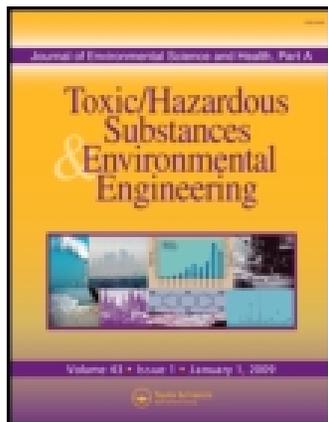


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Sobhan Iranmanesh<sup>a</sup>, Thomas Harding<sup>b</sup>, Jalal Abedi<sup>a</sup>, Fakhry Seyedeyn-Azad<sup>a</sup> & David B. Layzell<sup>c</sup>

<sup>a</sup> Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada

<sup>b</sup> Nexen Energy ULC, Calgary, Alberta, Canada

<sup>c</sup> Department of Biological Sciences & Canadian Energy Systems Analysis Research (CESAR) Initiative, University of Calgary, Calgary, Alberta, Canada

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# Adsorption of naphthenic acids on high surface area activated carbons

SOBHAN IRANMANESH<sup>1</sup>, THOMAS HARDING<sup>2</sup>, JALAL ABEDI<sup>1</sup>, FAKHRY SEYEDEYN-AZAD<sup>1</sup>  
and DAVID B. LAZZELL<sup>3</sup>

<sup>1</sup>Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada

<sup>2</sup>Nexen Energy ULC, Calgary, Alberta, Canada

<sup>3</sup>Department of Biological Sciences & Canadian Energy Systems Analysis Research (CESAR) Initiative, University of Calgary, Calgary, Alberta, Canada

In oil sands mining extraction, water is an essential component; however, the processed water becomes contaminated through contact with the bitumen at high temperature, and a portion of it cannot be recycled and ends up in tailing ponds. The removal of naphthenic acids (NAs) from tailing pond water is crucial, as they are corrosive and toxic and provide a substrate for microbial activity that can give rise to methane, which is a potent greenhouse gas. In this study, the conversion of sawdust into an activated carbon (AC) that could be used to remove NAs from tailings water was studied. After producing biochar from sawdust by a slow-pyrolysis process, the biochar was physically activated using carbon dioxide (CO<sub>2</sub>) over a range of temperatures or prior to producing biochar, and the sawdust was chemically activated using phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). The physically activated carbon had a lower surface area per gram than the chemically activated carbon. The physically produced ACs had a lower surface area per gram than chemically produced AC. In the adsorption tests with NAs, up to 35 mg of NAs was removed from the water per gram of AC. The chemically treated ACs showed better uptake, which can be attributed to its higher surface area and increased mesopore size when compared with the physically treated AC. Both the chemically produced and physically produced AC provided better uptake than the commercially AC.

**Keywords:** Naphthenic acid, activated carbon, CO<sub>2</sub> activation, adsorption, equilibrium.

## Introduction

The oil sands in Alberta contain some of the largest oil accumulations in the world.<sup>[1]</sup> Generally, two methods are used for extraction of bitumen from the oil sands deposits: surface mining for the near-surface deposits and in-situ recovery using steam injection for the more deeply buried resources. The surface mining approach employs conventional mining operations that involve large-scale shovel and truck removal to transport the whole oil sand to the central processing plant.<sup>[2,3]</sup> About 12 volumes of water are needed to produce one volume of bitumen in oil sands surface mining operations, with some of this water being released into tailings ponds.<sup>[4]</sup> The mining operations need 8 to 10 volumes of water for each volume of Synthetic

Crude Oil (SCO) produced. As 40 to 70% of the water is recycled and reused in the process, 2 to 4 volumes of water make-up is required.<sup>[2]</sup> Both surface mining, employing the hot water extraction process, and in-situ recovery, utilizing high pressure steam, result in organic contamination of the process water from contact of bitumen with hot water or steam.

Water in a tailings pond is generally saline, contaminated by organic materials and suspended clay. The main organic contaminant is Naphthenic Acids (NAs).<sup>[5]</sup> NAs are a mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids and are considered to be natural components of bitumen.<sup>[6]</sup> Studies have shown that the concentrations of NAs in tailings ponds are up to 120 mg/L.<sup>[4,7–9]</sup>

Several methods have been reported for the removal of NAs from water, such as catalytic reactions, membrane separation, microbial reaction and adsorption. Using biomass based AC or biochar as an adsorbent can also decrease the CO<sub>2</sub> footprint. In the study that was done by Lehmann and Joseph,<sup>[10]</sup> it was shown that physically AC can play a role in carbon sequestration and therefore act as a carbon sink.

Address correspondence to Jalal Abedi, Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr., NW, Calgary, AB, T2N 1N4, Canada; E-mail: jabedi@ucalgary.ca

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In order to produce activated carbon, two activation methods are commonly employed: physical (or thermal) activation and chemical activation. Chemical activation involves treating the precursor with a chemical agent, the most common of which are potassium hydroxide (KOH), phosphoric acid and zinc chloride.<sup>[11]</sup> Physical activation is carbonization or pyrolysis in an inert condition, usually done below 700°C followed by an activation step, which is a controlled gasification by an activation agent at high temperatures, up to 1100°C.<sup>[11]</sup> Steam and carbon dioxide (CO<sub>2</sub>) are the two most commonly used agents for physical activation.

Gamal El-Din et al.<sup>[12]</sup> investigated NA speciation and removal during petroleum-coke (petcoke) adsorption as a pretreatment step. They examined the impacts of pretreatment steps, including filtration and petcoke adsorption, on ozonation requirements and performance. Petcoke adsorption was found to be effective in reducing total acid-extractable organics by 91%, NAs content by 84%, and oil sands processed water toxicity units from 4.3 to 1.1 units.

The performance of AC in removal of NAs was investigated.<sup>[11,13]</sup> Barnard<sup>[11]</sup> used petcoke to produce AC using KOH as a chemical activation agent for the uptake of NAs. The effect of temperature on production of AC was studied in a constant KOH-petcoke ratio. It was concluded that the trend of temperature versus uptake capacity was curved and that the optimal temperature was 923 K. The removal of NAs for this sample was 80% for an initial concentration of 41 ppm. Small<sup>[13]</sup> varied other activation conditions, including the steam flow rate, activation time and activation temperature. In the case of CO<sub>2</sub> and steam, AC produced at 1173 K had a range of physical characteristics: total surface area from 426–578 m<sup>2</sup>/g, with mesopores accounting for 37–48% of the total pore volume, and carbon burn-off ranging from 44.2–58.8%. Small<sup>[13]</sup> concluded that, at the activation temperature of 1173 K, a CO<sub>2</sub> and steam flow rate of 0.5 mL/min and activation time of 6 h produced an AC with the highest total surface area of 578 m<sup>2</sup>/g.

The primary objective of this research was the preparation of an appropriate AC from saw dust by physical activation with CO<sub>2</sub> for adsorption of NAs. Sawdust was

selected as a raw material for producing AC due to its abundance and anticipated low cost. In addition, biomass-based AC can play a role as a carbon sink, so it can contribute to reducing the carbon emission footprint of oil sands operations. The removal of NAs by adsorption using AC was then investigated since among a variety of adsorbents, AC has been considered to be highly effective. The effect of the activation temperature on the burn-off and surface area of the produced AC was investigated. Chemical and physical activation methods were compared based on their characteristic properties, the adsorption capability of the produced AC was examined and the isotherm data presented.

## Materials and method

### Materials

The biomass selected for this research as the raw material for producing AC was a mixture of sawdust from different types of wood obtained from a waste wood recycling company in Calgary, Alberta, Canada. The main source of this sawdust was pinewood, which is abundant in Alberta. The sawdust was initially dried, crushed and sieved to different mesh sizes in the ranges of <590 μm, 590–1000 μm and 1000–1400 μm. The biomass was heated overnight in an oven at 100°C to remove any residual moisture. The elemental and ultimate analyses of the biomass are shown in Table 1. Due to the low sulfur and ash content of the feedstock, these two have not been included in Table 1.

The NAs used in this study was a commercial, technical grade, from Sigma-Aldrich (Oakville, ON, Canada). The commercial AC (Hydrarco C M-1629, St. Louis, MO, USA) used in this research was provided by Norit Company. This AC was produced by steam activation of lignite coal. This sample was considered to be applicable to wastewater treatment. Based on the information provided by Norit Company (Marshall, TX, USA),<sup>[14]</sup> their AC should have a surface area of 600 m<sup>2</sup>/g, but the test performed in our lab showed a surface area of 489 m<sup>2</sup>/g.

### Experimental procedure

The preparation of AC using physical activation had two steps: biochar production, and the activation step.

### Biochar production

The biochar production was performed in a horizontal, stainless steel, fixed-bed tubular reactor (internal diameter of 1.9 cm, external diameter of 2.2 cm, length of 50 cm) in an ultrapure nitrogen (N<sub>2</sub>) flow (99.999%), externally heated by a 1200 W electrical tube furnace. In each experiment, 10 grams of dried biomass were placed in the reactor and packed by glass fiber. The biomass was heated at a ramp of 10°C/min to reach 550°C and was kept at this temperature for 2 h. After the furnace cooled down to the

**Table 1.** Proximate and ultimate analysis of biomass.

	<i>As received</i>	<i>Dry basis</i>	<i>Dry, ash free</i>
Proximate analysis (wt. %)			
Moisture	5.96		
Ash	1.46	1.55	
Fixed carbon	11.42	12.14	12.34
Volatile	81.15	86.30	87.66
Ultimate analysis (wt. %)			
Carbon	47.37	50.37	51.17
Hydrogen	6.03	6.41	6.51
Nitrogen	2.40	2.55	2.59
Oxygen	36.78	39.11	39.73

ambient temperature, the residue (biochar) was collected and weighed. The biochar samples were named based on their particle sizes: biochar produced from sawdust with a mesh size below 590  $\mu\text{m}$  was called B500; and, biochars produced from sawdust with mesh sizes of 590–1000  $\mu\text{m}$  and 1000–1400  $\mu\text{m}$  were named B1000 and B1400, respectively. As a result of the carbonization process, some volatile materials were removed from the biomass. Therefore, at the end of the process, a reduction in the weight of the biomass was observed relative to the original sample. Yield is defined as the percentage of the remaining weight over the initial weight of the sample, i.e., the final weight of biochar over the weight of dry biomass. The yield represents the extent of the carbonization reaction.

### Activation

In this study, AC was produced by physical activation using  $\text{CO}_2$  with purity of 99.999%, except one sample, which was activated chemically for comparison purposes. The biochar produced in the carbonization step did not have enough surface area, and its pores needed to be widened. Therefore, physical activation was performed in the same reactor used for producing biochar using  $\text{CO}_2$  for 1 h at a temperature higher than the one used for the carbonization. To investigate the effect of temperature, the activation temperature was varied from 700 to 900°C. Following the activation step, the reactor was allowed to cool to ambient temperature, after which the AC was weighed and stored. The whole process from raw material to AC is shown in Figure 1.

Similar to biochar, the produced ACs were named based on the particle sizes: AC produced from sawdust with a mesh size below 590  $\mu\text{m}$  was called PH500; and, AC produced from sawdust with mesh sizes of 590–1000  $\mu\text{m}$  and 1000–1400  $\mu\text{m}$  were named PH1000 and PH1400, respectively. To investigate the effect of activation temperature

on the physical properties of the AC, a group of 6 samples of PH500 were activated with  $\text{CO}_2$  at various six different activation temperatures in the range of 700 to 900°C. Whereas for PH1000 and PH1500 groups, the activation temperature range was narrowed and only three samples of each group were activated at 800, 825 and 850°C.

As mentioned earlier, chemical activation is another way to produce AC. For this study, phosphoric acid was used as the activation agent. The sawdust sample was crushed and sieved to 590  $\mu\text{m}$  and then dried in an oven overnight at 100°C. A predetermined amount of phosphoric acid, which was acquired from BDH Chemicals with a purity of 85%, was used to impregnate the biomass. The biomass/acid ratio was 1/1 (w/w). In order to prepare chemically AC, 100 g of the acid was poured into a container, diluted with 100 g of deionized water and mixed with 100 g of biomass. The mixture was placed in a stirrer for 5 h and then dried in an oven overnight at 100°C. The dried impregnated biomass was then placed in the reactor inside a furnace. A quartz holder was also used to pack the reactor. The final temperature was set at 550°C, with a ramp-up of 10°C/min, and held for 2 h. The reactor was cooled to the ambient temperature, and the AC was collected.

The produced AC was impregnated with acid, which can reduce the porosity of the AC; therefore, the AC was washed with deionized water to establish a pH of 7. This sample was called CA, stand for chemical activation. The list of all the produced ACs and the experimental conditions are given in Table 2 along with the results presented later in this article.

In the activation process, which is basically a gasification reaction, the pore size was widened, and some weight was lost. Burn-off, which is defined as the weight loss of the carbon source relative to the initial carbon source, is a common index for the activation process.<sup>[15,16]</sup> Calculation of the burn-off is systematic for physically produced AC, because the weight of biochar can be easily obtained and it can be calculated from experimental data using the following equation:

$$\text{Burn-off} = 1 - \frac{\text{Activated carbon weight}}{\text{Biochar weight}}$$

For chemically AC, the burn-off is defined as the mass of the reacted carbon relative to the mass of the fixed carbon (FC) in the sample before activation and is calculated as follows:<sup>[15]</sup>

$$\begin{aligned} \text{Burn-off (\%)} &= \left( 1 - \left( \frac{\text{The weight of sample after activation}}{\text{The weight of FC in the sample before activation}} \right) \right) \\ &\times 100 \end{aligned}$$

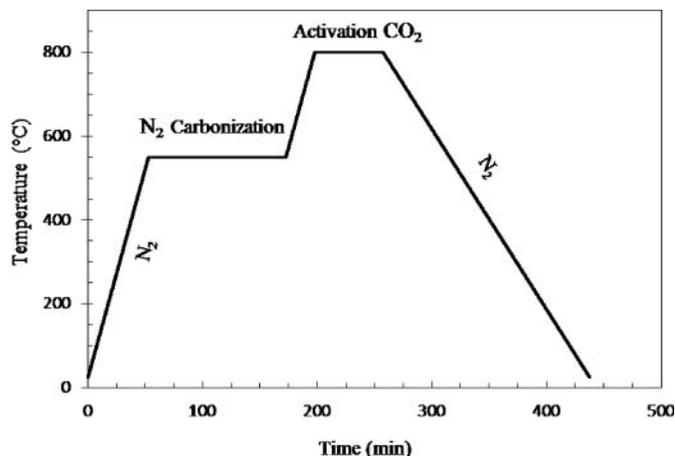


Fig. 1. Temperature versus time for producing AC.

**Table 2.** Production conditions, and the specifications of produced Acs.

Sample Name	Carbonation Step	Activation step	BET surface (m <sup>2</sup> /g)	Burn-off (%)	Yield base on initial biomass
PH500-1	550°C, 2 h, 10°C/min	700°C, 1 h CO <sub>2</sub>	397	4.67	24.32
PH500-2	550°C, 2 h, 10°C/min	750°C, 1 h CO <sub>2</sub>	524	17.73	20.98
PH500-3	550°C, 2 h, 10°C/min	800°C, 1 h CO <sub>2</sub>	630	37.64	15.90
PH500-4	550°C, 2 h, 10°C/min	825°C, 1 h CO <sub>2</sub>	750	43.14	14.50
PH500-5	550°C, 2 h, 10°C/min	850°C, 1 h CO <sub>2</sub>	525	67.59	8.27
PH500-6	550°C, 2hr, 10°C/min	900°C, 1 h CO <sub>2</sub>	367	82.35	4.67
PH1000-1	550°C, 2hr, 10°C/min	800°C, 1 h CO <sub>2</sub>	663	27.05	18.20
PH1000-2	550°C, 2 h, 10°C/min	825°C, 1 h CO <sub>2</sub>	720	46.30	13.80
PH1000-3	550°C, 2 h, 10°C/min	850°C, 1 h CO <sub>2</sub>	507	43.75	14.46
PH1400-1	550°C, 2 h, 10°C/min	800°C, 1 h CO <sub>2</sub>	690	33.94	17.11
PH1400-2	550°C, 2 h, 10°C/min	825°C, 1 h CO <sub>2</sub>	731	55.21	11.60
PH1400-3	550°C, 2 h, 10°C/min	850°C, 1 h CO <sub>2</sub>	501	55.21	11.60
CA	No carbonization	550°C, 2 h N <sub>2</sub>	895	45.31	NA

### Adsorbent characterization

For measuring the BET (Brunauer, Emmett, Teller) surface area, pore size distribution, average pore size and total pore volume, the Micrometric Tristar II analyzer was used (Micrometric, Norcross, GA, USA). Nitrogen gas was used for estimating surface area, pore size distribution, average pore size and total pore volume of ACs. The cryogenic temperature of N<sub>2</sub> was 77 K, which was consistent with that of the liquid nitrogen bath. The pressure range in this apparatus was set at 0.01–0.95 P/P<sub>0</sub>, where P<sub>0</sub> is the saturation pressure and P indicates the equilibrium pressure. However, attempts using N<sub>2</sub> for measurement of the BET surface area for biochar failed. Therefore, measurement of biochar surface area was performed using CO<sub>2</sub> instead of N<sub>2</sub>, due to the capability of CO<sub>2</sub> for measuring microporosity.

Elemental analyses were performed with a Perkin-Elmer (Waltham, MA, USA) 2400 Series II element (carbon, hydrogen, nitrogen, sulfur and oxygen, CHNSO) analyzer for the biochar and AC to gain a better understanding of the carbonization and activation processes.

Thermogravimetric analysis (TGA) was used to determine precise changes in weight relative to a change in temperature or time. With the TGA data, the kinetics and extent of a reaction can be determined for a given time or temperature and the yield and other gravimetric parameters can be compared to the data obtained using the reactor. Approximately 10–13 mg of raw biomass was placed in the chamber of a TGA system and weighed with accuracy of 10<sup>-4</sup> g. The balance recorded the weight with an assigned time interval of 1 sec or 1°C for each sample.

### Adsorption test

NA solutions with various concentrations were prepared according to the following procedure. First, a solution of almost 50 mg/L NAs was produced by mixing the commercial NAs with deionized water. The mixture was

sonicated for approximately 3 min to increase the dissolution of NAs in the deionized water and create a more homogeneous solution. More deionized water was then added to the solution and the diluted solution was stirred at least for 3 h. To ensure that the solution was homogeneous, several samples were taken, and their TOC values were compared to ensure consistency.

Adsorption tests were performed with NAs samples having various TOC values from 18 to 42 ppm to investigate the presence and profiles of isotherms. This TOC range was selected as it was reported that the NA concentrations in Athabasca oil sands tailings ponds have been in the range of ~40–120 mg/L.<sup>[11]</sup> Without changing the pH of water from its natural value of 7, the solubility of NAs in water is about 40 mg/L.

The NAs/deionized water solution and AC mixture was placed in 20 mL vials. The ratio was set as 1 g of AC to 1 L solution. The vials were placed in an incubating shaker at 298 K and 175 rpm for 24 h. For replication purposes, three vials with the same concentration were used for each adsorption experiment for each different produced AC at different conditions. The vials were then agitated in a shaker for 24 h. The standard NAs solution (without AC) was mixed with silica sand. After 24 h, the samples were taken out of the shaker, and left to settle for 1 h before they were filtered using a 0.45-micron nylon syringe filter. The filtrate was then injected into a clean vial for TOC measurement. For reproducibility, each of the three vials was tested three times. The standard deviations of the TOC data were calculated and the deviation percentages were less than 1%.

The measurement of the total organic carbon (TOC), which refers to the amount of carbon bound in an organic compound, was used for quantity. The TOC was measured using a Shimadzu TOC-VE TOC analyzer (Columbia, MD, USA). TOC can be calculated by subtracting inorganic carbon from the total carbon. The main source of inorganic carbon was CO<sub>2</sub>, which dissolves in water and creates carbonic acid salts.

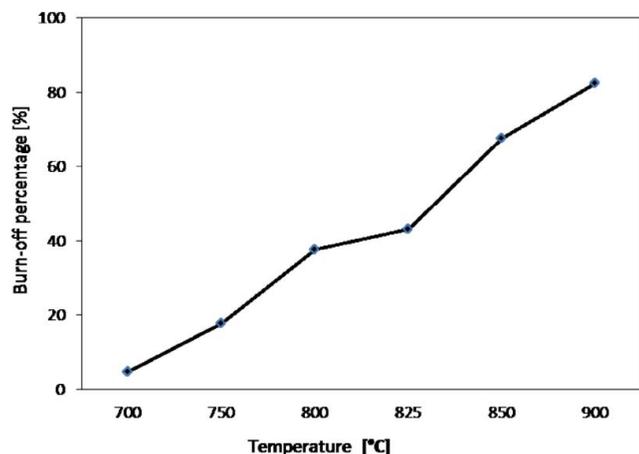


Fig. 2. Burn-off of the PH500 series versus activation temperature.

## Results and discussion

In production of biochar, biomass is converted to a material with a higher carbon density.<sup>[10]</sup> This is normally achieved by distilling off any volatile material in the biomass. Pyrolysis, the process of heating organic materials in an inert atmosphere, is used to achieve this purpose.<sup>[10]</sup> The yield of carbonization and burn-off, which indicates the extent of the reaction, are presented in Table 2. Figure 2 illustrates burn-off percentage versus activation temperature for the PH500 series. As the temperature increased, the burn-off also increased from 27 to 82%, indicating that the extent of the reaction enhanced. For the PH500 series with lower particle size, the burn-off was between 20 and 80% for the activation temperature range of 700 to 900°C.

For the PH1000 and PH1400 series, the burn-off was 27–56%, indicating that the burn-off percentage was similar for all 3 different particle sizes for any activation

temperature. The effect of particle size on the burn-off and yield was also not significant. It seems that only the temperature had a significant impact on the activation process, in terms of yield.

The production yields of the AC from biomass were between 5% and 15%, based on the initial biomass before carbonization. As the temperature increased, the yield decreased. The low yield can be attributed to the low fixed carbon and the high percentage of volatile material in the raw material. Interestingly, the burn-off and surface area for all 3 different mesh sizes at the same activation temperatures were almost the same. The discrepancy can be attributed to experimental error.

The BET surface area was also measured for all of the ACs as shown in Table 2. For the PH500 series, the surface area was plotted versus the activation temperature, which is presented in Figure 3. As the temperature increased, the surface area also increased to a certain activation temperature (825°C), after which the surface area started to decrease. The optimal activation temperature based on surface area was 825°C, at which the surface area was 750 m<sup>2</sup>/g.

The same trend can be seen in Figure 4, in which the surface areas of the PH1000 and PH1400 series are plotted versus the activation temperature. The optimal activation temperature was again 825°C, at which the surface areas of the PH1000 and PH1400 samples were 720 and 739 m<sup>2</sup>/g, respectively. This trend was also reported by Lua et al.<sup>[16]</sup> They concluded that the ACs produced at an activation temperature of 950°C had a lower surface area than at 850°C at the same conditions and that the carbon–CO<sub>2</sub> reaction was so severe at high temperatures that it caused high burn-off and resulted in detrimental effects on the quality of the AC.

The pore size distribution and microposity of AC were examined. Table 3 shows BET surface area, *t*-plot of the micropore area and *t*-plot of the micropore volume.

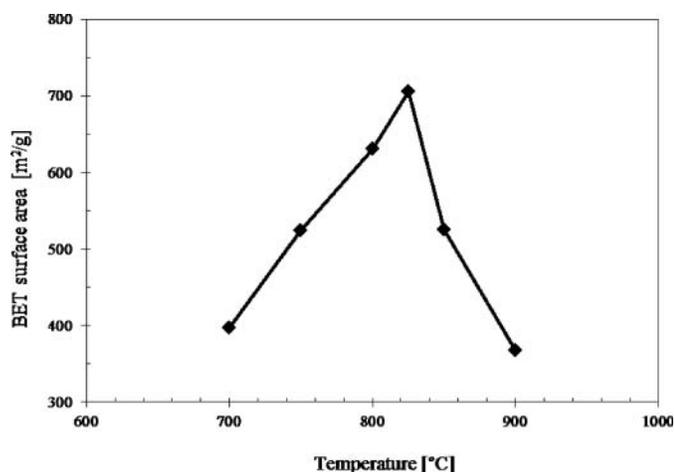


Fig. 3. Surface area of the PH500 series versus activation temperature.

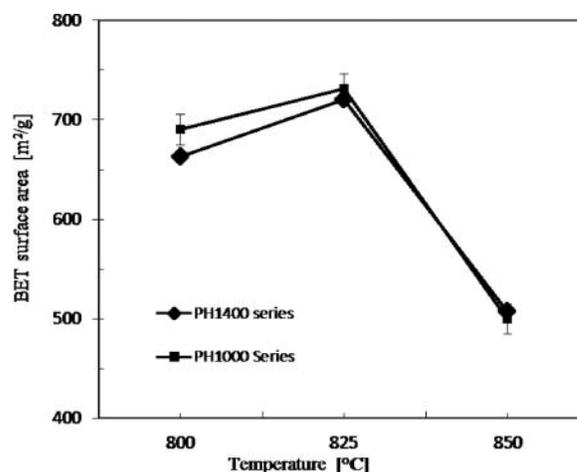


Fig. 4. Surface area of the PH1000 and PH 1400 series versus activation temperature.

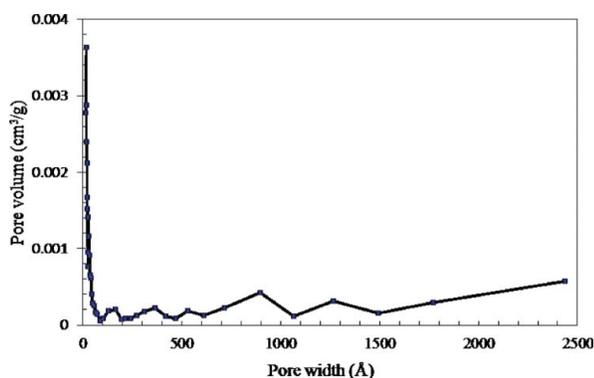
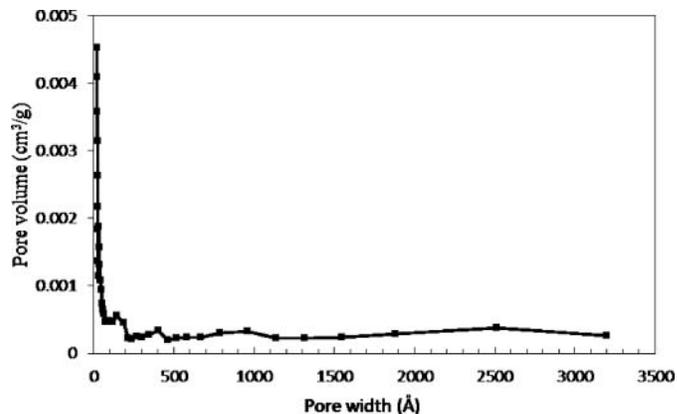
**Table 3.** BET surface area and microporosity of Acs.

Sample Name	BET Surface area (m <sup>2</sup> /g)	<i>t</i> -plot micropore area (m <sup>2</sup> /g)	<i>t</i> -plot Micropore Volume (cm <sup>3</sup> /g)
B500	233.93	NAs	NAs
B1000	296.34	NAs	NAs
B1400	290.05	NAs	NAs
PH500-1	396.55	392.36	0.1617
PH500-2	524.47	467.67	0.2340
PH500-3	632.36	619.52	0.2547
PH500-4	705.27	596.68	0.2678
PH500-5	525.78	487.66	0.2456
PH500-6	365.14	308.57	0.19882
PH1000-1	663.60	576.46	0.2800
PH1000-2	731.65	618.87	0.2974
PH1000-3	507.21	439.44	0.2706
PH1400-1	690.61	586.23	0.2834
PH1400-2	720.24	607.46	0.2944
PH1400-3	501.35	422.45	0.2698
AC Com*	489.51	229.00	0.1133
CA**	895.23	613.01	0.2980

\*Commercially activated carbon.

\*\*Chemically activated carbon.

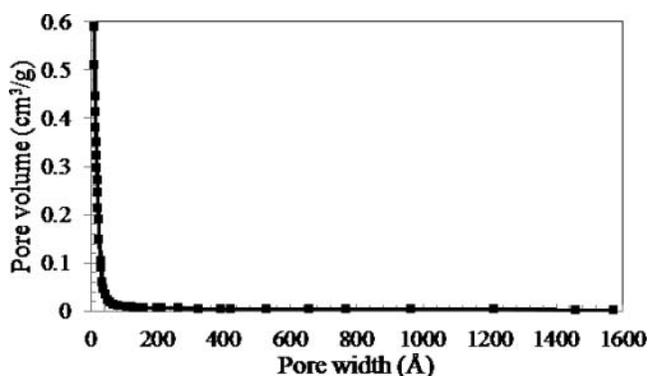
As shown, the physically ACs were mainly micropores; and, the chemically AC had more mesopore surface and therefore, it may be concluded that the microporosity is the result of physical activation of the samples by CO<sub>2</sub>. Having a larger surface area and more mesopores makes the chemically AC more favorable for adsorbing organics in water. The commercial AC that was provided by the Norit Company was considered to be applicable for wastewater treatment. Interestingly, all the physically produced ACs had almost the same average pore diameter, i.e., about 30 Å, which is in the mesopore range. From Table 3, one can notice that regardless of the particle sizes, the ACs had almost the same properties. In other words, mesh size did not affect the surface area, micropore

**Fig. 5.** Pore volume versus pore width of sample PH1000-1.**Fig. 6.** Pore volume versus pore width of sample PH1000-2.

volumes and micropore areas, whereas temperature did have a significant effect on these properties.

In Figures 5 to 8, the pore size volume versus the pore width is shown for different AC samples. The types of the pores are generally defined as: micropores (pore diameter <2 nm, 20 Å), mesopores (2–50 nm, 20–500 Å) and macropores (pore diameters >50 nm, 500 Å) according to the definitions established by the International Union of Pure and Applied Chemistry (IUPAC). As shown in Figures 5 and 6, the two physically treated ACs showed almost the same trend for the relationship between pore volume and pore width, which represents the pore size distribution. This trend was also observed for all other physically activated carbons. As shown, the pores for physically treated AC are in the range of micro, meso and macro, but dominated by the micro size. In chemical activation (Fig. 7), most of the pore volume was in the micropore range, and in the commercial AC, the distribution showed several peaks, indicating that most of the pore sizes were in the meso range.

The results show that all three biochar samples had similar BET surface area. The effect of activation can be understood by comparing the surface area of biochar prior

**Fig. 7.** Pore volume versus pore width of sample CA.

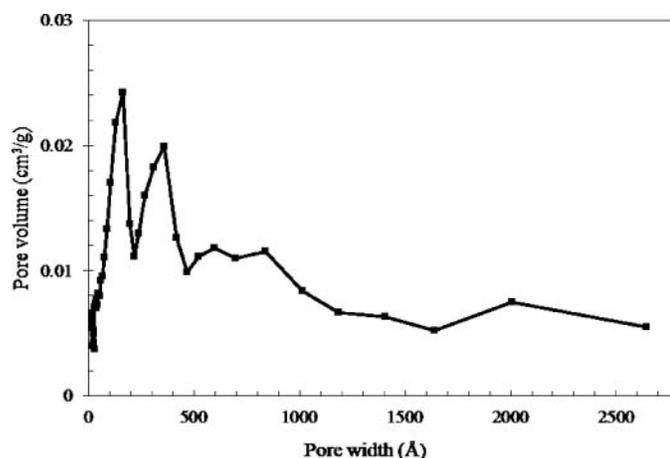


Fig. 8. Pore volume versus pore width of commercial AC.

to activation with that of the AC. Significantly increased surface area resulted. The effect of the temperature on the production of AC can be explained in terms of the creation of more surface area rather than changing pore width, thus increasing the pore size. TGA tests were performed to compare the physical activation results effect on the properties of the AC produced inside the reactor with those of the small TGA chamber with precise measurements. The TGA samples underwent the same steps as those of the biomass in the larger reactor, such as the heating ramp, final temperature and change of the gas from  $N_2$  to  $CO_2$ . The resulting final weight can be found with the TGA data shown in Figures 9 and 10, where plots of weight versus time and weight versus temperature are presented, respectively.

These are consistent with the results from the larger reactor, As is shown in the figures, the major weight loss happened at the beginning of the process, i.e., during the

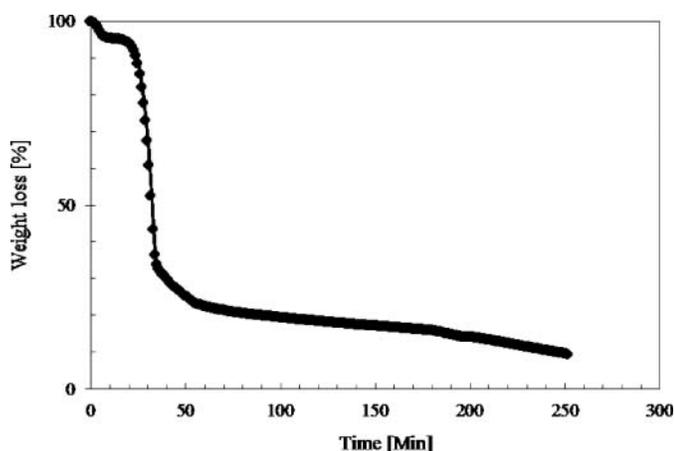


Fig. 9. Thermogravimetric results for sample PH1000-1 (weight versus time).

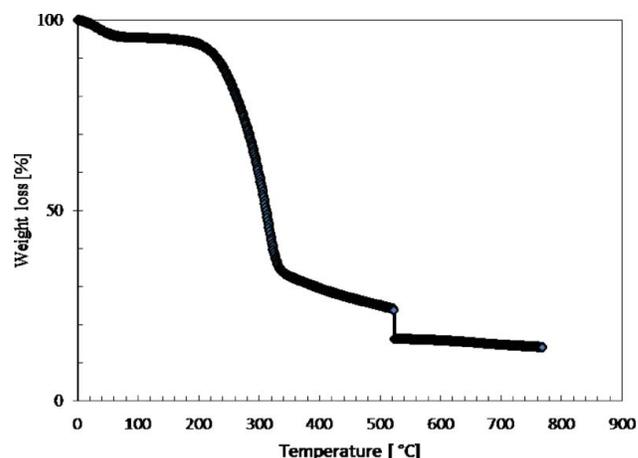


Fig. 10. Thermogravimetric results for sample PH-1000-2 (weight versus temperature).

carbonization, where a material richer in carbon was produced and volatile material was removed, as expected according to the work of Lehmann and Joseph.<sup>[10]</sup> In the second step, not much weight loss occurred. This trend was almost the same for all of the physically ACs.

The final yield calculated from TGA was very close to the experimental data. There was a small discrepancy that can be attributed to the difference between the heat transfer in the reactor and that of the small TGA chamber. It is remarkable that the yield calculated from TGA was slightly lower than that of the experimental data; however, this is most likely because a more uniform heat distribution was provided in the TGA chamber, allowing a greater extent of reaction.

The elemental analyses for produced AC are shown in Table 4. The carbon content was about 64–88%, which was predictable from the initial biomass analysis due to the removal of humidity and volatile material. Chemically

Table 4. Elemental analysis of produced AC.

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)
B500	83.41	1.82	2.31	0.46
PH500-1	85.33	0.03	0.97	1.18
PH500-2	80.99	0.76	1.27	1.17
PH500-3	74.76	1.92	2.06	1.16
PH500-4	71.07	1.99	1.92	1.78
PH500-5	68.89	2.4	1.86	1.22
PH500-6	63.18	2.64	1.90	1.62
PH1000-1	72.98	2.06	1.63	1.18
PH1000-2	68.89	2.45	1.86	1.22
PH1000-3	63.18	2.64	1.90	1.62
PH1400-1	74.12	1.88	1.64	1.82
PH1400-2	65.34	2.32	2.15	1.14
PH1400-3	65.34	2.39	1.88	1.28
CA	54.24	3.40	1.75	1.27
AC <sub>Com</sub>	64.13	0.97	0.49	0.55

AC had the lowest carbon content (almost 54) among the ACs; and, the carbon content of the commercial AC was around 64%. A comparison of these carbon content values to those of the biochar showed that the carbon content decreased; therefore, the lost carbonaceous material can be associated with volatile material. As shown in Table 4, as the activation temperature increased, the carbon content also decreased. Another reason for the decrease in the carbon content of the produced AC can be the carbon-CO<sub>2</sub> reaction, which leads to a decrease of the carbon in the produced AC. Regarding the effect of particle size on the carbon content of the AC, those that were produced at the same activation temperature had almost the same carbon content, regardless of particle size. The same conclusion can be reached for the effect of particle size on the BET surface area.

The carbon content of the PH500 series samples is plotted versus activation temperature in Figure 11. It shows that, as the activation temperature increased, the carbon content of the produced AC decreased. This trend can also be seen in the PH1000 and PH1400 series. The PH500-1 sample had richer carbon content than the rest of this series and was close to the carbon content of biochar. The same phenomenon can be seen for the PH1000 and PH1400 series. The PH1000-1 and PH1400-1 samples, both of which were produced at 800°C, had richer carbon content compared to the rest of the samples of those series which were produced at higher temperatures (825°C and 850°C).

### Adsorption tests

Biochar samples, two samples of each group of physically ACs with higher surface area, chemically produced AC and commercially produced AC, were tested for adsorption of NAs. The results of the adsorption tests for various initial concentrations are shown in Tables 5 and 6 for all biochar and AC samples, respectively. In the tables, for each

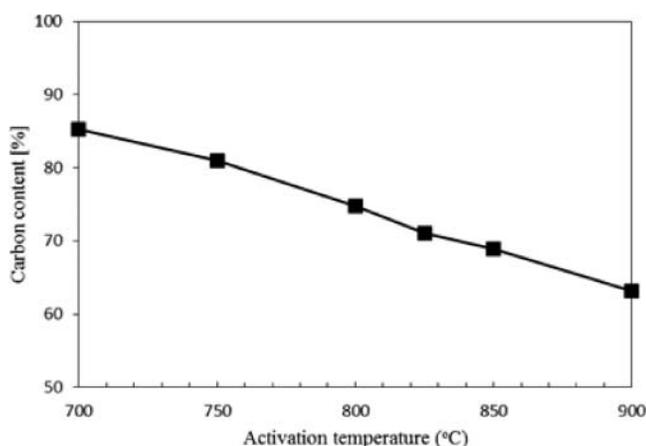


Fig. 11. Carbon content of AC versus activation temperature.

Table 5. Adsorption results for biochar samples for various initial TOC of NAs.

	TC (ppm)	IC (ppm)	TOC (ppm)
Initial TOC of NAs (18 ppm)			
B590	29.68	2.00	27.68
B1000	26.34	2.35	23.99
B1400	25.75	2.26	23.49
Initial TOC of NAs (28.4 ppm)			
B500	34.50	2.01	32.49
B590	32.14	2.35	29.79
B1000	31.45	2.26	29.19
Initial TOC of NAs (32 ppm)			
B500	38.47	2.31	36.16
B590	36.24	2.80	33.44
B1000	34.14	2.43	31.71
Initial TOC of NAs (37 ppm)			
B500	42.41	2.01	40.4
B590	37.78	2.35	35.43
B1000	36.68	2.26	34.42

initial total carbon shown, the total organic level after adsorption is also provided. In the calculation of the total organic carbon (TOC), inorganic carbon must be subtracted from total carbon. As the result of adsorption, TOC must decrease after adsorption.

As shown in Table 5, biochar adsorption showed an increase in the TOC level. This does not necessarily mean that there was no adsorption, but may have been caused by the inability to distinguish NAs from other organics. The biochar may have released some volatiles into the water.

The chemically produced AC had the best adsorption uptake (in the range of 50–80%) compared to the other ACs. This may be due to a higher surface area, more mesopores or a functional group on the AC.

The PH1400-2 sample showed the best adsorption among the physically produced ACs. The PH1000-1 sample showed a similar performance to the commercially produced AC. The PH500 series samples almost showed a little increase in TOC, which may be addressed using different methods, such as decreasing the pore size of the nylon membrane from 1 μm and 0.45 μm to 0.2 μm.

The PH1000-3 and PH1400-3 samples were not used in adsorption, because of the very low yield of the physically AC. An increase in inorganic carbon was observed through the use of physically activated carbon. The reason for that may be related to the usage of carbon dioxide for activation. Carbon dioxide may be attached on the surface of AC and then dissolved in the water creating bicarbonate and carbonate, which are sources of inorganic carbon. Silica sand, which was used with the standard NAs solution (no AC), showed NAs adsorption of 2 to 3 ppm.

In order to investigate the leaching of organics from biochar into the water, 3 biochar samples were placed in

**Table 6.** Adsorption results for AC for various initial TOC of Nas.

	<i>TC</i> (ppm)	<i>IC</i> (ppm)	<i>TOC</i> (ppm)	<i>Uptake</i> percentage (%)
Initial TOC of NAs (18 ppm)				
PH500-3	20.56	4.25	16.31	
PH500-4	21.45	4.51	16.94	
PH1000-1	9.85	4.60	5.25	71
PH1000-2	9.05	6.00	3.05	83
PH1400-1	7.01	3.01	4.00	78
PH1400-2	7.5	3.43	4.07	77
Com	7.03	2.03	5	72
CA	3.5	0	3.5	81
Initial TOC of NAs (28.4 ppm)				
PH500-3	30.48	4.30	26.18	
PH500-4	32.01	4.51	27.5	
PH1000-1	12.97	3.97	9.00	68
PH1000-2	11.48	5.98	5.50	81
PH1400-1	10.26	4	6.26	78
PH1400-2	11.9	4.9	7.00	75
Com	12.88	1.88	11	61
CA	5.5	0	5.5	81
Initial TOC of NAs (32 ppm)				
PH500-3	33.14	4.45	33.14	
PH500-4	35.04	4.71	30.33	
PH1000-1	14.85	2.87	11.98	63
PH1000-2	13	5.98	7.02	78
PH1400-1	11.43	3.4	8.03	75
PH1400-2	12.54	3.86	8.03	75
Com	14.6	1.6	13	59
CA	6.5	0	6.5	80
Initial TOC of NAs (37 ppm)				
PH500-3	38.35	3.84	34.51	
PH500-4	39.25	3.45	35.8	
PH1000-1	16.5	3.11	13.39	64
PH1000-2	15.58	5.98	9.6	74
PH1400-1	14.15	3.8	10.35	72
PH1400-2	15.62	3.7	11.92	68
Com	18.6	1.6	17	54
CA	8	0	8	78
Initial TOC of NAs (42 ppm)				
PH500-3	43.20	3.25	39.95	
PH500-4	44.15	3.51	40.64	
PH1000-1	20.15	3.11	17.04	59
PH1000-2	16.15	4.15	12	71
PH1400-1	14.99	3.49	11.5	73
PH1400-2	17.17	3.187	13.983	67
Com	21.8	1.8	20	52
CA	10.5	0	10.5	75

deionized water with the same conditions as the adsorption conditions. The TOC level was measured after 24 h of shaking. The results are shown in Table 7. The TOC level of the deionized water increased dramatically with the biochar samples. It seems that biochar leached out some organics. In ACs with particle sizes bigger than 590 μm (PH1000 and PH1400 samples), the TOC

**Table 7.** Biochar sample's TOC level in deionized water in the adsorption condition.

<i>Sample name</i>	<i>TC (ppm)</i>	<i>IC (ppm)</i>	<i>TOC (ppm)</i>
B590	19.34	1.32	18.02
B1000	12.75	1.82	10.93
B1400	13.23	1.73	11.50

remained the same, but there was an increase in the inorganic carbon material, such as carbonate and bicarbonate that can come from CO<sub>2</sub> on the surface of AC.

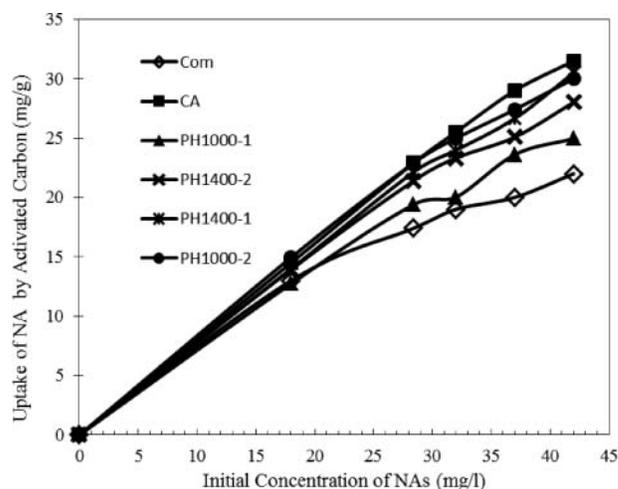
For plotting the isotherm and comparing ACs in a wider range, the adsorption capacity, *q*, was used. The adsorption capacity is defined as follows:

$$q = \frac{(C_0 - C_e)V}{W}$$

where *C*<sub>0</sub> is (mg L<sup>-1</sup>) the initial NAs concentrations, *C*<sub>*e*</sub> is the equilibrium concentration, *V* is the volume of the solution (L), and *W* is the mass of dry adsorbent used (g). The unit *q* is mg of adsorbed NAs per 1 g of AC.

For investigating the isotherm, *q* was plotted versus the initial NAs concentration. The results showed that the chemically produced ACs (CA) had the best adsorption at all initial NAs concentrations and that the commercially produced ACs had the lowest adsorption ability among ACs.

For comparison purposes, plots of *q* versus the initial concentration are depicted in Figure 12. This figure represents isotherms as the relationship between uptake of NAs by activated carbon and the initial concentration of NAs. As shown in Figure 12, the chemically produced ACs had better uptake at all initial concentration. The performance of the ACs were CA > PH1000-2 > PH1400-2 > PH1400-1 > PH1000-1 > commercial AC.



**Fig. 12.** Adsorption ability of different AC versus initial NAs concentration.

## Conclusion

The AC samples produced from wood waste were effective for the removal of NAs from aqueous solutions, showing better performance than a commercial AC sample. Among the physical activation conditions, the activation temperature had the most significant effect on the extent of the pyrolysis reactions, which is reflected in decreased carbon content and increased burn-off. Increasing the activation temperature resulted in increased surface area of the AC up to a certain point, after which the surface area decreased as the temperature increased. The optimal temperature was found to be 825°C. The decrease of surface area at temperatures higher than 825°C can be attributed to an extensive carbon–CO<sub>2</sub> reaction and increased ash content in the AC.

Particle size did not seem to have a significant effect on production characteristics, such as surface area and burn-off. All of the physically produced ACs in this study, regardless of their process conditions, displayed similar trends in micropore and mesopore distribution. It is noticeable that although chemically produced ACs had more micropores, the adsorption capacity was high due to the greater surface area. As the surface area increased, the adsorption ability increased. But, mesh size did not have a significant effect on the surface area or adsorption ability of the AC.

For the biochar samples regardless of the size and for physically AC with particle sizes below 590 μm, the base biochar showed an increase in total organic carbon in the aqueous solution. This increase was shown to be caused by the leaching out of organics in the biochar and passing of fine carbon particles through the filter.

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