalytic wet peroxide oxidation, activation, surface areas.

### INTRODUCTION

Water pollution, particularly in developing countries, is a serious problem which requires vital consideration. It is a leading worldwide cause of death and diseases as it is reported to account for deaths of more than 14,000 people daily (Water pollution - [http://en.wikipedia.org/wiki/water\\_pollution#\\_note-death2](http://en.wikipedia.org/wiki/water_pollution#_note-death2)). Among the potential sources of ground and surface water pollutants are discharges from industrial processes and agricultural activities. Wastewaters such as those from chemical, petroleum, pharmaceutical, coke, pesticides, electroplating industries and paper manufacturing, are difficult to treat. Such pollutants include phenols and its derivatives. It is important to find out a suitable cost effective treatment

technology for such pollutants. However, several technologies for degrading toxic wastes have been discovered by mankind overtime for the purpose of safeguarding human health, aquatic the desired removal efficiency, effectiveness, environmental conditions and cost (Masende et al., 2003; Taylor and Weygandt, 1974). However these methods are now losing popularity due to high operation cost and poor level of conversion of pollutants.

The catalytic wet oxidation (CWO) process is becoming more popular these days for oxidizing toxic organic wastes. It involves contacting of oxygen gas or air and organic compound like maleic acid and a catalyst in

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**Abbreviations:** BET, Brunauer Emmett-Teller; NIST, National Institute of Standards and Technology; AC, activated carbon; BPR, backpressure regulator; CV, on/off valve; CNS, cashew nut shells; CWPO, catalytic wet peroxide oxidation; DFT, density functional theory; dP, differential pressure; LI, level indicator; MFC, mass flow controller; PI, pressure indicator; pHI, pH indicator; PFS, palm fruit shells; PS, peach stone; SEM, scanning electron microscopy; TGA, thermal gravimetric analysis; RV, relief/vent valve; SI, stirrer speed indicator; TC, temperature controller; TI, temperature indicator; WI, weight indicator.

aqueous medium.

Application of catalysts in CWO has improved the old supercritical water oxidation and wet air oxidation processes (Debellefontaine et al., 1996; Masende et al., 2003; Mises, 2001; Santos et al., 2002).

However, one of the major drawbacks of catalysts is deactivation during liquid phase oxidation. The main causes for catalyst deactivation during CWAO are the leaching of the active metal phase (Fortuny et al., 1999) and/or the formation of carbonaceous deposits hampering access to the catalytic sites (Hamoudi et al., 1998). This problem could be avoided or minimized by employing activated carbon as catalyst or as catalyst support.

Activated carbon has broad range of applications in different fields such as food, chemical and pharmaceutical industries. Activated carbon is broadly defined to include a wide range of amorphous carbon based materials prepared in such a way that they exhibit a high degree of porosity and an extended surface area (Cecen, 2011). The primary use for activated carbon is in the treatment of water, including potable water; wastewater and groundwater remediation (Baker et al., 1992). They are also effective as catalysts and catalysts' supports (Jüntgen, 1986; Semikolenov, 1992). However, not every carbon is suitable for each use. The carbon skeleton products (after carbonization and/or activation), which result into porosity development inside the carbon particles, depend on the nature of the source materials and conditions of preparation. This need for task specificity among activated carbons necessitates careful selection of source material and conditions of preparation to suit the intended use.

Maleic acid was chosen as model compound in this study. Phenol reaction steps, in supercritical wet oxidation (SCWO), have been reviewed in which the formation of dimers and other intermediates like single-ring compound (e.g. hydroquinone) products, ring-opening products (e.g. maleic acid, glyoxylic acid, acetic acid and other organic acids) and gases (e.g. CO, CO<sub>2</sub>) are reported (Devlin and Harris, 1984; Masende et al., 2003). Some of these partial oxidation products and intermediates, especially the dimers are relatively more toxic than phenol. According to the reaction scheme proposed by Devlin and Harris (1984) for phenol oxidation, maleic acid found to be a crucial intermediate product as it appears almost at all reaction conditions, though in trace amounts (Mises, 2001; Santos et al. 2002). Furthermore, the oxidation of maleic acid over a number of catalysts showed a performance similar to phenol oxidation.

Nevertheless, many studies showing CWPO of phenolic compounds using activated carbons as catalysts or catalyst supports have been reported (Ayril et al., 2010; Missenden et al., 2003; Mohamed et al., 2013; Quesada-Peñate et al., 2012). However, many of them are commercially too expensive especially for developing

countries. There is a need to explore locally available and cost effective activated carbons and use them in waste water treatment. This paper presents characteristics of locally activated carbons prepared from cashew nut shell, palm fruit shell and peach stone and their performance in CWPO of maleic acid.

## EXPERIMENTAL SECTION

Chemicals and materials used include: maleic acid 99% (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) (May & Baker), phosphoric acid 99% (H<sub>3</sub>PO<sub>4</sub>) distilled water, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), nitrogen gas, carbon dioxide gas, palm fruit shells, peaches stones, and cashew nut shells. The equipments used are: CARBOLITE furnace type CTF 12/65, Autosorb-1 system from Quanta chrome Corp, thermo gravimetric analysis instrument 951, scanning electron microscopy and three-phase slurry batch tank reactor with a set of high performance liquid chromatography (HPLC).

### Activation

Two-step CO<sub>2</sub> activation was performed in a horizontal tube furnace (CARBOLITE furnace type CTF 12/65). The equipment contains horizontal tubular heater and a EUROTHERM 808 temperature controller unit used for setting required temperatures. In each run, approximately 5 g of sample material was used and the system was then purged with 150 cm<sup>3</sup>/min of N<sub>2</sub> for 15 min to ensure inert conditions in the reactor. The reactor was then heated at a rate of 20°C/min to a final temperature of 900°C, while the ACs wastes were thermally decomposed to porous carbonaceous materials. The sample was kept at 900°C for 90 min in the inert atmospheric of nitrogen. After carbonization while maintaining the temperature at 900°C the nitrogen stream was replaced by CO<sub>2</sub> for 30 min. The furnace was then switched off to allow it to cool to room temperature in the atmosphere of nitrogen. The samples were grinded and screened by using sieve of < 50 μm.

### Characterization of activated carbons

#### Textural characterization

An Autosorb-1 system from Quanta chrome Corp. was used to determine the surface area and porosity characteristics of the activated carbons, according to IUPAC classification. Density Functional theory (DFT) was applied to investigate sample microporosity. DFT Kernel applied in this research was N<sub>2</sub> at 77K on carbon, (slit pores, NLFDF equilibrium model). The BET surface area was calculated from N<sub>2</sub> adsorption isotherms by using the Brunauer-Emmett-Teller (BET). The total pore volumes were found from the amount of nitrogen adsorbed at a relative pressure of 0.99. A reference material, 8571 Alumina, (U.S. Department of Commerce National Institute of Standards and Technology (NIST)), was used to check the performance of the Autosorb-1. NIST reports the mean BET specific surface area for 8571 Alumina to be 158 m<sup>2</sup>/g, but with a variation from 150 to 165 m<sup>2</sup>/g. Autosorb-1 instrument therefore was tested and calibrated quite frequently to ascertain its performance. The surface areas of calibration material were measured to be 152 m<sup>2</sup>/g, which is in total agreement with NIST published value.

The surface characteristics of samples were analysed using scanning electron microscopy (LEO 1500). The different powder samples were placed on aluminum SEM specimen mount stubs from Electron Microscopy Sciences (EMS) using carbon coated conductive adhesive tabs, with the accelerating voltage of 2500.

**Table 1.** Standard reactor operating condition.

Item	Standard	Range
Temperature, °C	50	50
Pressure, MPa *	1.2	1.2
Nitrogen flow rate (at room conditions)ml/min	90	10-120
Initial maleic acid concentration, mol/L	0.01	0.01
Volume of liquid in the reactor, ml	350	350
pH	Uncontrolled	2-7
Stirrer speed, rpm	350	350-1200
Activated carbons ACs, g/l	0.5	0.5

1.2 MPa \* is a backward pressure which was used to facilitate easy withdrawal of samples from the reactor.

### Thermogravimetric analysis

Thermal degradation characteristics of ACs waste were studied using a thermogravimetric method. Experiments were performed on TA instrument 951 using air (O<sub>2</sub>, 21%). Each sample of 5–6 mg was heated from room temperature to a final temperature of 800°C. Fixed carbon, volatile, and ash analyses were carried out using a thermogravimetric analyser. When the sample is heated under an inert atmosphere to 800°C, the weight loss during this step is a volatile component. The gas atmosphere is then switched to air to burn off fixed carbon, finally, any residue left after the system is cooled to room temperature is considered as ash.

### Performance test

The experiments were conducted in a batch stirred Tank reactor (BSTR) in a temperature of 50°C and at an atmospheric pressure in the presence of H<sub>2</sub>O<sub>2</sub> as an oxidant. Other experimental and reactor operating conditions were as listed in Table 1. The reactor used was a 500 ml volume autoclave (Autoclave Engineers, Zipperclave Hastelloy) with two internal baffles, thermowell, cooling coil, two separate liquid inlets, a liquid outlet with catalyst filters (filter type: Millipore HV 0.45 µm and a stainless steel 0.5 µm), immersion-pipe for level measurement, and a gas dispersion impeller. The reactor set-up is presented in Figure 1. The detailed procedure was similar to that described elsewhere (Masende et al., 2003).

## RESULTS AND DISCUSSION

An effective use of activated carbon requires knowledge about the structure of its porosity obtained from equilibrium data namely: the pore-size distributions of the microporosity in particular, the pore-size distributions of the mesoporosity, the composition of the carbon surfaces onto which adsorption occurs and the knowledge of the dynamics of adsorption to indicate its effectiveness (Marsh et al., 2006). Traditional activated carbons possess a wide range of pore size, typically from 2 to 2000 Å (Martinez et al., 2003). The pores are divided into three groups, the micropores with diameter less than 20 Å, mesopores with diameters ranging between 20 and 50 Å and macropores with diameter greater than 50 Å. The micropores constitute a large surface area (about 95% of

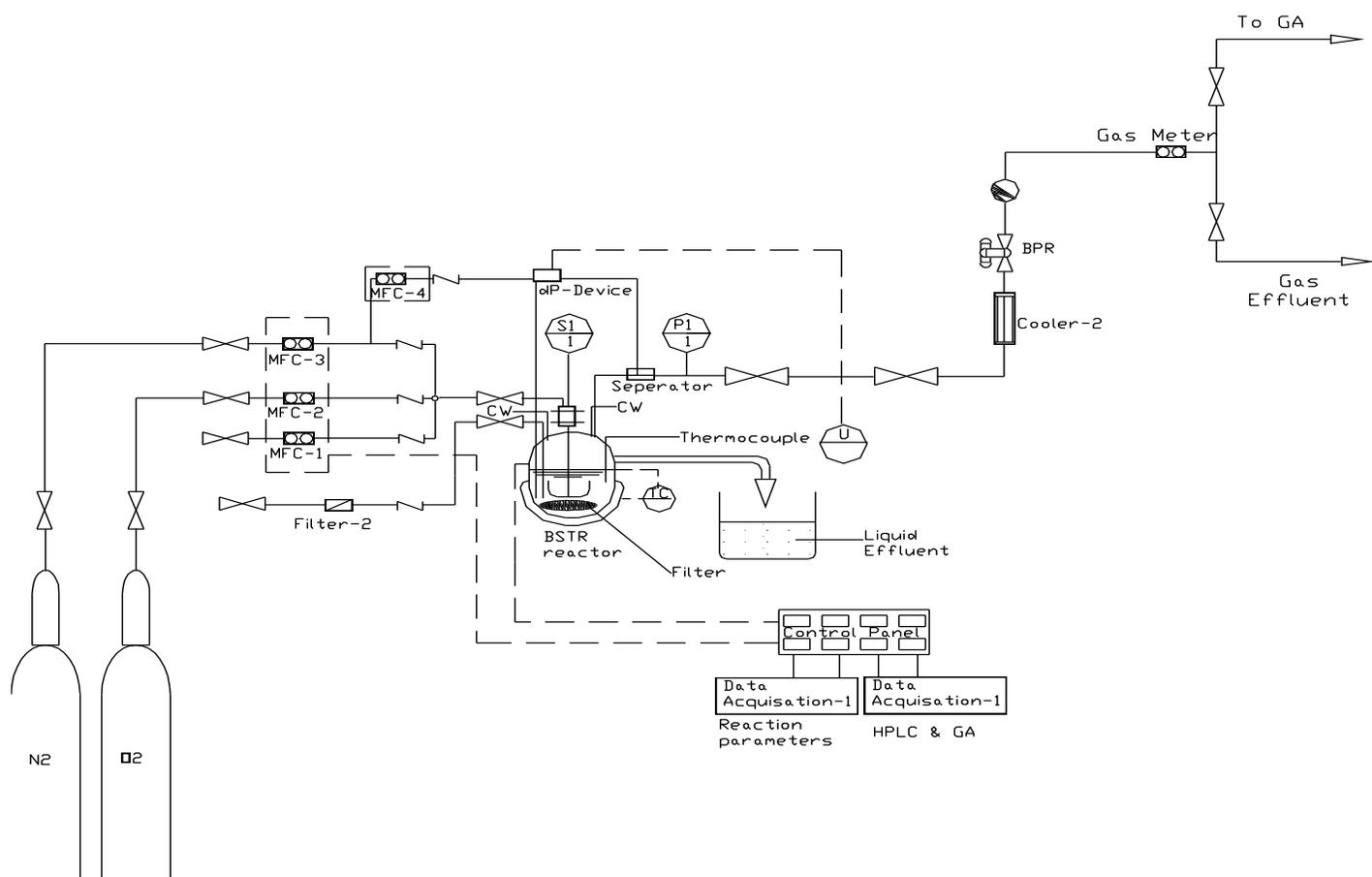
total surface area of activated carbon) and microvolume and therefore determine to a consideration extent of the adsorption capacity of a given activated carbon. However the molecular dimensions of the adsorbate are not too large to enter in micropores (Encyclopaedia of Surface and Colloid Science, Wikipedia). Macropores are not of considerable importance to the process of adsorption in activated carbon as their contribution to surface area does not exceed 0.5 m<sup>2</sup>/g. Accordingly the surface areas and porosity characteristics obtained in this study are accepted as shown in Table 2.

The surface area of cashew nut shell was much higher compared to that found in Peach stone (PS) and palm fruit shells (PFS). In addition the cashew nut shell (CNS) had higher microporosity of 69.0 compared to PFS and PS, 68.2 and 67.3%, respectively. The total pore volume of cashew nut shell was 0.4637 cc/g, which was also higher than that found in peach stone and palm fruit shell, 0.3097 and 0.2654 cc/g, respectively. However, CNS showed poor performance in CWPO of maleic acid compared to other ACs. This might be due to thermal stability structure of CNS, from thermal stability data CNS showed poor thermal stability compared to other ACs.

From the BJH adsorption (Dv (d) in (cc/Å/g)) data of the activated carbons show that, Cashew nut shell, peach stone and palm fruit shell had diameters ranging between 13.00 to 17.54 Å, 12.03 to 16.36 Å and 12.02 to 16.38 Å respectively. It has been reported that micropores carbons like the one obtained in this study are more effective to retain small molecules (Martinez et al. 2003). On the other hand, the mesopores carbon are better for adsorbing large molecules. Table 2 clearly shows that CNS, PS and PFS have both micropores and mesopores carbon properties.

Figures 2 to 6 show micrographs of activated carbons from SEM analysis for the three materials at different magnification. Figures 2 to 5 are micrographs of palm fruit shell and peach stone ACs, respectively. It can be seen that the particles have irregular shapes and consist of pores.

Figure 6 shows the SEM for cashew nut shell. The micrograph clearly shows that there are physical difference



**Figure 1.** A three-phase batch reactor BTR.

**Table 2.** Surface area and porosity characteristics of the three activated carbons under study.

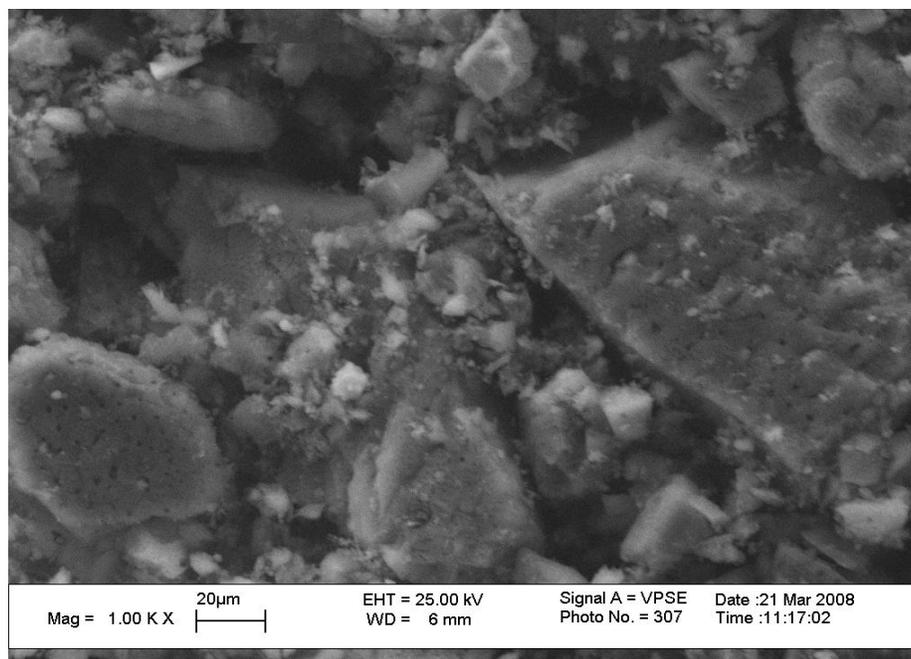
Sample name	Surface $m^2/g$	Micro-porosity (cc/g)	Micro-porosity (%)	Meso-porosity (cc/g)	Meso-porosity (%)	Macro-porosity (cc/g)	Macro-porosity %	Total porosity (cc/g)
PFS	389	0.1809	68.2	0.0643	24.2	0.0202	7.6	0.2654
PS	463	0.2138	69.0	0.0752	24.3	0.0207	6.7	0.3097
CNS	692	0.3120	67.3	0.1314	28.3	0.0203	4.4	0.4637

characteristics compared to PS and PFS. The micrograph also consists of irregular shapes.

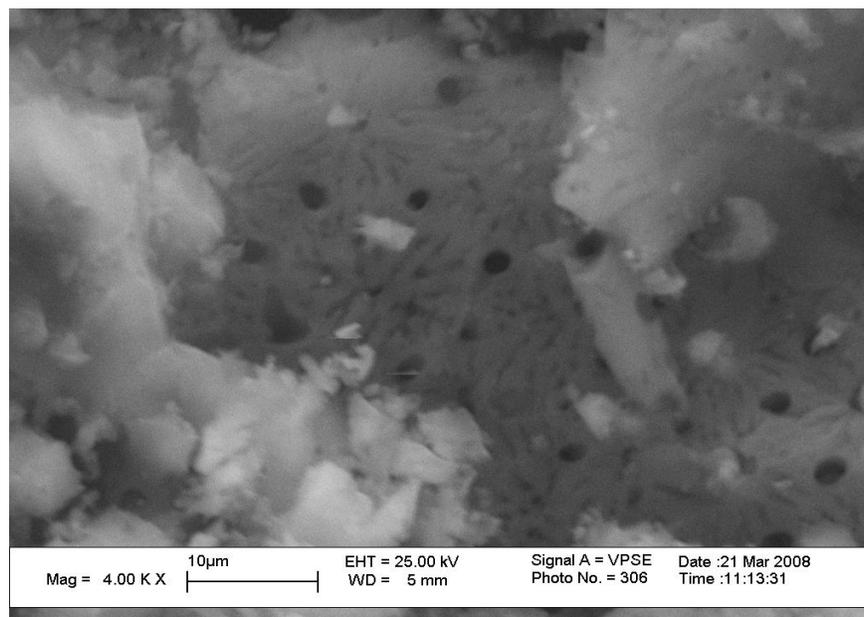
### Thermal stability

Thermogravimetric analysis (TGA) is an analytical technique for measuring the amount and rate of change in the weight of a material as a function of temperature or time. The changes in the mass can be caused by a variety of processes such as decomposition, degradation, sublimation, vaporization, adsorption, desorption, oxidation, and reduction (Vyazovkin, 2012). Figures 7

and 8 show results from thermogravimetric analyses (TGA) for the activated carbons. The maximum temperature of  $800^\circ\text{C}$  was used to ensure that the specimen weight was stable at the end of the experiment, implying that all chemical reactions were completed. This approach provided: oxidation temperature ( $T_{\text{max}}$ ) (Figure 7) and ash content (residual mass,  $M_{\text{res}}$ ) (Figure 8). In this context the oxidation temperature include temperature corresponding to the maximum weight loss rate ( $dm/dT_{\text{max}}$ ) and the temperatures corresponding to onset weight loss onset ( $T_{\text{onset}}$ ). The weight loss rate refers to the temperature of the maximum rate of oxidation, while the  $T_{\text{onset}}$  refers to the



**Figure 2.** Activated carbon from Palm fruit shell (low magnificatio 1.00X) SEM).



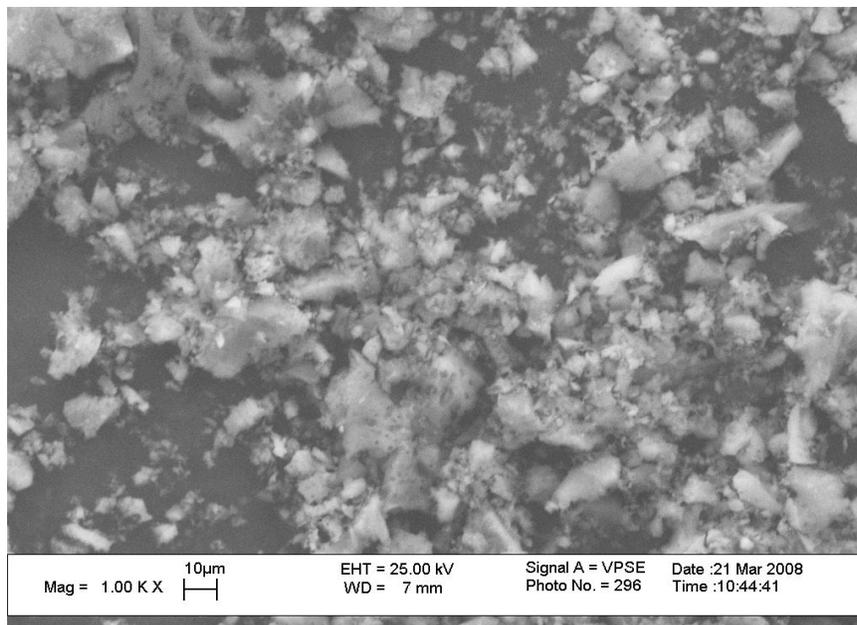
**Figure 3.** Activated carbon from Palm fruit shell (Modarately magnified (4.00X) SEM).

temperature when oxidation just begins.

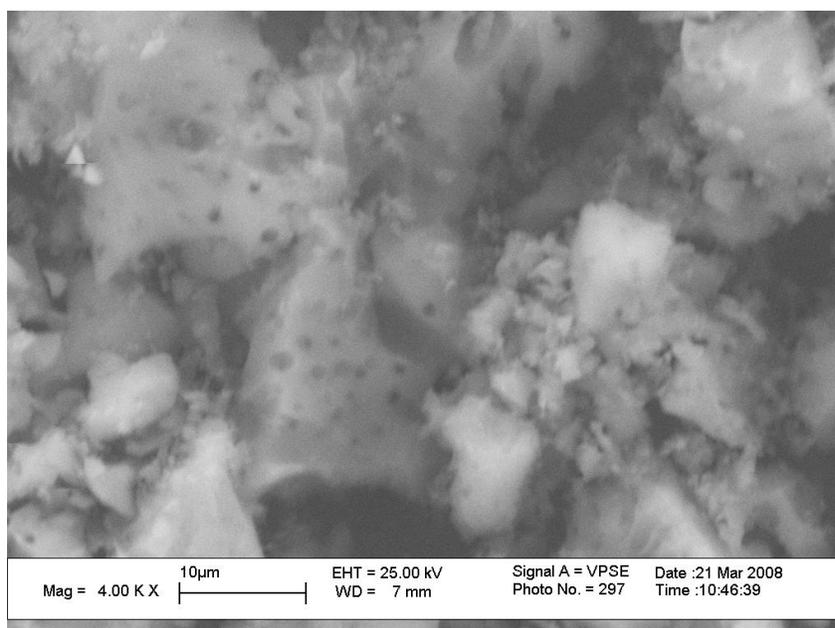
All the curves indicated that the activated carbons underwent a single-step weight loss process due to pyrolysis (Figure 7). The derivative thermogravimetric (DTG) curves in clearly show that the peach stone and palm fruit shell are thermally stable up to 400°C while cashew nut shells were stable up to 300°C (Figure 7). It

can also be seen that the mass loss graph vs. temperature/time for cashew nut shell is decreasing fast compared to other ACs Figure 8.

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of devolatilisation revealed that two pyrolysis stages occurred. The main pyrolysis stage was completed up to 600°C, while the



**Figure 4.** Activated carbon from peach stone (low magnification (1.00X) SEM).



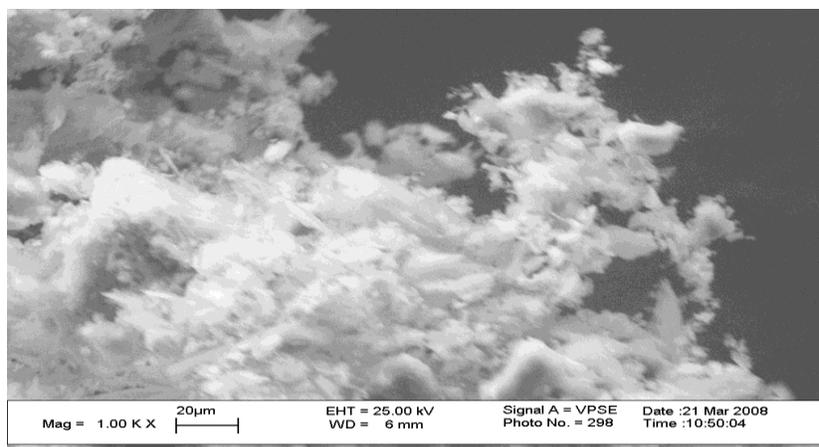
**Figure 5.** Activated carbon from peach stone.(Moderately magnified (4.00X) SEM).

second one continued until the test completion at 700°C. According to Skodras et al. (2005) and Tsamba et al. (2005) the pyrolysis for CNS was occurring in the same range. According to Fogler (1999) the DTG peak height is directly proportional to reactivity and the correspondent temperature is inversely proportional to this chemical activity parameter. Applying this theory, it can be concluded that reactivity of PFS is higher than that of

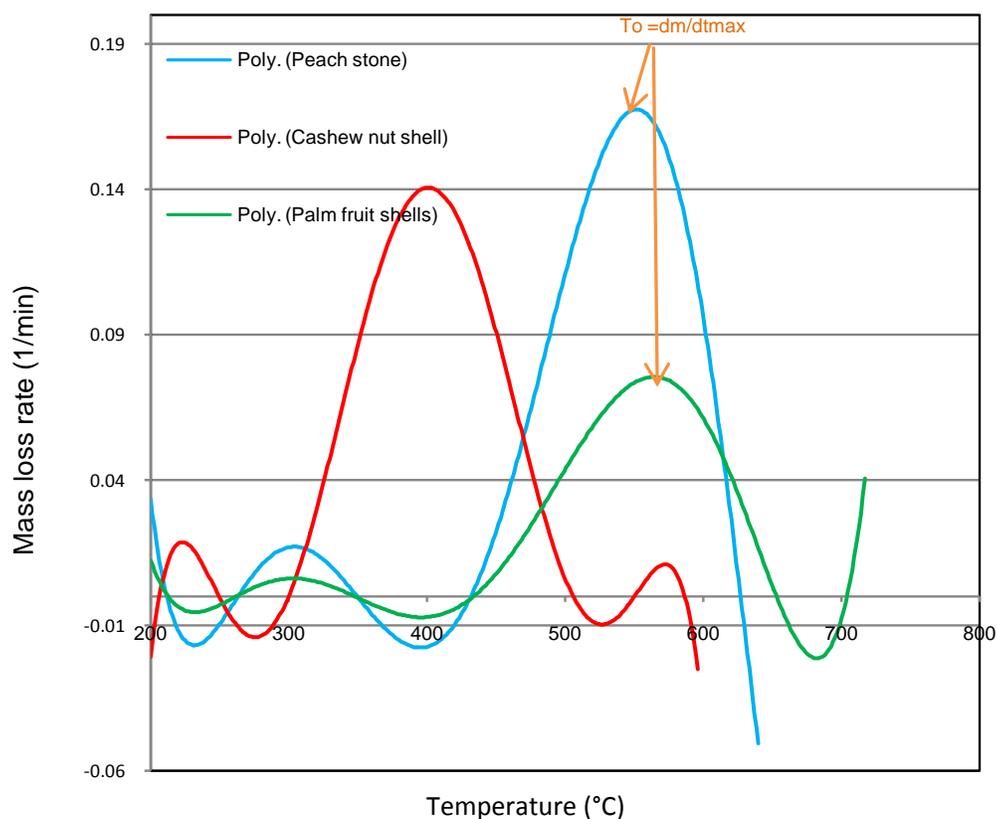
CNS and PS.

### Blank experiments

Blank experiments (that is with no activated carbons) were conducted under a nitrogen gas environment to determine whether a non-catalytic reaction, adsorption or vapour-liquid equilibrium effects were taking place under



**Figure 6.** Activated carbon from Cashew nut shell.



**Figure 7.** Mass loss rate (DTG) from the thermal decomposition of CNS, PS and PFS at 20°C.

experimental conditions. These experiments were performed at 50°C, atmospheric pressure and liquid residence time of 90 min. The results show that there was negligible maleic acid conversion (about 0.5% of the initial maleic acid concentration). Introduction of hydrogen peroxide in the reaction while maintaining the same

reaction conditions slightly improved the conversion to about 2%. This could be attributed to either homogeneous reaction of maleic acid with hydrogen peroxide or reaction caused by presence of impurities in the solution or catalytic activity of the reactor material. The similar blank results were reported by Daniel and

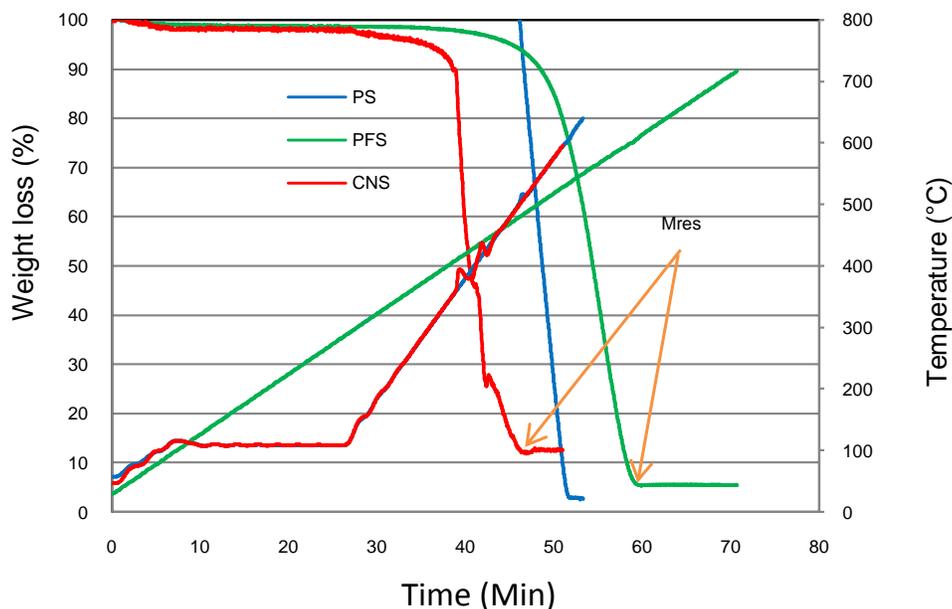


Figure 8. Weight loss %-Temperature with time for the PFS, PS and CNS.

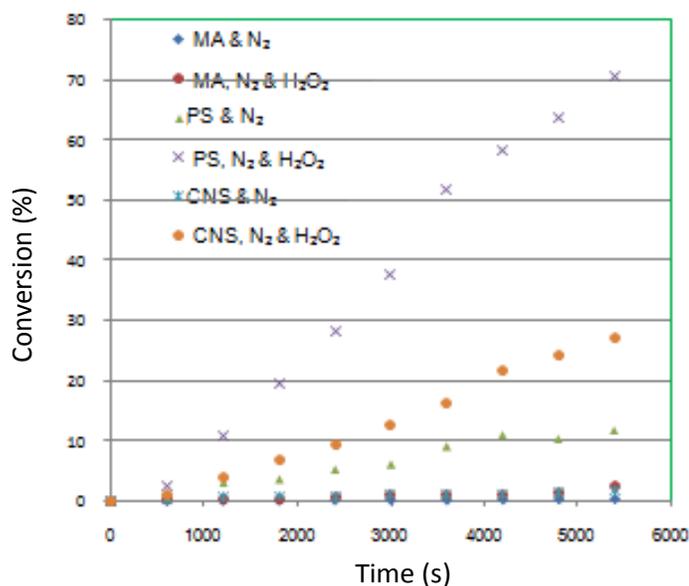


Figure 9. Blank experiments of conversion against time graph; Conditions: 50°C,  $C_0 = 0.01$  and effect of  $H_2O_2$ , activated carbons = 0.5 g/l.

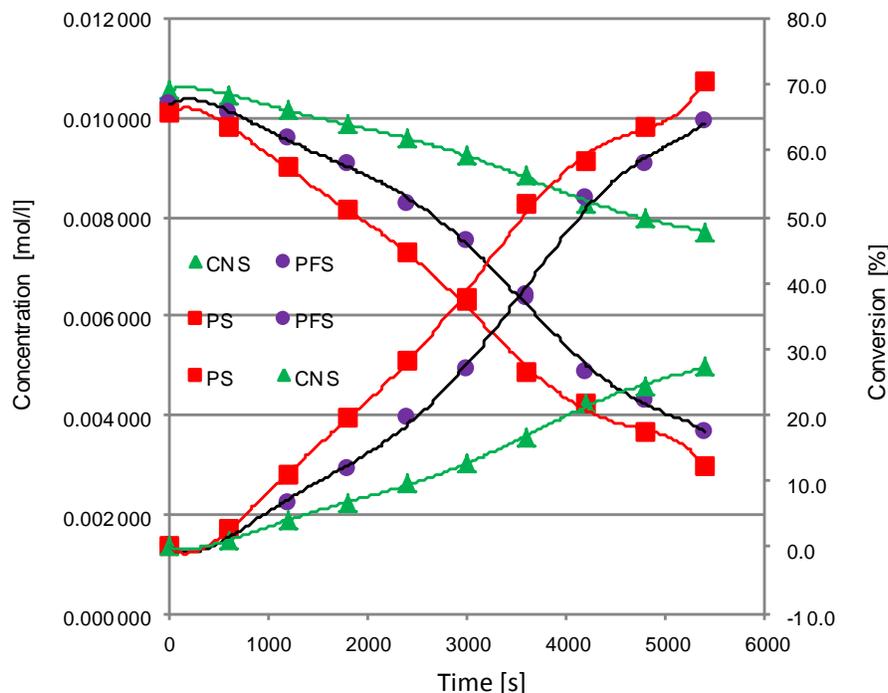
Katima (2009). The effect of ACs loading on the CWPO of MA is shown in Figure 9. Blank experiments were used as reference for zero ACs loading. In general, the conversion of MA is enhanced in the presence of  $H_2O_2$  and ACs. Two ACs among the three were tested in the blank experiments, the peach stone (the best performance in CWPO) and cashew nut shell (the least performance in CWPO). The introduction of peach stone

or cashew nut shell with  $N_2$  only in the reactor gave 11.9 and 1.8% of MA respectively, Figure 9. In the absence of  $H_2O_2$ , MA oxidation on ACs particularly CNS was comparable to that observed with  $H_2O_2$  and  $N_2$ .

The reaction between maleic acid, hydrogen peroxide, activated carbons and nitrogen gas has improved the conversion of maleic acid to 70.7 and 27.3% for peach stone and cashew nut shell respectively. These results revealed that without  $H_2O_2$  the conversion is low, suggesting that the performance of the peach stone or cashew nut shell (activated carbons) in the oxidation of maleic acid is highly influenced by the presence of  $H_2O_2$ . The catalytic oxidation using hydrogen peroxide is a more efficient process as compared to catalytic oxidation using air, since hydrogen peroxide is a stronger oxidant (Britto et al., 2008). Hydrogen peroxide is highly reactive and non-selective oxidants, which has been used to degrade many organic compounds (Hu, 2001). Rubalcaba et al. (2007) reported that, adding  $H_2O_2$  to the CWAO process not only increases pollutant removal but also leads to higher mineralisation of the remaining oxidation products. This is because hydrogen peroxide acts as a free radical initiator, providing hydroxyl radicals that increase pollutant removal (Valkaj, 2011).

#### Performance of the three activated carbons in catalytic wet peroxide of maleic acid

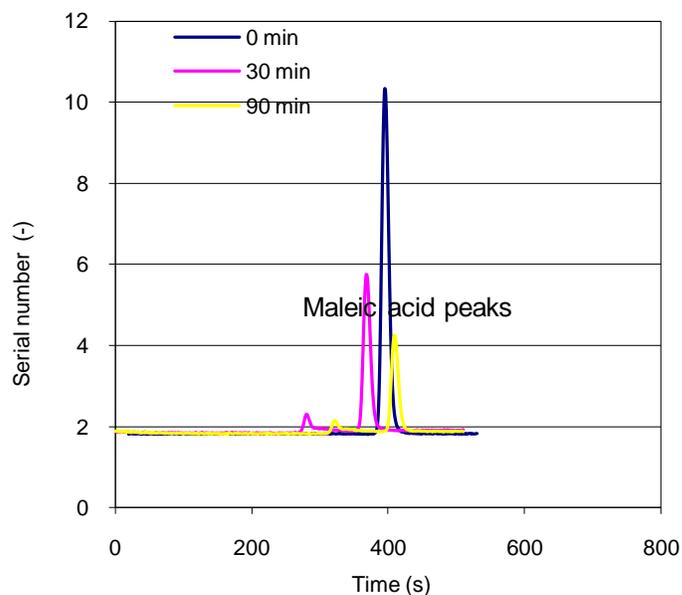
Figure 10 shows the conversion/concentration of MA vs. time. The ACs were used as catalysts and hydrogen peroxide was used as oxidizing agent. The influence of the activated carbons on the degradation of maleic acid



**Figure 10.** Influence of catalyst supports in CWPO of maleic acid. Conditions,  $C_{a_0}$  = 0.01 mol/L, Temperature = 50°C, activated carbons = 0.5 g/l.

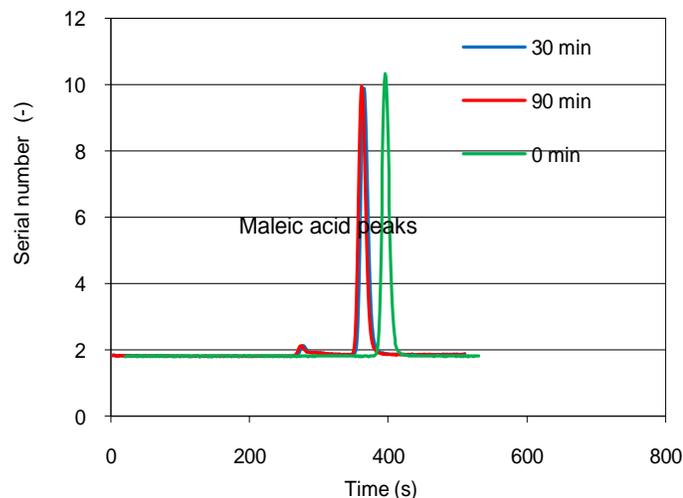
was studied at 0.01 mol/L of maleic acid, 50°C and 0.5 g/l of activated carbons. It was found that cashew nut shell posses very low catalytic activity and had little adsorption capacity for maleic acid of about 27.3% after 90 min of reaction time. In contrast, due to suitable properties of the peach stone and palm fruit shell showed better catalytic activity in the degradation of maleic acid. The conversion of maleic acid using peach stone and palm fruit shell were 70.7 and 64.4%, respectively after 90 min of the reaction time. This might be due to their good porosity characteristics, thermal stability and porous structure of PFS and PS. Activated carbon alone is a good adsorbent for non-biodegradable organic waste pollutants (Stuber et al., 2005). Most forms of activated carbon are non-polar in nature, so they have the greatest affinity for other non-polar substances. As a result, they are most effective in the removal of a variety of organic pollutants. Activated carbon is an effective absorbent primarily due to its extensive porosity and very large available surface area (Jason, 1996). Ash et al. (2006) reported that the adsorption capacity of certain carbon is known to be a function of porous structure, chemical nature of the surface and pH of the aqueous solutions. Figures 11 and 12 show maleic acid chromatograph peaks for peach stone and cashew nut shell respectively.

It is clearly seen that the maleic acid peaks are decreasing when peach stone was employed as catalyst and after 90 min the maleic acid peak was almost a quarter of the original peak (Figure 11). Aguilar et al.



**Figure 11.** Chromatograph peak for peach stone; conditions  $C_{a_0}$  = 0.01 mol/L; Temperature = 50°C; activated carbons = 0.5 g/l.

(2005) used a commercial peach stone AC in the catalytic wet oxidation of aqueous methyl and dimethylamines and it was found to be a good catalyst, it has also been proven in this study that peach stone was the best catalyst. On the other hand, cashew nut shell



**Figure 12.** Chromatograph peak for cashew nut shell; conditions  $C_{a_0} = 0.01$  mol/L; Temperature =  $50^\circ\text{C}$ ; activated carbons =  $0.5$  g/l.

proved to perform poorly in the degradation of maleic acid (27.3% conversion of maleic acid). After 20 and 90 min, the maleic acid peaks (Figure 12) were almost the same and small difference was observed between 20/90 min and the original peak which explained that the conversion of maleic acid in the presence of CNS as catalyst was low though it had the best porosity characteristics compared to other ACs. This might be due to the stability structure of CNS. Thermal stability data for CNS showed less thermal stability compared to other ACs.

The catalytic wet peroxide oxidation of maleic acid using activated carbons has been reported elsewhere (Kaale, 2008). All these reasons and good preparation of the sample make the activated carbons to be used as catalyst.

## Conclusions

Ps, PFS and CNS pyrolysis was successfully prepared, characterized and tested. Differences and similarities between these biomass wastes were found and discussed. The activated carbons had maximum Brunauer Emmett-Teller (BET) surface areas of 389, 428 and  $692$   $\text{m}^2/\text{g}$  for palm fruit shell, peach stone and cashew nut shell, respectively. TG and DTG results showed that, the PS and PFS materials are thermally more stable than CNS. The catalytic wet peroxide oxidation (CWPO) of maleic acid was carried out using the three activated carbons. The PS and PFS showed better conversion of maleic acid, 70.7 and 64.4%, respectively as compared to CNS which had the conversion of 27.3%. The result demonstrated that, the PS and PFS are effective catalysts for liquid phase

oxidation of maleic acid than cashew nut shell and can therefore be applied for catalytic wastewater treatment systems.

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