

## Characterisation of Activated Carbons Obtained from Rice Husk

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### Abstract

Rice husk derived activated carbons doped with nitrogen have been studied using low temperature nitrogen adsorption, scanning electron microscopy, mercury porosimetry, thermogravimetric analysis combined with mass-spectrometry, differential scanning calorimetry and X-ray photoelectron spectroscopy. It has been shown that N-doped activated carbon produced by high temperature treatment of the starting material soaked with urea, has a significantly higher anion exchange capacity than the other samples studied, which correlates with its higher adsorption capacity towards nitrate ion removal from aqueous solutions with the initial concentration of 5 and 15 ppm.

## 1. Introduction

Activated carbons, ACs, were prepared from rice husk (CRH), which is an abundant waste material, with the aim of investigating their potential for removing nitrate from the water. Nitrate ( $\text{NO}_3^-$ ) is a common pollutant of surface water in Kazakhstan, which is difficult to remove.

For CRH characterization we used the following techniques.

(i) Low temperature nitrogen adsorption (LTNA) analysis and mercury porosimetry are both used to obtain quantitative data on the material porosity and pore structure [1, 2].

(ii) Scanning electron microscopy (SEM) is a high resolution imaging technique which provides images of the sample surface structure.

(iii) Differential scanning calorimetry (DSC) is a technique for measuring the energy required to obtain a near zero temperature difference between a test sample and an inert reference material, which are both subjected to an identical heating, cooling or constant temperature cycle.

(iv) Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of carbon materials can be measured as a function of increasing temperature

(with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss).

(v) In X-ray Photoelectron Spectroscopy (XPS) the energy and number of electrons released from the surface of a sample owing to X-ray irradiation is measured. This information is used to determine the chemical state of elements in the uppermost layer of the material and the semi-quantitative elemental composition of the layer to the depth of 10 nm.

(vi) Acid-base (Boehm) titration has been proposed as one of the simplest methods for the characterisation of surface properties that can be used to identify surface functional groups of different carbons [4].

(vii) Ion chromatography method was selected for determination of dissolved ions in water [3].

In this work the pore structure and physico-chemical properties of AC materials prepared from rice husk have been studied.

## 2. Methodology

The initial AC, designated as CRH-I, was obtained from rice husk by carbonisation at 700 °C in inert atmosphere followed by chemical activation with potassium carbonate at 950 °C. In order

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to form oxygen and nitrogen-containing groups on the surface, CRH-I sample was first ozonated at 120–124 °C (24 h) and then heat treated in the atmosphere of ammonia at 350 °C giving AC product CRH-II. In an alternative modification route, CRH-I sample was first oxidised with concentrated nitric acid, washed till neutral pH and dried, then soaked in urea solution, dried and heat treated in inert atmosphere at 950° to produce AC material CRH-III. All samples were washed with hot distilled water until neutral pH was reached.

The porous structure, texture and physicochemical properties of the activated carbons were studied using pH-potentiometric titration, LTNA and SEM techniques. The carbon adsorbents were analysed and nitrogen adsorption isotherms determined using an Autosorb-1 (Quantachrome, UK) in the range of relative pressures from 0.005 to 0.991. The data were analysed using Quantachrome data analysis software. The following mathematical models were used: Brunauer-Emmett-Teller (BET) theory and the QS density functional theory (QSDFT) for slit/cylindrical pores, in order to calculate the materials specific surface area, pore volume and pore size distribution [1, 2]. The surfaces of materials were examined using the SEM imaging obtained with field emission SEM (Zeiss NTS). CRH carbons were investigated by Dynamic DSC using the cooling and heating range from -50 °C to 500 °C at a controlled heating rate 10 °C/min and monitored over 1 h. Thermogravimetric analysis was performed using TGA analyser Q500 (TA Instruments) coupled with mass spectrometer (TGA-MS). XPS was performed using an ESCALAB 250 Xi system (Thermo Scientific) equipped with a monochromated Al K $\alpha$  X-ray source, a hemispherical electron energy analyser, a magnetic lens and a video camera for viewing the analysis position. Wide scans (step size 1 eV, pass energy 200 eV) and narrow scans (step size 0.1 eV, pass energy 20 eV) of the N1s (binding energy, BE ~399 eV), C1s (BE ~285 eV), O1s (BE ~531 eV), and Si 2p (BE ~100 eV) regions were acquired from three separate areas on each sample. Data were transmission function corrected and analysed using Thermo Avantage Software (Version 5.952) using a smart background.

In our experiments we applied a simple Boehm titration using 0.025 M NaOH or 0.05 M HCl in 0.1 M NaCl to determine the total surface density of acidic or basic groups, respectively, measured by Glass Combination Electrode (BDH, UK). The back titration with 0.025 M HCl of NaOH solution after the latter's contact with carbon or with 0.05 M NaOH of HCl solution after its contact with activated carbon was performed in triplicates for each

sample. In each case 0.100 g of activated carbon was shaken with 20 mL solution of NaOH or HCl overnight.

The carbon materials of CRH series were tested for their ability to remove oxyanions such as nitrate from solution using an Ion Chromatograph Metrohm IC 930 system.

### 3. Results and Discussion

The low temperature nitrogen adsorption data for the CRH carbons are presented in Table 1. The surface areas show comparable values, and the calculated micropore and mesopore volumes demonstrate a larger proportion of the total pore volume attributed to the mesopores.

The LTNA surface area and pore volume results calculated by the QSDFT method show that CRH-III has the largest surface area and the ratio between micropore and mesopore volumes shows that a larger proportion of the total pore volume can be attributed to the mesopores, with sample III having a significantly higher value (Figs. 1 and 2) [2]. Samples CRH-I and CRH-II have a similar pore size distribution and surface area.

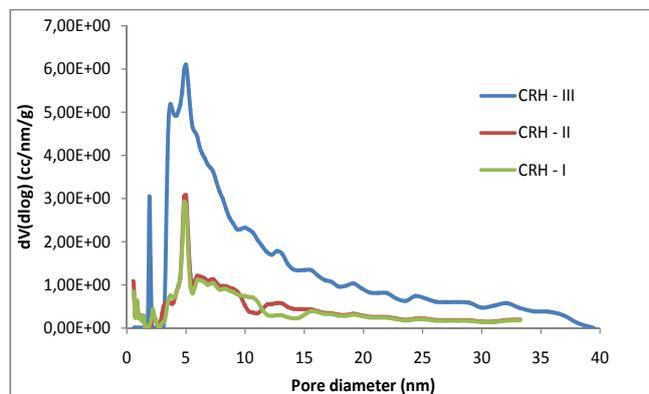


Fig. 1. Pore size distribution of carbons CRH-I, CRH-II and CRH-III measured by LTNA porosimetry and calculated by the QSDFT method.  $dV/d\log D$

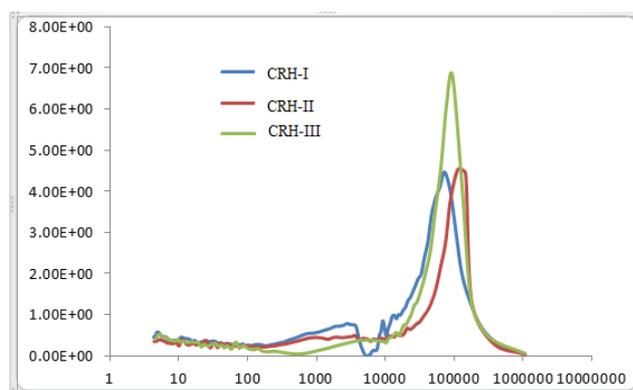
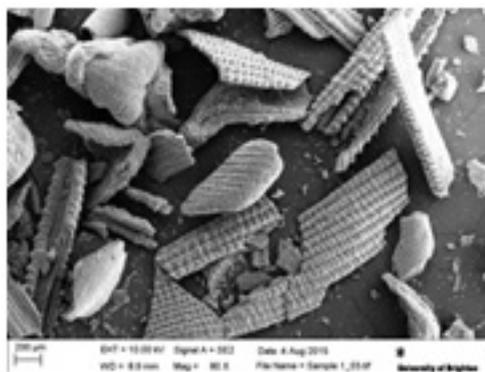


Fig. 2. The results of mercury porosimetry analysis plotted as incremental pore volume versus pore diameter.

**Table 1**  
The surface area and pore volume of materials measured by LTNA

| Material | BET surface area (m <sup>2</sup> /g) | QSDFT surface area (m <sup>2</sup> /g) | Pore volume (cc/g) | Micropore volume (cc/g) | Mesopore volume (cc/g) |
|----------|--------------------------------------|--|--------------------|-------------------------|------------------------|
| CRH-I    | 1174.6                               | 1270                                   | 0.968              | 0.265                   | 0.703                  |
| CRH-II   | 1290.2                               | 1420                                   | 1.06               | 0.296                   | 0.762                  |
| CRH-III  | 2322.4                               | 1820                                   | 2.576              | 0.100                   | 2.48                   |



(a) CRH-I



(b) CRH-II



(c) CRH-III

Fig. 3. SEM images of CRH activated carbons.

The results of the study porous structure of the samples by mercury porosimetry show that the sample CRH-I has higher porosity in the large mesopore size range and small macropore size range from 20 to 800 nm (200 to 8000 Å, Fig. 2). The peak around 100,000 Å, or 10 micron, for all three carbons originates from interparticle distances rather than intraparticle pores.

The SEM images (Fig. 3) show that all three ACs have the same or similar texture. All of them have a very heterogeneous particle size distribution including nanoparticles in the range from 20 to 80 nm (CRH-I), 40–140 nm (CRH-II) and 40–100 nm (CRH-III). All samples were mechanically fragile and formed dust.

The DSC results are shown in Fig. 4. The plots show the dependence of heat flow variations, mass and its time derivative on temperature. The time

derivative of mass helps to clearly identify the dehydration stage in the temperature range from 50 to 120 °C.

The plot for CRH-II displays three small peaks on the rate of the sample mass change, whereas two peaks are observed for CRH-I and one large peak for CRH-III. The first peak corresponds to the desorption of (free) water in the temperature range of 50–120 °C, after which there is no adsorbed water left on the surface. The peak observed on the DSC curve of CRH-II most likely characterises the process of dehydroxylation of the surface bound functional groups in the temperature range between 170 °C and 220 °C. Thus, it appears that the processes of dehydration and dehydroxylation do not overlap as heating of the material occurs at a high rate (10 °C/min) and in the natural environment, similar processes occur at lower temperatures (10–50 °C).

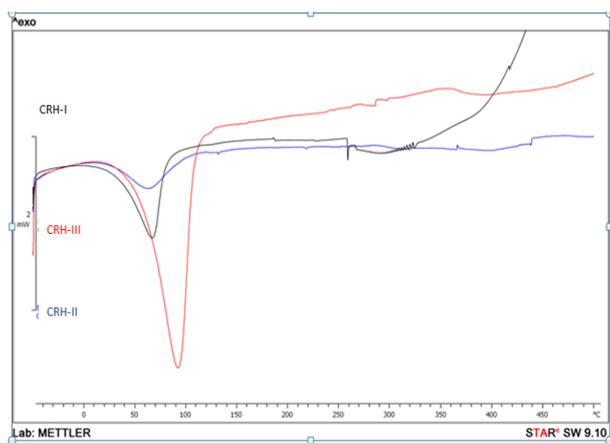


Fig. 4. Differential scanning calorimetry of CRH carbons.

Decarboxylation, that is, removal of CO/CO<sub>2</sub> groups from the surface oxygen-containing groups, takes place at a higher temperature in the range of 260 °C. The results of TG-MS analysis are presented in Table 2. Samples CRH-II and CRH-III showed a limited amount of water released (fragments 18<sup>+</sup> – H<sub>2</sub>O<sup>+</sup>, 17<sup>+</sup> – OH<sup>+</sup>, 16<sup>+</sup> – O<sup>+</sup>, 19<sup>+</sup> – HDO<sup>+</sup>). CO<sub>2</sub> was the main component released from the sample CRH-I (44<sup>+</sup> – CO<sub>2</sub><sup>+</sup>, 22<sup>+</sup> – CO<sub>2</sub><sup>++</sup>, 12<sup>+</sup> – C<sup>+</sup>). All samples released NO<sup>+</sup> fragments, however S<sup>+</sup> was only detected for CRH-II and CRH-III, which was confirmed by EDAX (electron-dispersive X-ray analysis) results. The origin of the latter fragment is

not clear. At higher temperature the intensity of the 30<sup>+</sup> ion is slightly increased. It is not clear whether it is an artifact or it belongs to the released NO<sup>+</sup>. As for NH<sub>3</sub>, the signal 15<sup>+</sup> (NH<sup>+</sup>) in general selectively corresponds to NH<sub>3</sub> unless CH<sub>3</sub><sup>+</sup> is present.

The results of XPS survey scan analysis (atomic percentage of elements) are presented in Table 3.

The XPS results show that CRH-II and CRH-III have significant amount of nitrogen in amine groups (Fig. 5) and there is no presence of amide in these carbons and areas analysed. The distribution of N-containing groups in CRH-III is different from CRH-II, which was expected owing to the different synthetic routes of these two carbons. As per sample description, nitrogen was not expected in sample CRH-I. The amount of nitrogen present in CRH-I is below detection limit of the instrument, i.e. below 0.1 atomic%. However, small quantity of nitrogen was detected while carrying narrow scan analysis (Fig. 5). All samples have shown the presence of usual functional oxygen-containing groups C-O, and Si, the latter originating from the raw material, rice husk. Si was not completely removed in the process of synthesis of CRH-II and CRH-III. Interestingly, some Mg and Mn were detected in CRH-I and CRH-II suggesting that they were also present in the starting raw material. Apparently, treatment with nitric acid eliminated the traces of these metals from carbon.

**Table 2**  
The results of TG-MS analysis

| Sample  | Level of temperature |                      |                      |                      |                      |                      |                               |                      |                       |                       |                              |                              |                       |
|---------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|-------------------------------|----------------------|-----------------------|-----------------------|------------------------------|------------------------------|-----------------------|
|         | 1<br>12 <sup>+</sup> | 2<br>15 <sup>+</sup> | 3<br>16 <sup>+</sup> | 4<br>17 <sup>+</sup> | 5<br>18 <sup>+</sup> | 6<br>19 <sup>+</sup> | 7<br>22 <sup>+</sup>          | 9<br>26 <sup>+</sup> | 12<br>30 <sup>+</sup> | 14<br>42 <sup>+</sup> | 16<br>44 <sup>+</sup>        | 18<br>46 <sup>+</sup>        | 20<br>64 <sup>+</sup> |
| CRH-I   | C <sup>+</sup>       |                      | O <sup>+</sup>       | OH <sup>+</sup>      | H <sub>2</sub> O     | HDO <sup>+</sup>     | CO <sub>2</sub> <sup>++</sup> |                      | NO <sup>+</sup>       |                       | CO <sub>2</sub> <sup>+</sup> |                              |                       |
| CRH-II  | C <sup>+</sup>       |                      |                      |                      |                      |                      | CO <sub>2</sub> <sup>++</sup> |                      | NO <sup>+</sup>       |                       | CO <sub>2</sub> <sup>+</sup> | NO <sub>2</sub> <sup>+</sup> | S <sup>+</sup>        |
| CRH-III | C <sup>+</sup>       | NH <sup>+</sup>      |                      |                      |                      |                      | CO <sub>2</sub> <sup>++</sup> | CN <sup>+</sup> ?    | NO <sup>+</sup>       | CNO <sup>+</sup> ?    | CO <sub>2</sub> <sup>+</sup> | NO <sub>2</sub> <sup>+</sup> | S <sup>+</sup>        |

**Table 3**  
XPS survey scan data of samples CRH-I, CRH-II and CRH-III. Survey scan data were acquired from three areas on each samples and standard deviation were calculated from these data.

| Name  | CRH-I         | CRH-II        | CRH-III       |
|-------|---------------|---------------|---------------|
|       | Avg. Atomic % | Avg. Atomic % | Avg. Atomic % |
| Mg1s  | 0.9 ± 0.1     | 0.4 ± 0.1     | 0             |
| Mn2p3 | 0.1 ± 0.1     | 0.2 ± 0.1     | 0             |
| O1s   | 8.8 ± 0.4     | 6.7 ± 0.5     | 3.5 ± 0.3     |
| N1s   | 0             | 1.3 ± 0.1     | 1.3 ± 0.1     |
| C1s   | 88.6 ± 0.8    | 90.3 ± 0.8    | 94.1 ± 0.6    |
| Si2p  | 1.6 ± 0.2     | 1.1 ± 0.2     | 1.1 ± 0.2     |

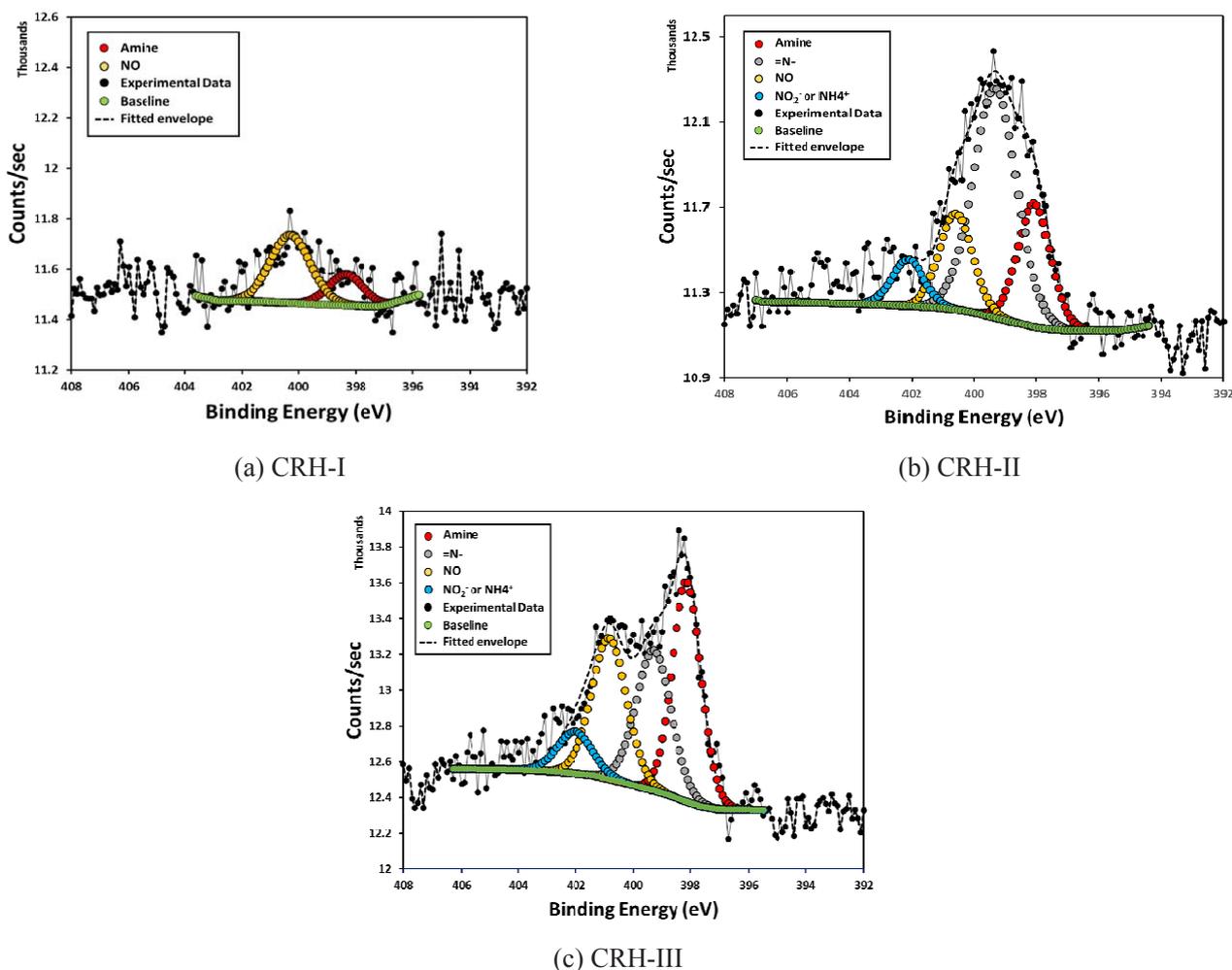


Fig. 5. Narrow scans of N1s spectra.

**Table 4**

Ion-exchange groups on CRH carbons determined by potentiometric titration and their adsorption capacity towards nitrate ion

| Carbon  | Acidic groups, meq/g | Basic groups, meq/g | Adsorption of nitrate, mg/g |            |
|---------|----------------------|---------------------|-----------------------------|------------|
|         |                      |                     | 15 ppm                      | 5 ppm      |
| CRH-I   | 1.20                 | 1.65                | 0.1                         | negligible |
| CRH-II  | 1.36                 | 1.90                | 0.1                         | negligible |
| CRH-III | 0.90                 | 3.40                | 4.4                         | 1.35       |

Potentiometric titration showed the difference between the ion exchange properties of AC samples with CRH-III having the highest anion exchange capacity and CRH-II having the highest cation exchange capacity (Table 3). According to the preliminary data supported by XPS results [5], all samples are characterised by the presence of both basic and acidic groups.

Assessment of the adsorption of nitrate (and nitrite) by CRH carbons from model solutions con-

taining high concentration of nitrate (60 to 150 ppm) did not show significant differences in their adsorption capacity towards nitrate. The difference between nitrate adsorption by the three carbons studied was clear when the initial concentration was lowered (5 to 15 ppm).

The experimental results on nitrate adsorption (Table 4) correlate with the concentration of basic groups on the carbon surface.

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