Surface modification of activated carbon using an atmospheric pressure dielectric barrier discharge (DBD) plasma jet

R W Lubis\textsuperscript{1}, T E Saraswati\textsuperscript{1}, U H Setiawan\textsuperscript{1}, K Kusumandari\textsuperscript{2}
\textsuperscript{1}Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan, Surakarta 57126 Indonesia
\textsuperscript{2}Department of Physics, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan, Surakarta 57126 Indonesia

*Email: teguh@mipa.uns.ac.id

Abstract. We successfully modified an activated carbon layer using an atmospheric pressure plasma jet. The plasma was generated in dielectric barrier discharge (DBD) configuration using Cu wire and Cu tape separated by dielectric glass with an inner diameter of \(~1\) mm. An alternating current of \(1.5\) kV was supplied to the electrodes to generate the plasma using a mixture of Ar gas and ammonia vapor at varied flow speeds of \(1\) to \(7\) L/min for one-minute treatment. The changes to the wettability of the carbon surface were estimated from the contact angle of a water drop. After plasma treatment, a significant improvement in the surface hydrophilicity was observed. The contact angle decreased to \(~6\)\(^{\circ}\) from its initial contact angle of \(74\)\(^{\circ}\). This hydrophilic property was likely due to the successful attachment of an amino group supplied by the NH\textsubscript{3} plasma. An amino-functional group was covalently bound to the carbon, which happened after etching by Ar plasma during the plasma jet processing. In addition, Fourier transform infrared (FTIR) profiles were taken to provide definitive proof of the suggested amino surface modification. Overall, the plasma treatment described in the present study may become a tool in surface treatment modification applications conducted in atmospheric conditions for carbon-based materials.

1. Introduction

Activated carbon is a carbon allotrope widely used in adsorption—for example, in wastewater processing for removing methylene blue [1], in the adsorption of heavy metal ions [2] or in the adsorption of CO\textsubscript{2} [3]. Activated carbon can be produced from carbonaceous material such as coal, fly ash, tree bark and nut shells [4], and it has a well-known large surface area, porous structures and a wide spectrum of surface functional groups [5]. The surface of activated carbon is known to have hydrophobic characteristics; however, in its application, hydrophilic surface characteristics are required because they provide more effective activity. This change in surface properties can be achieved using plasma treatment [6].

Atmospheric pressure plasma jets have received attention due to their ability to produce reactive species at ambient temperatures [6]. Plasma jets generate an ionized gas flow, forming plasma discharge shaped like a flare in the glass tube. The flare length can extend up to several centimetres, and it can be adjusted by increasing the gas flow, electrical current or pressure gradient [6]. However,
a further increase in gas flow will reduce the length of the plasma jet [7]. Plasma jets are efficient tools for surface material modification [6] because the gas flow from the nozzle guides the reactive species straight to the surface of the material. Plasma jets are employed in various fields, such as surface treatment, cancer treatment, biomedical treatment, material processing and pollutant control [8, 9]. Moreover, plasma jets can be used to modify the surface characteristics of cotton fibres [10], metals (Al, Cu, and stainless steel) [11, 12] and polymers (PMMA, PE, PP, PET) [6, 13] to be more hydrophilic.

In the present study, we investigated thin-layer activated carbon surface modification using an atmospheric pressure dielectric barrier discharge plasma jet utilizing 1, 3, 6 and 7 L/minute flows of argon and ammonia gas. The results achieved were compared to activated carbon without plasma treatment. In order to provide definitive proof and understand the chemical reaction of the phenomena achieved, Fourier-transform infrared (FTIR) and ultraviolet visible (UV-Vis) spectroscopy studies were used to determine the surface characteristics before and after plasma treatment.

2. Experimental setup

2.1. Materials
Activated carbon from a local commercial supplier was deposited in a thin layer with double tape stuck on mica. After the activated carbon was flattened, an air spray was provided to clean and further flatten the thin layer. Ar gas (UHP, PT Samator), ammonia 25% (analytical grade, Merck), copper tape, copper wire and distilled water were the other materials used.

2.2. Plasma Jet
The atmospheric pressure dielectric barrier discharge plasma jet used in this work consisted of two electrodes and a 30 cm glass tube that had an inner diameter of 1.0 mm and an outer diameter of 5.0 mm. The tube was sealed with Teflon tape to prevent gas leakage. The Ar gas and ammonia vapor streams had flow rates of 1, 3, 6 and 7 L/minute. Copper wire 0.5 mm in thickness was used as an electrode inside the glass tube; copper tape was wrapped around the outside of the glass to serve as another electrode. High voltages were supplied to the electrodes using HVAC (Neon Pro) at 1.5 kV with a frequency of 50-60 Hz. The HVAC was connected to the regulator supply (Matsumoto Slide Regulator) to adjust the desired voltage. The configuration was installed vertically; the configuration scheme can be seen in Figure 1.

![Figure 1. The schematic of the plasma jet setup.](image-url)
2.3. Plasma treatment
The samples had a 1.0 x 1.0 cm square area and were placed 10 mm from the nozzle. The plasma treatment was carried out for 1 minute by manually directing the plasma jet at 5 points on the sample, firing at the central area for 20 seconds and the points to the top, left, bottom, and right of the centre of the sample for 10 seconds each, as shown in Figure 2. The morphological and chemical modifications of the activated carbon that were induced by the plasma jet process are discussed in the next section.

![Figure 2. Area of the plasma treatment.](image)

2.4. Treated surface analysis
The effect of plasma on the surface of activated carbon was studied by measuring the contact angle between the surface of the sample and a water droplet dropped right into the middle of the plasma treatment area. The surface characteristics before and after plasma treatment were analysed by Fourier-transform infrared spectroscopy (FTIR; IRPrestige-21 Shimadzu).

3. Results & Discussion
3.1 Contact angle
The changing of the surface characteristics of activated carbon after plasma treatment was indicated by the changing of the contact angle. Figures 3(a) to (e) show the observed contact angle of the activated carbon before and after treatment in various gas flows. The water contact angle (WCA) between activated carbon without plasma treatment and with plasma treatment showed significant differences—the untreated activated carbon had a WCA of 74°, while activated carbon with plasma treatment in the Ar/NH₃ gas flow 1, 3, 6 and 7 L/min had WCAs of 10°, 6°, 11° and 12°, respectively. The sample that experienced 3 L/min treatment was more hydrophilic than the others, showing that a flow of 3 L/min produces the best hydrophilic surface. Further increasing the gas flow rate only leads to a decrease in plasma length and the weakening of active species transportation along the tube, while the radial movement of the active species is enhanced [7]. Gas flow rates greater than 3 L/min also reduced the effectiveness of plasma formation because the gas remained in the tube for a shorter period, thus the plasma-activated species were rarely produced.

![Figure 3. Comparison of the water contact angles of activated carbon before plasma treatment (a) and after plasma treatment in various gas flows (b-e; 1, 3, 6, 7 L/min, respectively).](image)
The WCA of the activated carbon surface decreased after plasma treatment, indicating that the surface changed from hydrophobic to hydrophilic. This phenomenon likely occurred because plasma made with Ar/NH₃ gas produces reactive species such as -NH₂, which can attach to carbon atoms after carbon etching by reactive Ar plasma. Moreover, during the plasma treatment, the carbon etching may also have been followed by the introduction of oxygen-related polar groups [6, 10, 13, 11, 14, 15] that bonded with the carbon atoms. These oxygen-containing groups might have come from the atmospheric gas. Both amine- and oxygen-containing groups induced the formation of the hydrophilic surface of the sample.

3.2 FTIR Spectroscopy
In order to understand the chemical change on the surface of the activated carbon, an FTIR spectrometer was used to investigate the functional groups attached. In the spectra shown in Figure 4, the plasma-treated samples show several definitive peaks located at around 1400 cm⁻¹, 1600 cm⁻¹ and 3240 cm⁻¹. These peaks correspond to the absorption of C─N amine, N─H bending and N─H stretching [16], respectively. The untreated activated carbon also shows a peak at 1400 cm⁻¹, which may indicate the peak of C=C stretching. C=C stretching generally has an absorption band around 1400-1600 cm⁻¹. The FTIR peak observed in the treated sample at 1400 cm⁻¹ might overlap with C─N, as the peak at 1400 cm⁻¹ in the treated sample spectra is stronger than that of the untreated sample.

![Figure 4. FTIR Spectra of untreated and plasma-treated activated carbon.](image-url)

Sakudo et al. [17] explained that some of the treated surfaces were etched by plasma treatment. After the etching, the ionized particles from the plasma could attach to the sample surface, i.e., carbon atoms in the case of in this study. Even though the FTIR spectra profiles shown in Figure 4 are likely the same, however, the intensity of the FTIR absorption peaks in the treated sample are significantly higher than in the untreated one, indicating that the amounts of the represented functional groups increased after plasma treatment.
4. Conclusions

Atmospheric pressure plasma jet treatment was carried out to modify the surface of activated carbon using Ar/NH$_3$ plasma with gas flows of 1, 3, 6 and 7 L/min. The hydrophobic nature of activated carbon changed to produce a hydrophilic surface after plasma treatment, as indicated by a significant decrease in the contact angle from 74° to less than 15°. The changing of the surface characteristics was also confirmed using FTIR spectra, which showed the presence of C—N amines, N-H bending and N-H stretching, indicating the plausible attachment of hydrophilic amine groups covalently bonded to the carbon atoms.

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