

The Influence of Microwave Irradiation on Physicochemical Characteristics of Nitrogen-Enriched Carbon and Its Performance in Biogas Desulfurization

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Research Article

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Abstract

In this work, palm shell activated carbon (PSAC) was functionalized with nitrogen groups via urea impregnation, followed by the synthesis of microwave (MW) and conventional heating (TH) at temperature of 950 °C, 500 ml/min of N₂ flow rate and 30 minutes of heating time. The effects of MW and TH heating on the modified PSAC adsorbent were analyzed and compared towards hydrogen sulfide (H₂S) removal. The efficiency of H₂S removal was calculated based on adsorption capacity of the adsorbent samples. Nitrogen-functionalized PSAC that was synthesized via MW heating (PSAC-MW) has shown better performance with adsorption capacity of 356.94 mg/g. The chemical and physical characteristics of all adsorbent samples were studied and analyzed by using CHNS elemental analysis, N₂ adsorption-desorption analysis, SEM, TGA and FTIR analysis. The adsorbent sample that was synthesized via MW heating showed significant characteristics, such as high surface area with sponge-like structure, in which there are additional pores developed inside the existing pores. Instead of that, there was an observation on 'hot spot' appearance during the MW heating process, which is believed to be responsible for the development of physical and chemical characteristics of the PSAC-MW adsorbent. These characteristics indirectly contribute to the high removal of H₂S.

1.0 Introduction

In recent years, Malaysia is listed as the second leading of palm oil producer in the world. With the increase in the worldwide demand, the production of palm oil products indirectly lead to the environmental pollution. In 2015, up to 75 million m³ of palm oil mill effluent (POME) has been generated annually (Ahmed et al. 2015). To encounter this challenge, POME has been used in anaerobic digestion as a feedstock for biogas production (Ahmed et al. 2015; Foong et al. 2021). In general, POME biogas can be classified as the source of greenhouse gases (GHG), with a composition of 65% of methane (CH₄), 35% of carbon dioxide (CO₂) and traces of hydrogen sulfide (1000 – 3000 ppm of H₂S) (Asis et al. 2016). The GHG potential of CH₄ is incredibly high, which is predicted to a hundred years of global warming potential (Unece 2021). As a result, this concern urges the researchers to benefit the utilization of CH₄ as a renewable energy. Prior to recover high energy content in the biogas, the traces of H₂S need to be eliminated.

H₂S is a very toxic and harmful gas with unpleasant smell, that is not only dangerous to human health but also cause detrimental effect to the gas engine and metal parts, due to its corrosive behaviour (Ou et al. 2020). To accommodate this problem, numerous methods have been explored, such as chemical oxidation, biological treatment, electrochemical abatement, catalytic conversion, precipitation, chemical scrubbing, incineration, and adsorption (Wiheeb et al. 2013). Among these methods, adsorption onto lignocellulose adsorbent has been widely employed due to its effectiveness in removing gaseous pollutant (Supanchaiyamat et al. 2019; Georgiadis et al. 2020).

Significant interest on the use of lignocellulose derived materials in the adsorption application is due to it is cheaper and abundantly available. Activated carbon (AC) derived from lignocellulose biomasses have been utilized for various gas pollutant adsorption, such as H₂S, CO₂ and SO₂ (Nor et al. 2013; Supanchaiyamat et al. 2019). AC is a promising adsorbent due to its high adsorption capacity in capturing target pollutants. This is contributed by its high surface area, well-developed pore structure, and availability of various functional groups. Palm shell biomass consists of physical and chemical characteristics that are suitable to be converted into AC. The selection of palm shell as a precursor in this research work due to it is relatively economic and abundantly available (Phooratsamee et al. 2014; Habeeb et al. 2017; Nor et al. 2018). Furthermore, the conversion of this biomass into palm shell activated carbon (PSAC) could contribute to zero carbon emission, as palm shell and biogas are by-products that were produced from the palm oil mill.

To craft different types of functional groups onto AC's structures, chemical activation/modification need to be introduced. The modification is responsible for the oxidation of H₂S to be converted into elemental sulfur during the adsorption process (Zhang et al. 2018). There are various types of chemicals that could improve the adsorption capacity of AC, which includes the cooperation of metal oxide nanoparticle (i.e., CuO, NiO, Fe₂O₃) (Thanakunpaisit et al. 2017; Orojlou et al. 2018; Yang et al. 2019) and the modification of surface chemistry of the carbon matrix (i.e., KOH, NaOH, NaCO₃, urea, NH₃), in which created additional elements onto the carbon's surface (Adib et al. 2000; Habeeb et al. 2017; Lau et al. 2018; Chen et al. 2021). Among these modifications, the introduction of nitrogen element onto the carbon matrix has caught the attention, where the association of nitrogen functional groups within the carbon matrix could enhance the carbon's basicity, which provides the best platform for the oxidation of acidic gas such as H₂S to be happened (Chen et al. 2021). As reported by (Kan et al. 2019), the use of nitrogen-doped ordered mesoporous polymer spheres could capture the H₂S up to 13.4 mmol/g, where the adsorbent was enriched with nitrogen sites of pyridinic and pyrrolic groups, that showed strong interaction with H₂S. (Yang et al. 2019) also proved the fact that the addition of nitrogen element into AC in capturing the H₂S show twice increment, with 62.5 mg/g of breakthrough capacity compared to unmodified adsorbent. The modification of nitrogen functional groups onto AC's structure is usually prepared via thermal synthesis of nitrogen chemical-driven (i.e., urea, melamine, NH₃) at temperature ranging from 300 to 950°C (Nor et al. 2018; Yang et al. 2019; Chen et al. 2021).

Typically, the synthesis of AC was usually done via conventional thermal heating method, where the external heat source is directly supplied to transfer the heat into the system. However, this conventional approach leads to non-uniform heating, longer heating duration and high synthesis temperature, which directed to high energy and cost consumption (Kazmierczak-Razna et al. 2016). MW heating method is an interesting alternative that caught researchers' attention to cater the conventional heating problems (Kazmierczak-Razna et al. 2016; Darvishi et al. 2017; Nor et al. 2018). The use of MW heating source could promote an efficient heating mechanism, which requires a short contact time. Furthermore, it was reported that MW energy can be easily converted into heat and quickly absorbed by activated carbon (Ibrahim et al. 2020).

Herein, this work is focusing on investigating the incorporation of nitrogen functional groups onto the PSAC's porous structure through urea impregnation at 950°C under different heating mechanisms (conventional thermal and MW heating). For this purpose, the optimized parameters from our previous research studies (Nor et al. 2018) were employed to compare the effect of conventional thermal and MW heating method on nitrogen-modified PSAC adsorbent. The physicochemical characteristics of the raw and modified PSAC adsorbents were correlated with the performance of H₂S adsorption capacity. The results demonstrate that the MW heating method demonstrate a great potential in H₂S removal at room temperature, whilst improving the adsorbent's characteristics via tailored nitrogen functional groups.

2.0 Methodology

2.1 Chemicals and Materials

Commercial palm shell activated carbon was purchased from KD Carbon Sdn. Bhd., Malaysia. The raw sample is indicated as PSAC. Nitric acid, HNO₃ (AR, 65%), urea, CO(NH₂)₂ (AR, 99%), ethanol, C₂H₅OH (AR, 96%) were obtained from Merck, Malaysia. Gases used in this work consists of H₂S in CH₄ gas (10,000 ppm of H₂S in CH₄ as balance, 99.995%) was purchased from KNY Industrial Gas Sdn. Bhd., while CH₄ gas (99.995 %), CO₂ gas (99.9 %) and N₂ (99.999 %) were supplied by Goldengas Industrial Supply Sdn. Bhd.

2.2 Adsorbent Pre-oxidation

The PSAC was ground and sieved to 1 – 2 mm size. It was pre-oxidized by using 50 wt% of HNO₃ for 4 h at ambient temperature. Then it was washed out with distilled water to remove excess acid and water-soluble products. The purpose of pre-oxidation of the PSAC is to enhance surface oxidation state of the adsorbent (Adib et al. 2000). The pre-oxidized PSAC sample was then dried at 110°C for 24 h, to remove excess water.

2.3 Urea Impregnation

Prior to the conventional thermal and MW heating, the pre-oxidized PSAC sample was impregnated with urea, to tailor nitrogen functional groups onto the adsorbent structures. The mixture containing pre-oxidized PSAC (30 g), urea (20 g), and ethanol (100 ml) was stirred (200 rpm) at room temperature for 5 h. Next, the mixture was boiled to evaporate the alcohol, and was dried at 110°C in a drying oven (Yang et al. 2019).

2.4 Conventional Thermal Heating

The conventional thermal heating of urea impregnated PSAC was synthesized by using a vertical-type furnace (Carbolite, CTF 1200). The heating parameters were set to temperature of 950°C with the heating rate of 15°C/min. The heating time was set to 30 min, under 500 ml/min of N₂ flow rate. The N₂ gas was supplied to provide inert condition for lignocellulose carbon throughout the heating process. To remove

excess urea, the final adsorbent sample was washed with boiling water and was dried in an oven at 110°C for 24 h. The sample was indicated as PSAC-TH.

2.5 Microwave Heating

MW heating was introduced to urea impregnated PSAC at temperature of 950°C with 500 ml/min of N₂ flow rate and 30 min of heating time. The sample was first placed into a double-walled quartz annular column (inner diameter: 1.5 cm, outer diameter: 3.5 cm, height: 30 cm) prior to locate in a MW oven as illustrated in Fig. 1. The MW heating unit consists of a multimode domestic microwave oven (Cornell, CMO-EL17L) with a maximum power output of 1150 W and frequency of 2.45 GHz, a double-walled quartz annular reactor, mass flow meter, N₂ gas cylinder and temperature controlling unit. For MW's temperature controlling unit, a K-type thermocouple, 25 cm long with sheath diameter of 1.5 mm was placed inside the quartz annular column. The MW's heating temperature was maintained by modification of the power supply circuit that has been equipped with PID controller. The MW heating apparatus (magnetron) was modulated in an on-off cycle to maintain a constant MW's heating temperature. The final product was washed and dried similar as PSAC-TH sample. The sample prepared by MW heating was indicated as PSAC-MW.

To study the effect of various MW heating temperature on the nitrogen-modified adsorbent, the MW temperature were varied from 500 to 900°C, with constant N₂ flow rate and heating time. The samples were indicated as MW500, MW600, MW700, MW800, and MW900.

2.6 H₂S adsorption Analysis

A custom designed H₂S desulfurization rig as shown in Fig. 2 was employed to study the performance of the modified adsorbents toward H₂S removal. An amount of 0.75 g of the adsorbent sample was placed in the middle of a fixed bed stainless-steel adsorption column (length: 450 mm, internal diameter: 12.5 mm) that was supported with approximately 0.5 g borosilicate glass wool. A simulated biogas that consists of 59.7 vol% of CH₄, 40 vol% of CO₂ and 3000 ppm of H₂S was passed through the column at constant flow rate and temperature of 200 ml/min and 30°C, respectively. The biogas mixture was simulated to imitate the actual composition of biogas collection pond in Felda Besout palm oil mill, Malaysia. The composition of the simulated biogas was manipulated by regulating the flow rate of individual gas using mass flow controllers (Aalborg, AFC26). To achieve 40% of relative humidity (RH) prior entering the column, the H₂S gas was mixed with CH₄ and CO₂ gases that were passed through the humidification system at a water bath temperature of 40°C. The outlet concentration of H₂S was analysed using an electrochemical H₂S sensor (IMR500 gas analyser), that was calibrated for 0-5000 ppm range. To ensure the safety of workstation, a ventilation system equipped with exhaust fan was installed on top of the biogas desulfurization rig, to aerate the H₂S gas to the fume hood scrubber.

2.7 Adsorbent Characterizations

The pH of the modified adsorbent was measured using a mixture of dried adsorbent (0.4 g) and water (20 mL) that was agitated for 24 h to reach equilibrium. The pH of the solution was measured by using desktop pH meter (Mettler Toledo). The elemental analysis was performed by using a Perkin Elmer 2400 CHNS Analyzer. N₂ adsorption-desorption test was done in an Autosorb-1-MP instrument (Micromeritics ASAP 2020) to determine the specific surface area (S_{BET}), average pore diameter and pore volume of the adsorbent. The samples were heated at 120°C, followed by 5 h of degassing process. The proximate analysis (moisture, volatile organic matter, fixed carbon, and ash) was carried out using thermogravimetric analyser (TA Instrument SDT Q600). Fourier Transform Infrared (FTIR) of nitrogen-modified samples were analysed using Thermo Scientific (Nicolet iS10) equipment. The spectrum of the sample was displayed after 64 seconds with corrected background noise. The adsorbent surface morphologies were analysed by using of Scanning Electron Microscopy (SEM) (Quanta FEG 450) at an accelerating voltage of 3kV at magnification of 5k.

3.0 Results And Discussion

3.1 H₂S Adsorption Study

To understand the performance of nitrogen modified PSAC adsorbents towards H₂S removal, the adsorbents that were synthesized via thermal heating (PSAC_TH) and microwave heating (PSAC_MW) were analysed by using H₂S adsorption study. The physical and chemical characteristics of the modified adsorbents were investigated and will be discussed in detail in the following sections. Commercial raw palm shell activated carbon (PSAC) adsorbent was used as a baseline to evaluate the performance of the nitrogen modified adsorbents in this work. To be noted, the nitrogen modified adsorbents that were synthesized via conventional thermal and MW heating methods were performed under similar parameters.

Figure 3 illustrated the H₂S breakthrough curves for all PSAC-based adsorbents (PSAC, PSAC-TH and PSAC-MW). Among all, the breakthrough curve of PSAC-MW shows better performance, due to it shows prolonged breakthrough time and extended exhaustion time compared to the PSAC and PSAC-TH. The breakthrough capacity was calculated at breakthrough time, where $C_t/C_o = 0.05$ and the total adsorption capacity was calculated at $C_t/C_o = 0.95$ (exhaustion time), where C_t is the H₂S concentration at time t and C_o is the H₂S's inlet concentration. Theoretically, the H₂S breakthrough capacity is defined as the mass of the adsorbate (H₂S) removed by the adsorbent at breakthrough concentration or the maximum acceptable (desired), while the total H₂S adsorption capacity is defined as the total mass of the adsorbate (H₂S) removed by the adsorbent when the outlet concentration of H₂S is almost saturated or at exhaustion time (Shang et al. 2012). The H₂S breakthrough-curve characteristics along with the pH values of the adsorbents are shown in Table 1.

Table 1
H₂S breakthrough-curve characteristics and pH values of PSAC-based adsorbents

Sample	pH	Breakthrough time, $t_{0.05}$ (min)	Exhaustion time, $t_{0.95}$ (min)	Breakthrough capacity (mg/g)	Total adsorption capacity (mg/g)
PSAC	7.48	2.0	116.17	3.25	61.14
PSAC-TH	8.02	30.0	150.33	32.57	78.31
PSAC-MW	8.31	87.17	771.0	94.20	356.94

Compared to the PSAC and PSAC-TH, the PSAC-MW shows the highest H₂S breakthrough capacity and total adsorption capacity, with 94.20 mg/g and 356.94 mg/g, respectively. From results in Table 1, the presence of surface basicity with a pH value of 8.31 indicates that it influences the adsorption capacity of the PSAC-MW. The PSAC-MW had the highest surface basicity compared to others. Thus, it can be presumed that the basicity is one of the factors that could lead to the efficient H₂S adsorption. The presence of surface basicity in the adsorbent could improve the chemisorption of acidic H₂S to sulfur (S). The chemisorption caused more S deposited onto the adsorbent, in which the dissociation of H₂S covalent bond with nitrogen functional groups tailored happened. As reported by (Adib et al. 2000), the presence of basicity condition of the adsorbent with a typical pH value in the range of 6 to 8 could contribute to high oxidation of H₂S. In this work, the pH values of the PSAC-TH and PSAC-MW are pH 8.02 and 8.31, respectively, which indicates the PSAC-TH was less basic compared to the PSAC-MW. However, the same trend was not observed in the raw PSAC sample, where there is no nitrogen modification involved. This finding supports the high adsorption capacity of H₂S using PSAC-MW adsorbent.

3.2 Effect of Surface Characteristics

Generally, high H₂S adsorption capacity is frequently related to adsorbent's surface area, type of porous structure, available surface functional groups, and the possible chemisorption that might occurred within the adsorbent structure (Bazan-Wozniak et al. 2017). The physical and surface properties of the PSAC-based adsorbents are shown in Table 2. From the results, it seems the MW heating method could improve the physical characteristics of the nitrogen modified PSAC-based adsorbent, especially on surface area and pore structures. Referring to the previous works, impregnation of urea via conventional thermal heating method, results in enhancement of physical structure of carbon materials (Adib et al. 2000; Seredych and Bandosz 2008; Nowicki et al. 2015; Kaźmierczak-Raźna et al. 2019; Saad et al. 2020). Similar trend was observed in surface properties of the PSAC-TH, where its surface area and pore structure were well developed compared to the raw PSAC. (Adib et al. 2000) reported, AC that was undergo high thermal heating at temperature of 950°C, would reduce the carbon grains for about 30%, due to the increase in the adsorption energy. In consequence, this justifies the significance of the PSAC-TH's surface area was reduced by 10% compared to the raw PSAC.

Table 2
Physical and surface properties of PSAC-based adsorbents

Sample	BET surface area (m ² /g)	Micropore volume (cm ³ /g)	Total pore volume (cm ³ /g)	Average pore width (nm)	V _{mic} /V _t
PSAC	957.00	0.40	0.51	2.15	0.78
PSAC-TH	896.30	0.30	0.47	2.12	0.63
PSAC-MW	1000.62	0.35	0.51	2.03	0.69

Figure 4 shows the relationship between total surface area and total H₂S adsorption capacity that was further investigated by using nitrogen-modified PSAC-based adsorbents that were synthesized at different MW heating temperature, ranging from 500 to 900°C. The increase in MW heating temperature, caused enhancement in the PSAC's surface structure, where an increase in surface area of the adsorbents were observed. This clarifies that the increase in MW heating temperature could improves the degree of surface area development. Additionally, with the influence of nitrogen functional groups, the enhancement in surface area and porous structures offering spacious space to collect the H₂S, which indirectly increase the total H₂S adsorption capacity, as in MW900 performance. From Fig. 4, at 500°C of MW heating temperature, the total H₂S adsorption capacity is only 161.5 mg/g, whereas at 900°C of MW heating temperature, the total H₂S adsorption capacity is up to 356.9 mg/g. This contributes a remarkable difference in the H₂S adsorption capacity when the MW heating temperature increased. Surface characteristics of the PSAC-MW adsorbents play an essential role in the accessibility of nitrogen functional groups integration into the carbon structures. The influence of basicity in the PSAC-MW adsorbent could further assist in the chemisorption of H₂S, where the adsorbent small and narrow pore structures could help to immobilize the H₂S. Consequently, an increase in H₂S adsorption capacity was observed by the PSAC-MW adsorbent, as increase in MW heating temperature.

The growth in surface properties of the nitrogen-modified PSAC-based adsorbent is presumed related to the mechanism of MW heating itself. During the MW heating, carbon material is subjected to the electromagnetic field, where the delocalized π-electrons start to move through the broad areas within the material (Kaźmierczak-Raźna et al. 2019). (Menéndez et al. 2010) explained, carbon material that was subjected to the electromagnetic and induced current heating can further rise to hot spot establishment at a very high temperature, which indirectly subject to the absorption of MW energy into the carbon material. The hot spot establishment via MW heating is recognized as a great development for the adsorbent itself. The hot spot was discovered during the MW heating study as shown in Fig. 5. The hot spot was seen in red coloured, in the middle of the adsorbent's placement inside the Quartz column.

The correlation between pore size distribution and their involvement onto the porosity of the PSAC-based adsorbents is shown in Fig. 6. The PSAC-MW has high pore volume for average diameter of < 20 Å of pore width, which exhibits well pore distributions. Based on the average pore diameter, the PSAC-MW pore

width was narrower and had the highest pore volume compared to the PSAC and PSAC-TH. (Ren et al. 2020) suggested that carbon adsorbent that has small pore structure, preferably in micropore size are efficient for H₂S adsorption to be happened. The micropore size of the PSAC-MW could confine the H₂S molecules within the pores whilst keeping the molecules from escaping from the carbon material. The H₂S is a small molecule with a diameter of 3.6 Å (Shah et al. 2017), in which smaller pore structure is more preferable for the physisorption and chemisorption to occur. This occurrence may possibly improve the ability of H₂S adsorption, in which the reaction between the H₂S and nitrogen functional groups could effortlessly happen via trapping the gas molecules into smaller and narrower pore structure. The shrinkage of pore width in the MW modified adsorbent provides better structures compared to the PSAC, where the H₂S molecules could be trapped and adsorbed more. This theory can be applied for both PSAC-TH and PSAC-MW. The same trend was observed in the nitrogen modified PSAC-based adsorbents at different MW heating temperature (Fig. 7), where their micropore volumes observed were lesser than the PSAC. As increase in the MW heating temperature, the micropore volume of the adsorbents seem to be improved. Pore size distribution of the adsorbents at different MW heating temperatures indicates an increment in the micropore volume of pore widths < 40 Å.

3.3 Effect of Surface Chemistry

The results of proximate and elemental analysis of the PSAC-based adsorbents are presented in Table 3, whereas the elemental distribution of the adsorbents is illustrated in Fig. 8. The proximate analysis of all samples shows a high percentage in carbon content, which indicates the main component of the adsorbent is activated carbon. Compared to the nitrogen modified adsorbents, the PSAC was rich in volatile and moisture content. The elemental analysis data show significant amounts of nitrogen element in the PSAC-TH and PSAC-MW compared to the PSAC. The presence of nitrogen element in both PSAC-TH and PSAC-MW are owing to the easiness of nitrogen functional groups incorporated into the carbon matrix as aromatic ring component, especially at high temperature (Li et al. 2020). Thus, the use of high temperature (950°C) in producing both PSAC-TH and PSAC-MW, assisted in the integration of nitrogen functional groups into the carbon matrix. It was observed that the PSAC-MW contains higher nitrogen content (2.89 %) compared to the PSAC-TH (0.49%). Apart from that, an increase in carbon content for both PSAC-TH and PSAC-MW was also observed. The increase in the carbon content was due to the high degree of re-heating during the pyrolysis process of the modified adsorbents that underwent both thermal and MW heating. Besides the influence of high MW temperature, high surface area of the PSAC-MW (1000.62 m²/g) is another factor that allows the accessibility of nitrogen functional groups to be integrated into carbon's crystalline edges. This finding strengthens the theory that the use of MW heating possibly will enhance the AC characteristics that consists of high content of heteroatom (in this case nitrogen functional groups). The significant amount of nitrogen functional groups in the adsorbents helps in the adsorption of H₂S. Consequently, adsorbent that has high nitrogen content is relatively promotes to high H₂S adsorption capacity, as shown by the PSAC-MW (Table 1).

Table 3
Proximate and elemental analysis of PSAC-based adsorbents

Sample	Proximate Analysis (wt %)				Elemental Analysis (wt %)			
	Carbon	Moisture	Volatile	Ash	C	H	N	S
PSAC	78.20	6.05	9.61	6.14	61.61	1.48	-	-
PSAC-TH	87.53	4.78	5.32	2.37	79.92	0.90	0.49	-
PSAC-MW	90.38	2.16	5.72	1.74	88.76	1.50	2.89	-

From Fig. 8, a substantial amount of nitrogen content and an increase in carbon content were identified in all nitrogen-modified adsorbents, which consistent with nitrogen to carbon (N/C) ratio. The increase in carbon content in the nitrogen-modified adsorbent is relative to the raise of MW temperature. This happened due to the high degree of carbonization during the pyrolysis process of urea impregnated PSAC that experiences both thermal and MW heating, where the adsorbent encounters twofold of high temperature, where the first one is during the production of AC (before urea impregnation). Nevertheless, as for hydrogen content, the amounts are significantly reduced as the MW temperature raised.

To investigate the influence of urea impregnation and MW heating method on the surface chemistry of the PSAC-MW, FTIR analysis has been performed as illustrated in Fig. 9. All adsorbents show significant spectrums between bands 600 to 900 cm^{-1} , which indicates various positions of hydrogen in aromatic rings, mostly out of plane deformation of C-H group that was located at the edge of the aromatic group (Simons 1978). Additionally, the spectrums detected all through the bands of 1150, 1300, 1600 and 1800 cm^{-1} are signifying the functional groups of -C-O and O-H stretches and bends that can be classified into alcohols and phenols (R-OH), ethers (R-O-R), hydrocarbon attached to oxygen (-O-R), ketones, aldehydes, carboxylic acids, esters, and organic carbonates (Simons 1978). Due to urea impregnation, the functional groups identified in nitrogen modified PSAC adsorbents were different at certain bands compared to the raw PSAC. The reaction of carboxylic and aromatic groups with urea at high temperature (950°C) increase in the bands' intensity at 850, 1300, 1600, 2250, and 3200 cm^{-1} wavelengths. This indicated that there was association of nitrogen occurred after the impregnation of urea. As there was an increase in the intensity of the bands, strong aromatic C-N stretch peaks at 1300 cm^{-1} had been incorporated into the carbon structures. The band at 1600 cm^{-1} was possibly the C=O stretch of amides and imides groups that have been incorporated with the NH_2 scissors group, while the band at 2250 cm^{-1} was presumed to be the nitriles group that comprise of $\text{C}\equiv\text{N}$ stretches of nitriles and the band at 3200 cm^{-1} was the vibration of NH_2 and N-H stretches. The PSAC-MW exhibited strong intensity of the nitrogen functional groups compared to the PSAC-TH.

3.4 Effect of Thermal Analysis

Thermal stability analysis of the PSAC-based adsorbents is shown in Fig. 10 and Fig. 11. The DTG (differential thermal gravimetry) curve can be classified into three different ranges, which are from 80 –

120°C, 150 – 450°C, and 500 – 950°C. The first range of the DTG curve denotes the weight loss of moisture in the material, where it typically contributed to substantial percentage of weight loss (Bazan et al. 2016). The weight loss of absorbed water for the PSAC-TH is the highest (4.8 %/°C) followed by the PSAC (4 %/°C), and the PSAC-MW (3 %/°C). This implied that the PSAC-based adsorbents contain hydrophilic characteristic that tend to absorb water. Hence, the PSAC-based adsorbent is recommended to be stored in a desiccator that contains silica gel, to prevent the humidity in the air affecting or deteriorating the adsorbents. The second range of the DTG curve represents the decomposition of volatile organic matters that are easily volatile, presence on the surface of activated carbon such as carboxylic groups (Bazan et al. 2016). Fig. 10 displays that both the PSAC-TH and PSAC-MW experience higher weight loss of volatile organic matters compared to the PSAC. This is due to both the PSAC-TH and PSAC-MW were impregnated with urea, which had high intensity of carboxylic group (refer to Fig. 9). The nitrogen modified adsorbents were exposed at high temperature and experienced significant weight loss of 5 – 6 %/°C. This happened because of rapid decomposition of urea-derived species and other organic components in the range of 500 – 700°C as indicated in the DTG curves. These nitrogen functional groups were identified as amide, imide, nitrile groups and pyridine nitrogen. This explains the theory studied by (Seredych and Bandoz 2008), where the nitrogen-modified adsorbent that was heated at high temperature is very stable. As increases in the MW heating temperature from 500 – 900°C for, the weight loss in the nitrogen modified adsorbents shows rapid decomposition of urea-derived species (nitrogen functional groups) and other organic components in the range of 500 – 700°C in the DTG curve. The DTG curve for the PSAC adsorbents at lower MW temperatures (MW500, MW600, MW700) shows significant weight losses compared to the MW900.

3.5 Effect of Surface Morphology

The surface morphology of the nitrogen-modified PSAC-based adsorbents is shown in Fig. 12. All adsorbents had been subjected to the SEM analysis at a magnification of 5kX. Apparently, the nitrogen modified PSAC-based adsorbents showed different pattern compared to the PSAC. The surface morphology of the PSAC-TH in Fig. 12 (b) displays the pore structure had been clogged by excess urea/impurities and the size of the pores seems smaller compared to the PSAC structure in Figure 12 (a). As for the PSAC-MW in Figure 12 (c), the pore structure was well-developed and fewer pores had been clogged with urea/impurities as in the PSAC-TH. Furthermore, the carbon structure in the PSAC-MW established the sponge-like structure, where there is another pore were being constructed inside the existing pores and the pore size observed was smaller compared to the PSAC-TH and PSAC. As discussed earlier, narrow pore size could assist in H₂S adsorption activity. Thus, the surface morphology of the PSAC-MW justified the relationship between physical surface characteristics data in Table 2 and its surface morphology, where it contributes to high H₂S adsorption capacity. As reported by (Halasz et al. 2010), the use of MW heating method on AC could significantly change the amorphous structure of AC, where the cavities were deepened, and the inner structure of the adsorbent was remarkable. The development of surface area and narrow pore structures in the PSAC-MW were clearly noticed and this confirmed the hypothesis, where additional pores have been developed inside the pores (as observed from the surface morphology). These new added pores were assumed to have additional pore created

inside the structure (sponge-like structure) as the mechanism of MW heating itself is irradiated from the inner to the outer surface of the material. Having evaluated the thermal heating method on the PSAC-TH, it appears to have a slight identical effect as the PSAC-MW on the morphology of the AC.

The surface morphology of the PSAC adsorbents that have been modified with urea under different MW heating temperatures is shown in Fig. 13. For the nitrogen modified PSAC adsorbents that undergo different MW heating temperatures, as increases in temperature, the fouling of urea on the adsorbent surface seems to be better, as well as the development of the pore structure. This caused in the increases of H₂S adsorption capacity as increases in the MW heating temperature. Fig. 14 shows surface morphology of the nitrogen modified PSAC was also tested on MW heating time parameter, where the shortest heating time = 10 min and the longest heating time 60 min. The nitrogen modified PSAC at 10 min of heating time exhibited uniform porous structure, where the pore walls were not disturbed compared to the nitrogen modified PSAC at 60 min of MW heating time. The sintering effect of the carbon structure at 60 min of heating time was probably due to the pore walls between the adjacent pores that were destroyed. This resulted in widening the micropores and mesopores, which led to the external shrinkage and collapse of the carbon framework. In addition, instead of longer heating time, the use of high MW heating temperature (950°C) could be one of the factors that facilitated the destruction of pore structure once exposed at a longer heating time (Nor et al. 2016). Thus, this occurrence explains the H₂S adsorption capacity toward MW heating time, where at short heating time (10 min), resulted to high removal of H₂S.

3.6 Conventional Thermal Heating versus MW Heating Method

Based on the above discussions, MW heating method shows promising performance on the H₂S adsorption capacity compared to conventional thermal heating method. The great performance of the MW heating method can be related to its heating mechanism, where the theory was deduced by (Garcia Reimbert et al. 1996). Referring to the theory, a carbon material that was exposed to induced currents (origin from electromagnetic field) would be heated due to electrical resistances within the material. These electromagnetic and thermal properties of the material were non-linear temperature dependent. Thus, if the rate of material's absorption of MW non-linearly increased with heating temperature, a non-uniform heating would be created within the material, and indirectly formed regions of very high temperature known as hot spot.

The formation of the hot spot shown in Fig. 5 throughout the MW heating can be defined as sparks or electric arcs, where it could be regarded as plasma at the microscopic level. According to (Rodriguez-Fernandez et al. 2020), these plasmas could be considered as microplasmas and they were observed as the very tiny sparks that could last for a fraction of a second. Activated carbon is a good MW absorber and it could enhance the hot spot formation. Since the temperatures of these hot spots were considerably higher, this occurrence increased the kinetic energy of π -electrons (make the electrons jump out of the substance) and ionized the surrounding atmosphere of the material (Menéndez et al. 2010). During the

MW heating process, the hot spot was believed to be responsible for the development of physical and chemical characteristics of PSAC-MW. Referring to all the reasons, the MW heating method was chosen over the conventional thermal heating method.

4.0 Conclusions

The impregnation of urea onto the PSAC adsorbent shows remarkable influences on the H₂S adsorption, where the nitrogen functional groups were tailored. The use of the MW heating method is recommended, where it provide a great assist in the H₂S adsorption activity compared to the performance of PSAC-TH that undergo conventional thermal heating method. Based on the H₂S breakthrough capacity, the performance of the PSAC-MW is 100% better than the PSAC and PSAC-TH adsorbents. The development of physical and chemical characteristics of PSAC-MW adsorbent is primarily important and give a remarkable influence in the H₂S adsorption performance. From the findings, the nitrogen modified PSAC via MW heating method could be a benchmark to further enhance the H₂S adsorption activity.

Declarations

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Competing interests

The authors declare that is no competing interests.

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Authors' contributions

Conceptualization, methodology, analysis, and investigation, preparing the original draft, and editing the manuscript: **Norhusna Mohamad Nor**, Project administration: **Lau Lee Chung**; Review, revise, funding

acquisition, supervision: **Abdul Rahman Mohamed**. All authors have read and agreed to the published version of the manuscript.

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Figures

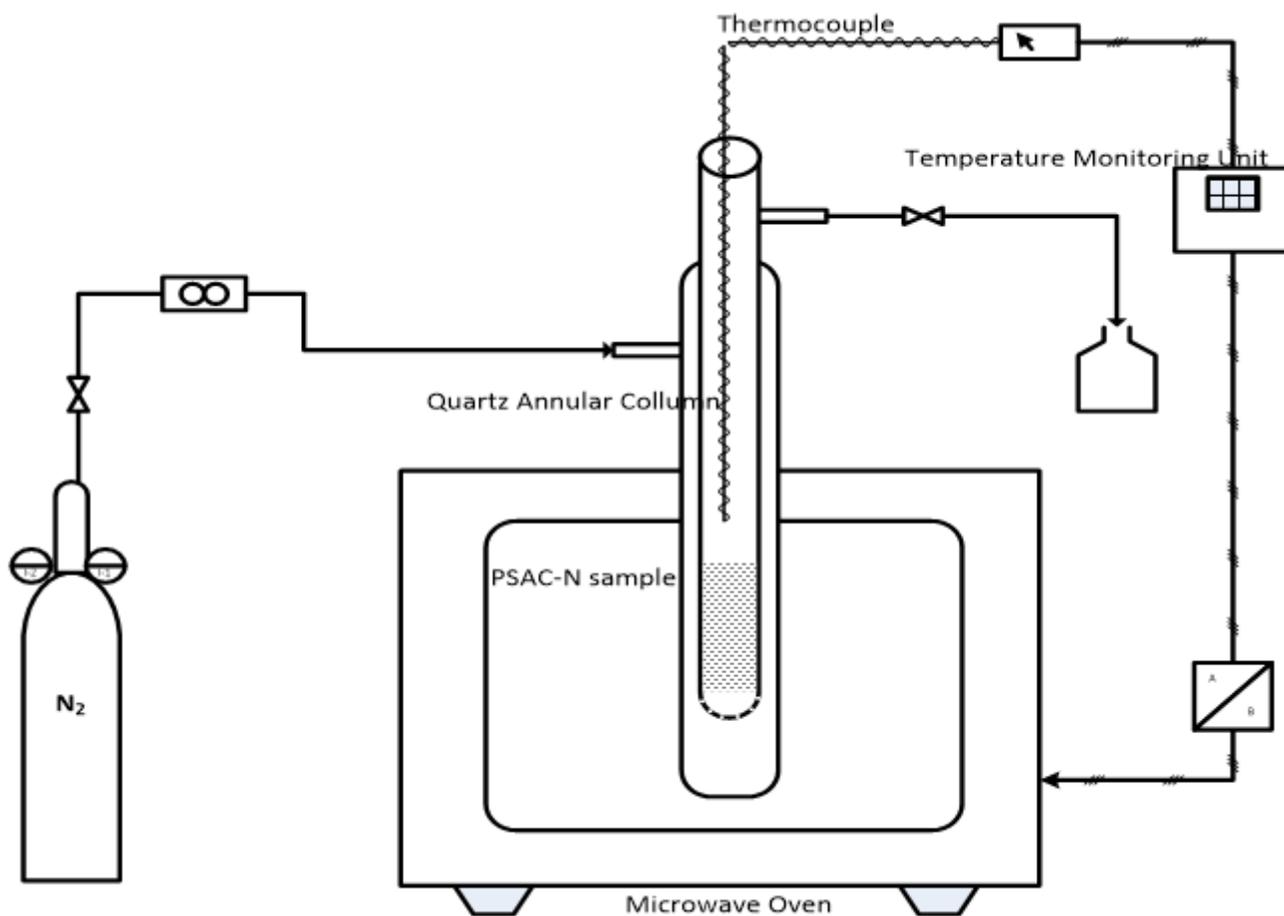


Figure 1

Schematic diagram of the set-up for MW heating rig.

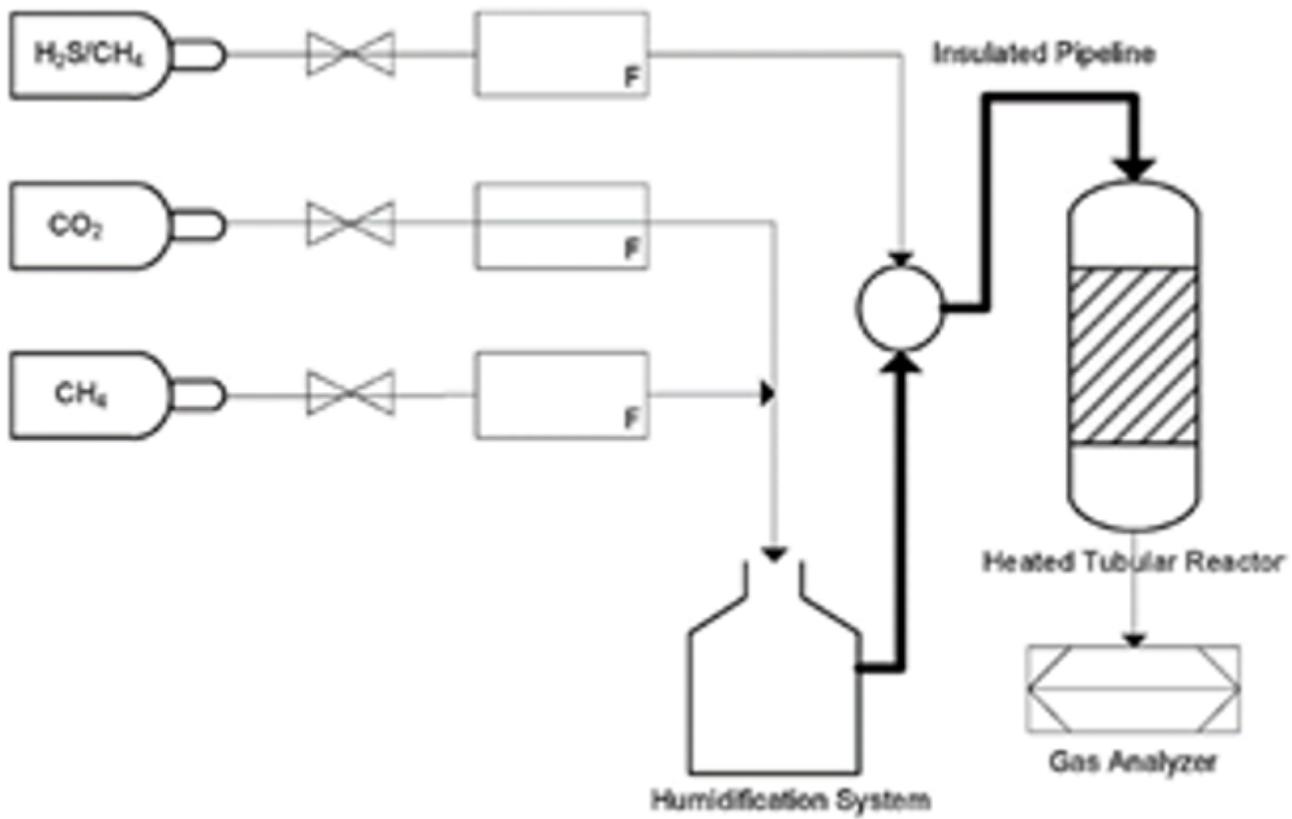


Figure 2

Schematic diagram of H₂S desulfurization rig.

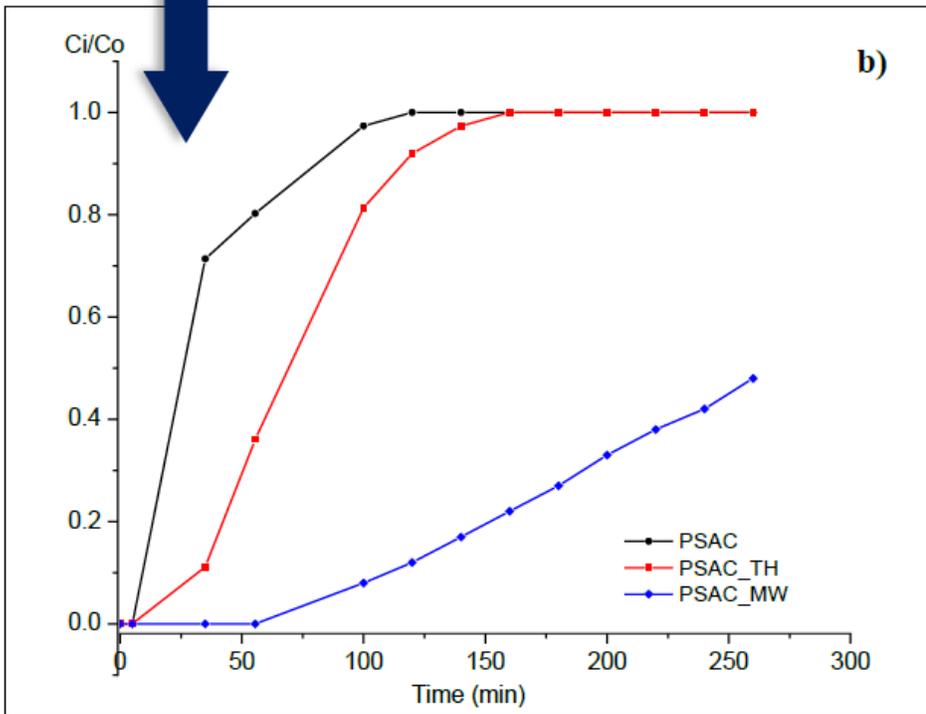
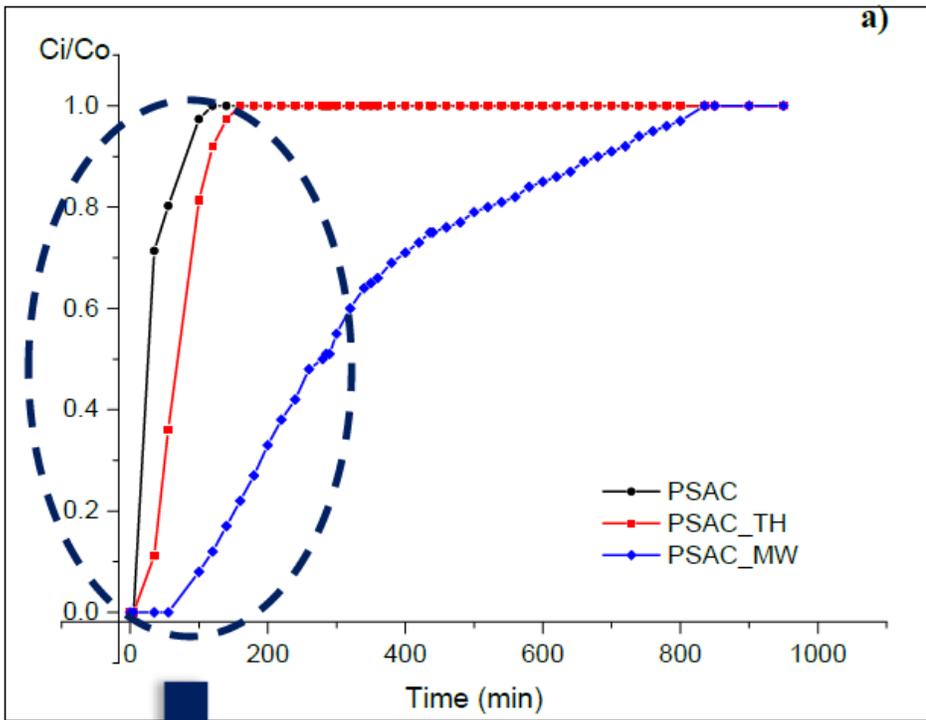


Figure 3

H₂S breakthrough curves of PSAC-based adsorbents a) overall layout and b) scaled-up layout.

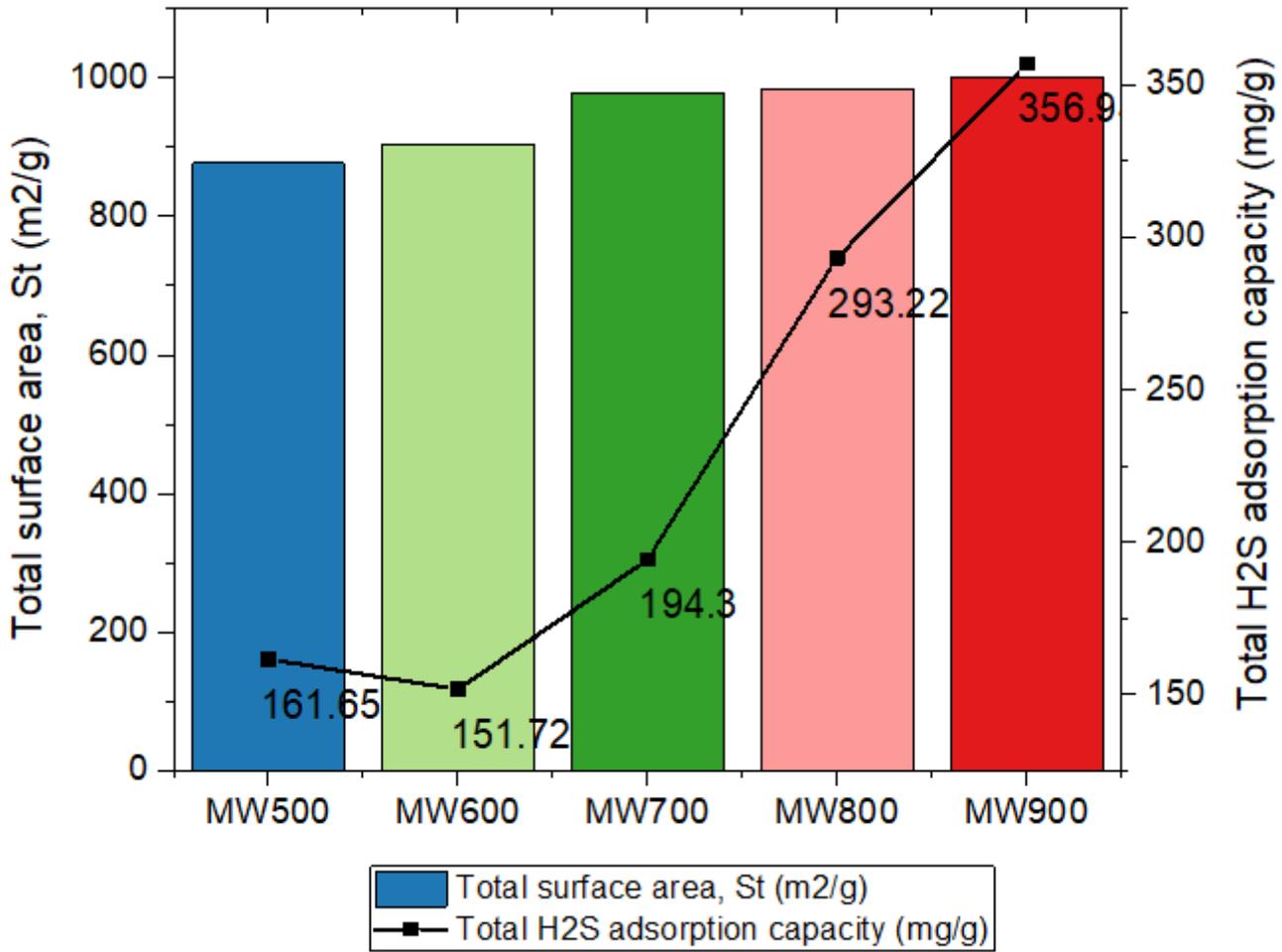


Figure 4

Effect of surface area and H₂S adsorption capacity of PSAC-based adsorbents at different MW heating temperatures.

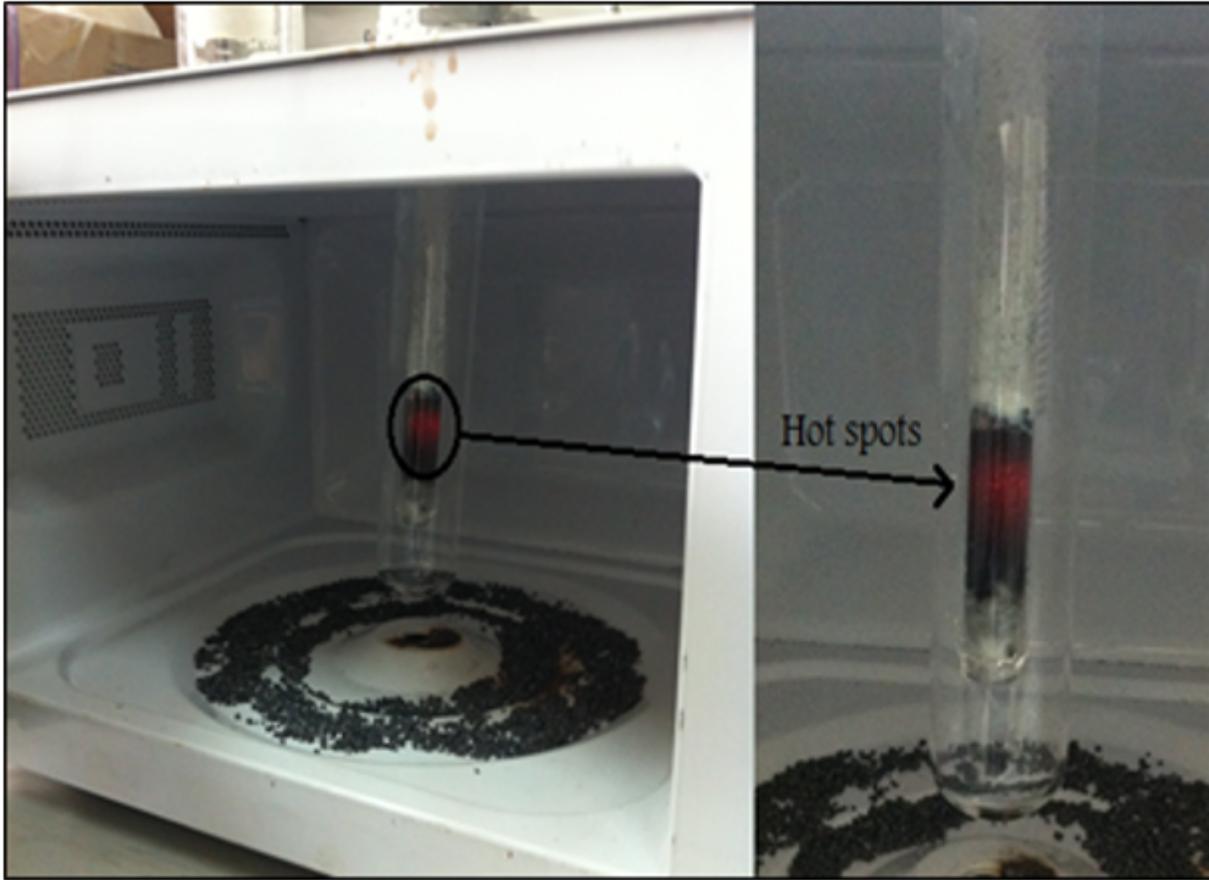


Figure 5

Hot spot observed during MW heating experiment.

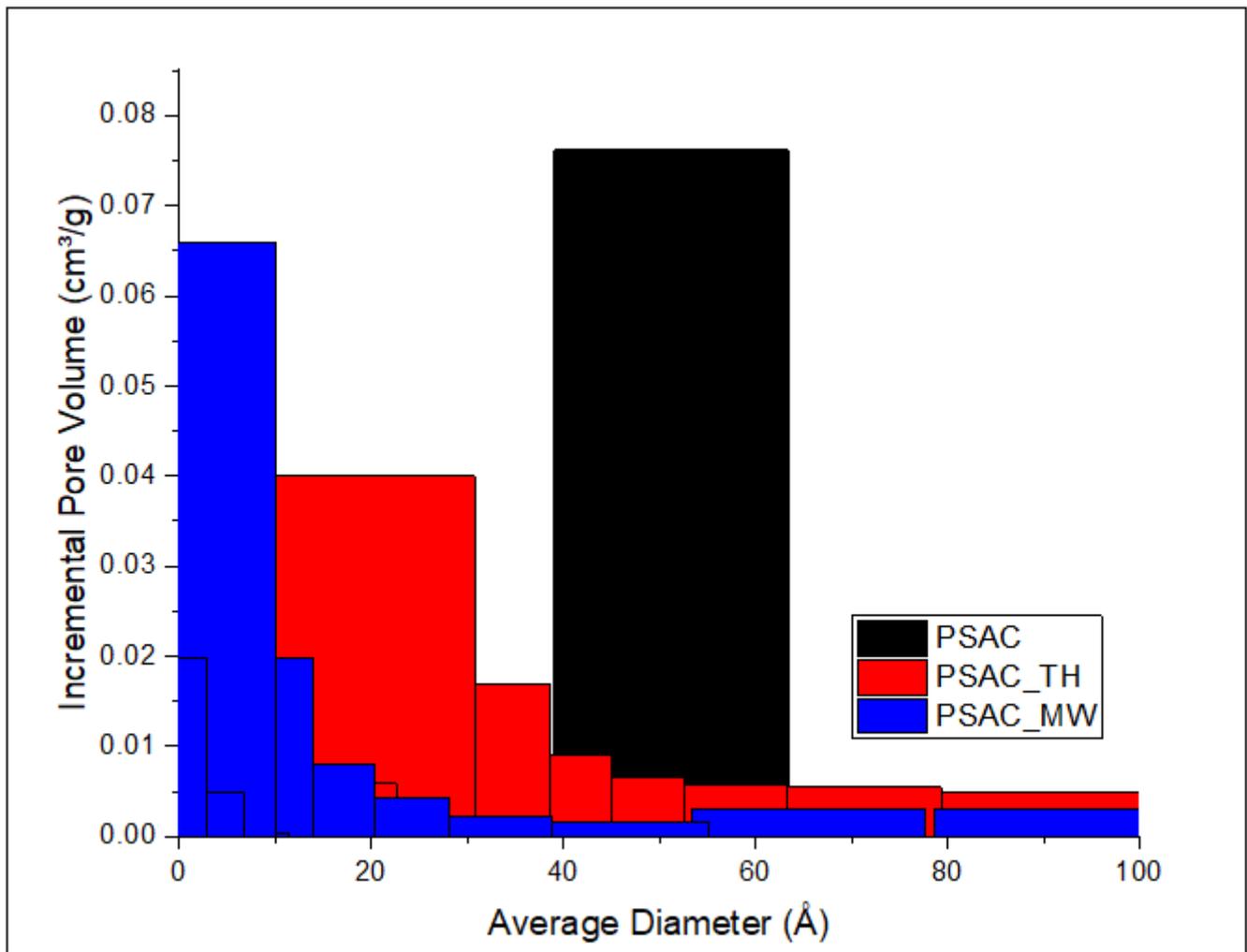


Figure 6

Pore size distributions (DFT) of PSAC-based adsorbents.

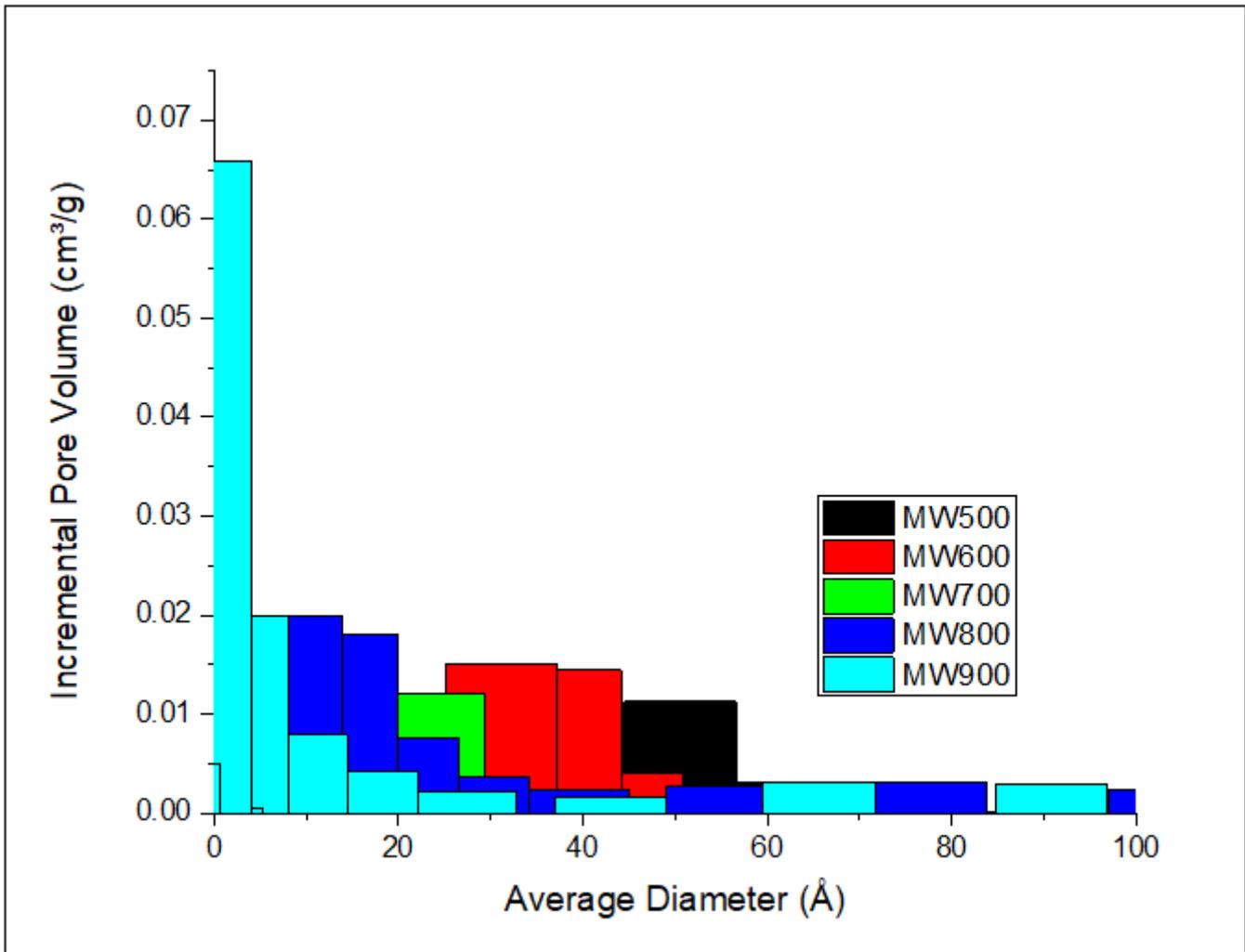


Figure 7

Pore size distribution (DFT) of PSAC-based adsorbent at different MW heating temperatures.

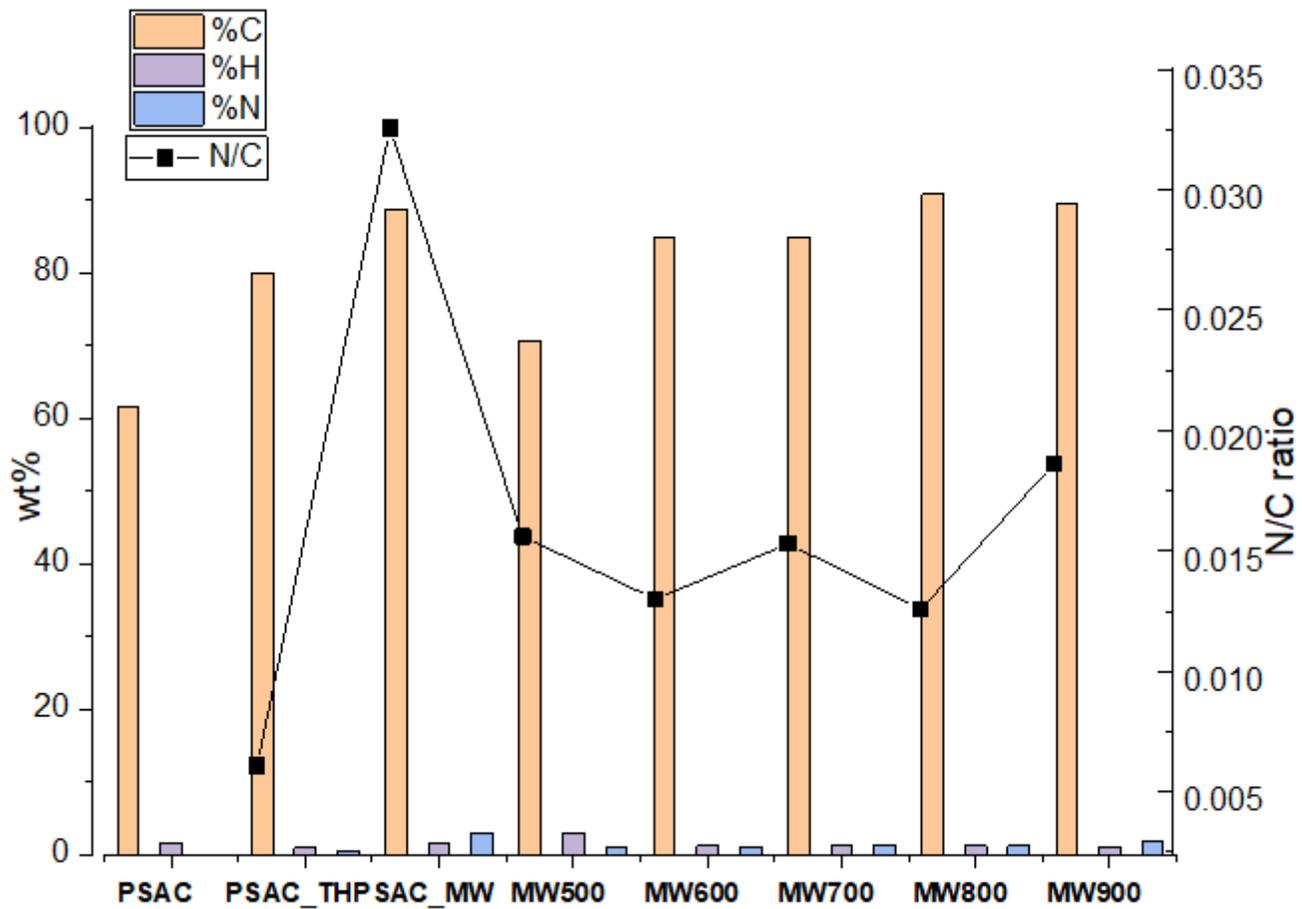


Figure 8

Elemental analysis of PSAC-based adsorbents with respect to N to C ratio.

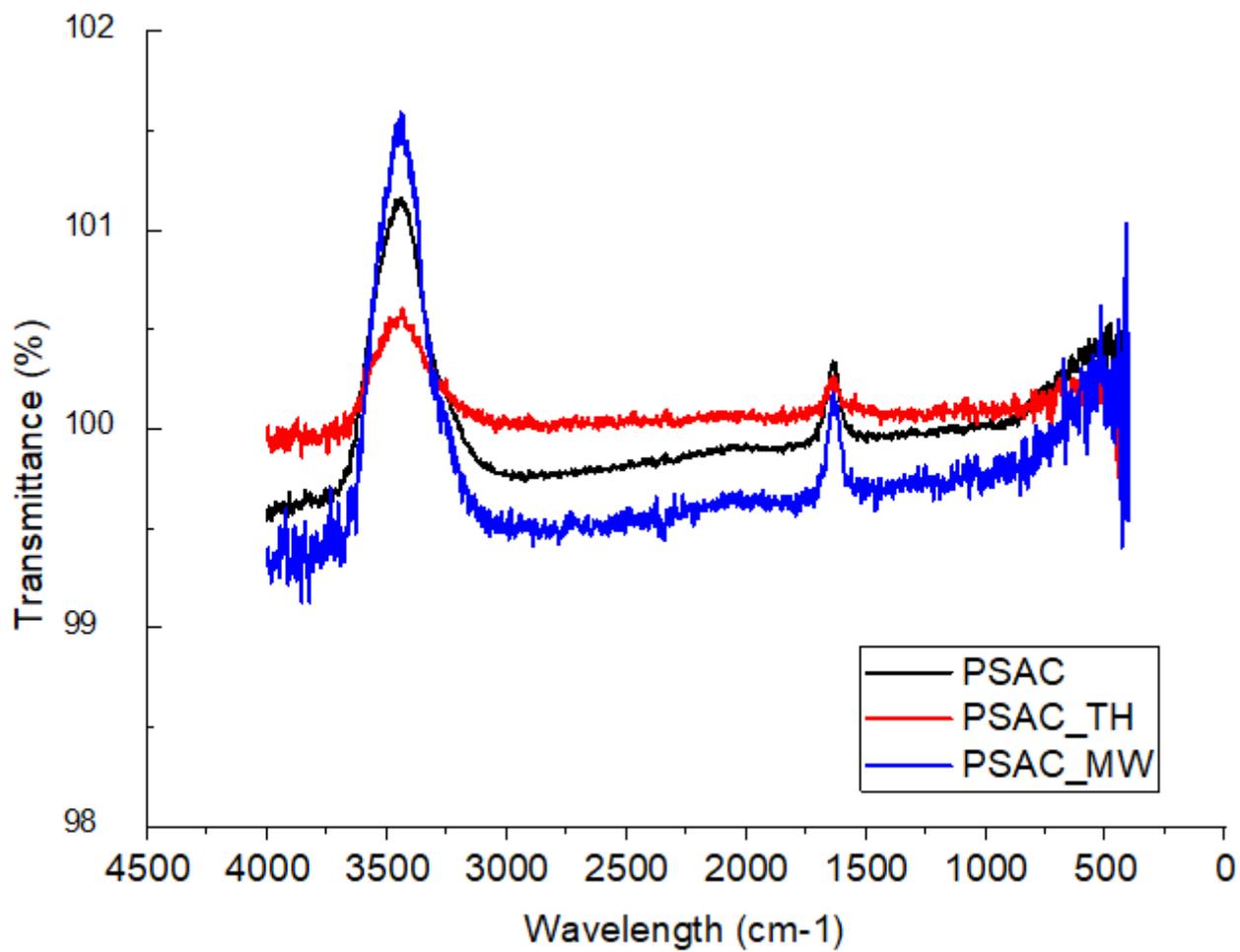


Figure 9

FTIR spectra of PSAC-based adsorbents.

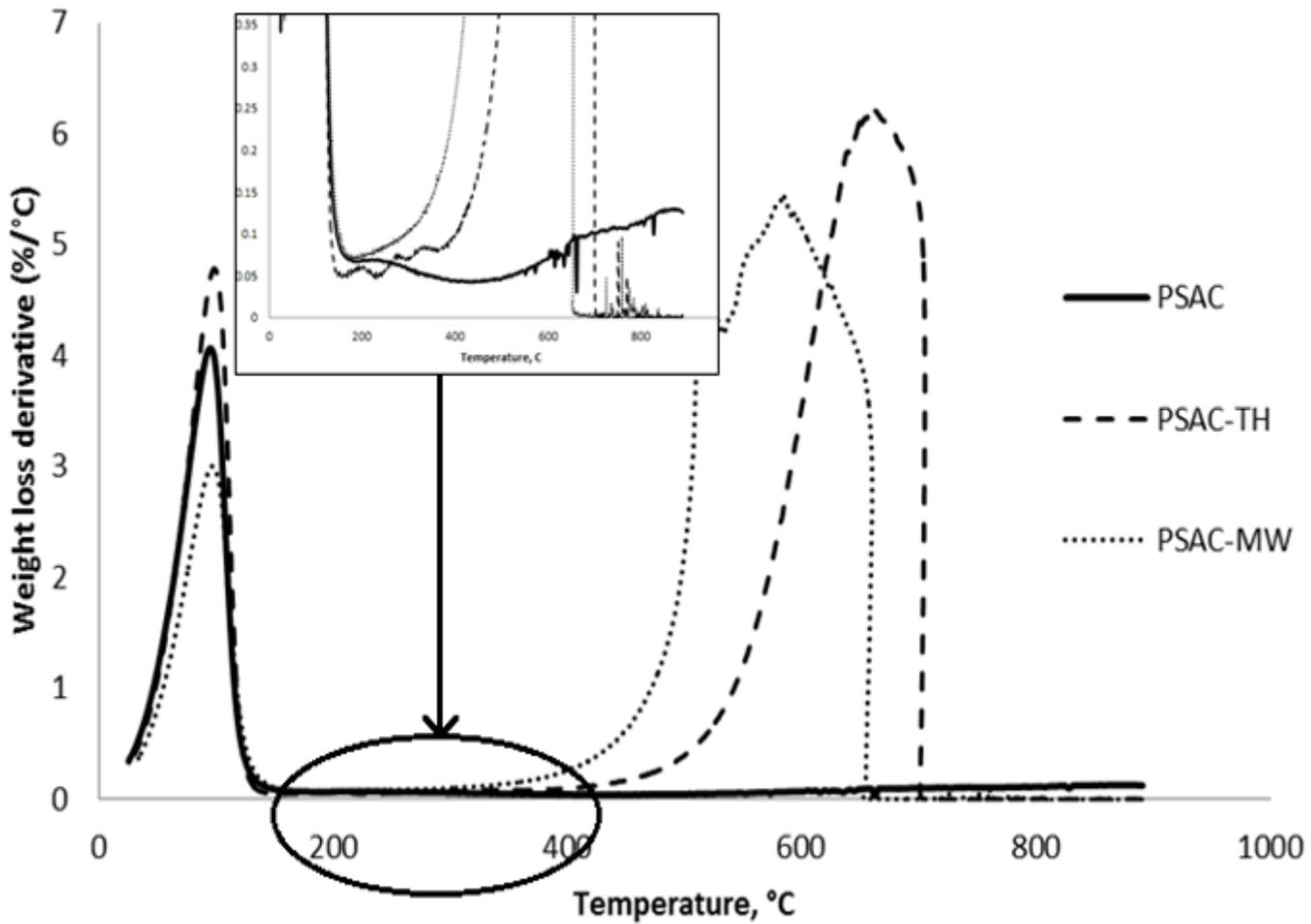


Figure 10

DTG curves of PSAC-based adsorbents.

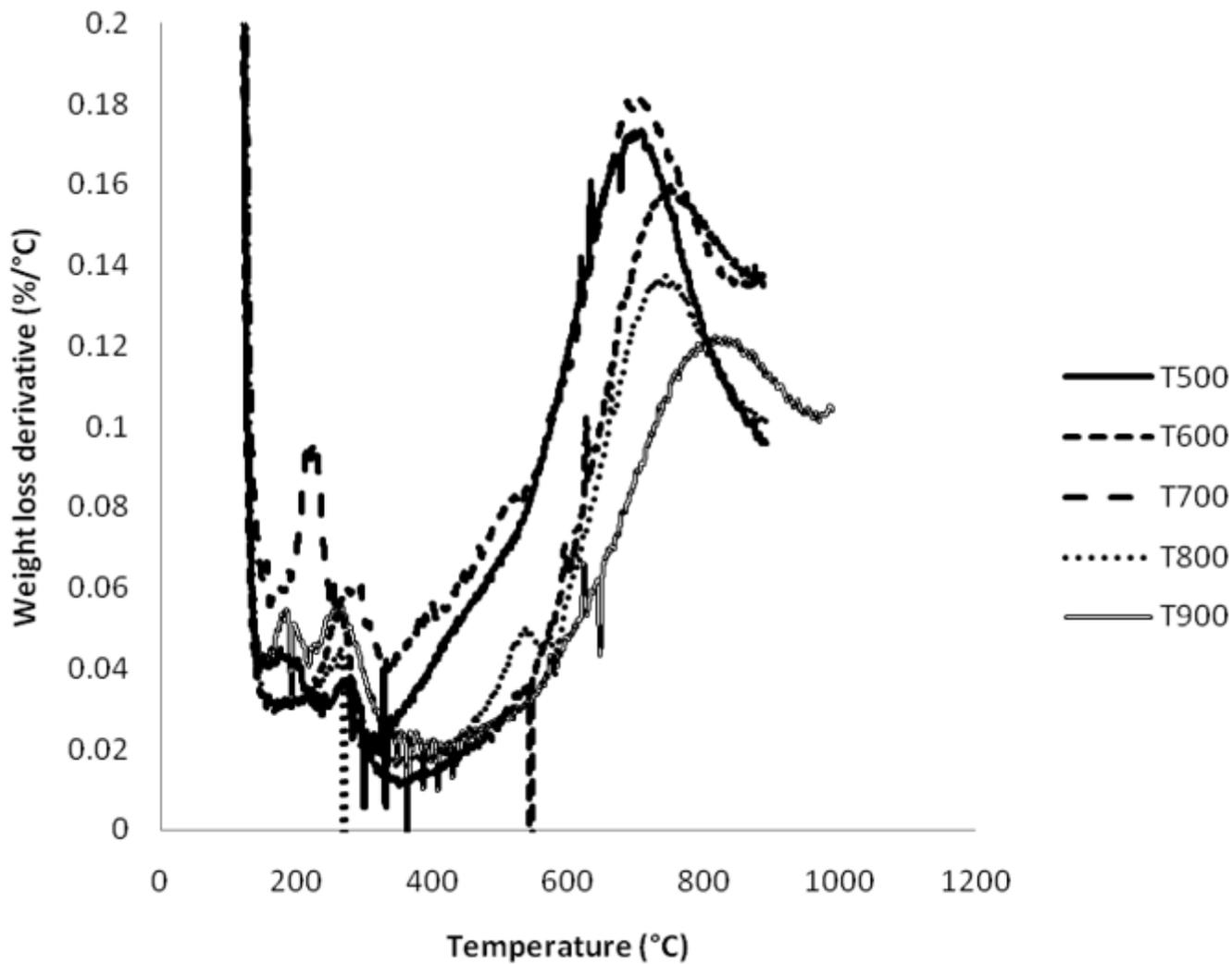


Figure 11

DTG curves of PSAC-based adsorbents at different MW heating temperatures.

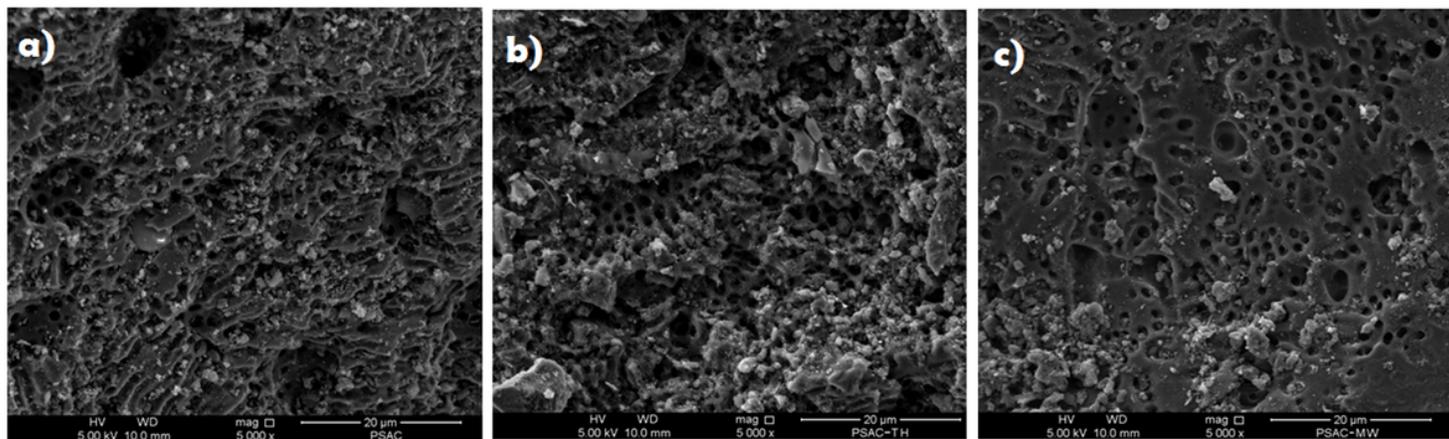


Figure 12

SEM images of (a) PSAC adsorbent (b) PSAC-TH adsorbent (c) PSAC-MW adsorbent at 5kx magnification.

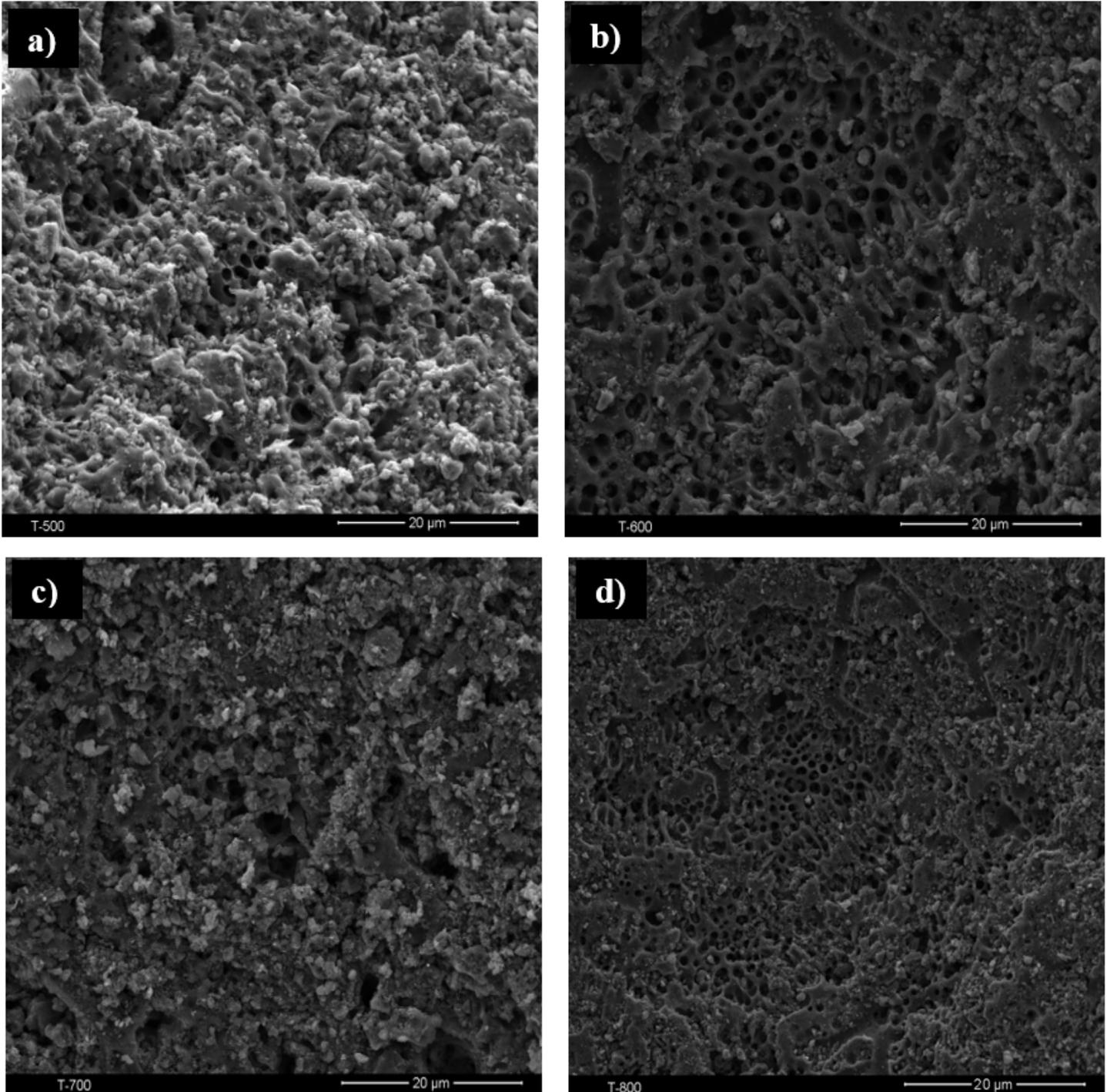


Figure 13

SEM images of PSAC-based adsorbents at different MW heating temperatures a) MW500, b) MW600, c) MW700, d) MW800 (5k magnification).

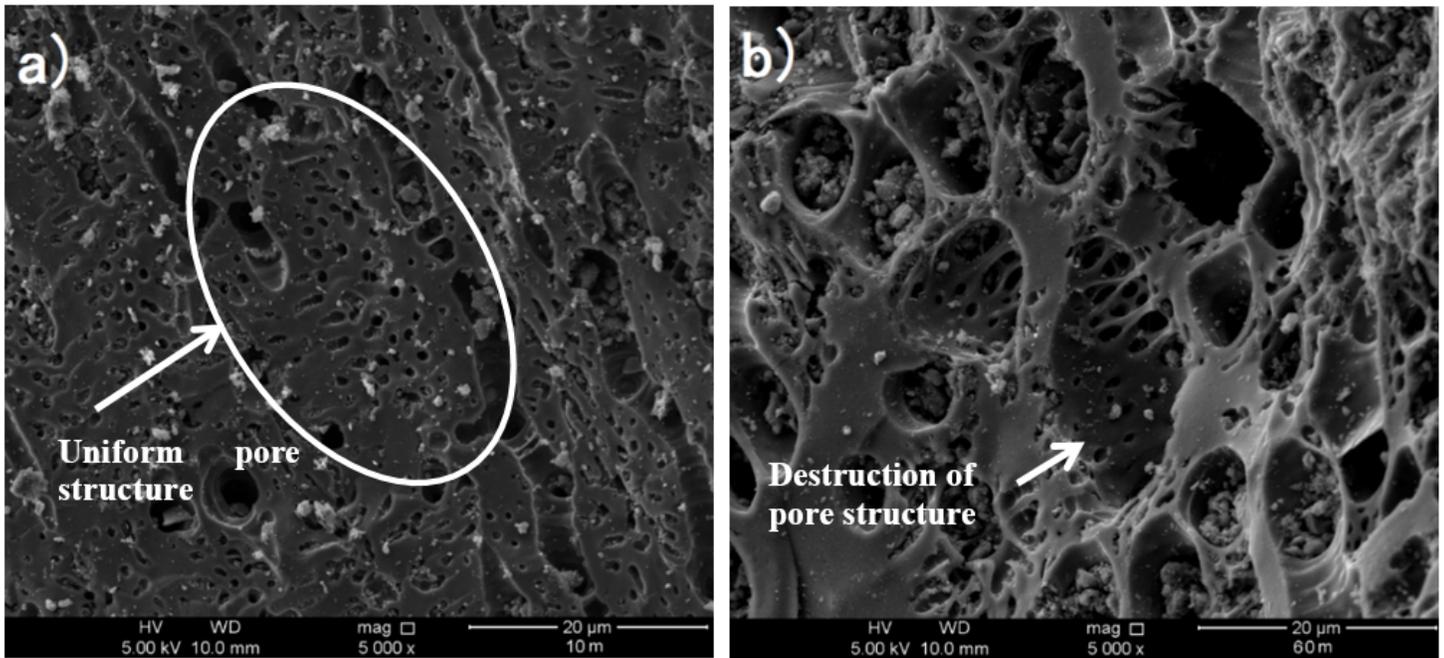


Figure 14

SEM images of a) PSAC-based adsorbent at 10min MW heating time b) PSAC-based adsorbent at 60 min MW heating time (5k magnification).