Aniline concentration-dependent surface area of emeraldine salt polyaniline

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Abstract. In this paper, we have reported a study on the surface area of emeraldine phase polyaniline prepared from different concentration of aniline. Polyaniline was prepared using oxidative polymerization at low temperature. A Fourier infrared spectrometer and X-ray diffractometer were used to confirm the formation of the conductive phase of polyaniline. The Brunner-Emmet-Teller (BET) surface area of polyaniline was obtained at a relatively low concentration of aniline. The highest BET value was 611.88 m²/g.

1. Introduction
Conductive polymers have become known as an alternative to other inorganic materials due to their properties, such as being environmentally friendly and having a unique morphology [1]. They also have attractive electrical, conductive, and optical properties among other advantageous attributes [2]. Polyaniline is one of the most popular conductive polymers, and it has many electronic [3], electrochemical [4], and catalytic [5] applications as well as being used for sensors [6]. Polyaniline can be used for many applications, as it is a low-cost monomer that is easy to synthesize and has good environmental stability and high tunable conductive properties [7].

In addition to its advantages in production, polyaniline also has unique properties, such as high stability, superior conductivity [8], colour reversibility [9], high electrochemical capacitance stability [10], and so on. As a conductive polymer, polyaniline has a unique morphology. Its fibrous and porous structure [11] may be the cause of its successful application in electrodes, catalysts, and sensors. Having a porous structure may affect the surface area of a material [12]. Large surface areas optimize electron transport and ion diffusion, which may explain polyaniline’s favourable electrochemical performance [13, 14]. Therefore, optimizing the surface area of polyaniline may enhance its useful properties.

We synthesized polyaniline at various aniline concentrations to optimize its surface area. We chose oxidative polymerization as a synthesis method, because it is an easy and low cost way to produce polyaniline [15]. We confirmed the formation of polyaniline using Fourier transform infrared spectroscopy and determined its surface area using the BET and Barret-Joyer-Halenda (BJH) methods. There was significant variation in the surface area of polyaniline formed at various concentrations of aniline. Polyaniline in the emeraldine salt phase had a mesoporous structure and the highest surface area of all samples in this study and was formed at an aniline concentration of 0.04 M.
2. Methods
Aniline was supplied by Sigma-Aldrich, and ammonium peroxodisulfate (APS) and HCl were supplied by Merck. Distilled water was the solvent used in reagent preparation. Various concentrations of aniline (0.4, 0.3, 0.2, 0.1, and 0.04 M) as the monomer were used in this work. The oxidative polymerization was carried out by adding HCl to all reagents, using APS (0.3 M) as an initiator. First, aniline was dissolved in 25 mL HCl 0.2 M and stirred continuously for 15 min. Then, we dissolved APS into 25 mL HCl 0.2 M. APS solution was then added into the aniline solution rapidly in an ice bath between 0 and 5°C. The color of the aniline solution changed to green, and we stirred it continuously for 2.5 h under cold temperature conditions. After polymerization, we filtered the green precipitate and washed it with distilled water before drying it. Fourier transform infrared spectroscopy was performed using a SHIMADZU Prestige-21 to confirm the formation of the conductive phase of polyaniline. Surface area was investigated using a Micromeritics ASAP 2020 surface area analyzer with degassing condition 150°C for 6 h. The specific surface area was determined using the BET method. Then, the BJH method was used to determine pore size and distribution.

3. Results and discussion
We confirmed the formation of polyaniline using Fourier transform infrared spectroscopy at a range spectrum of 4000–650 cm⁻¹ for 0.3 M and 0.04 M concentrations of aniline. The obtained fingerprint had a major band at around 3300–3200 cm⁻¹, which corresponded to an N-H stretching secondary amine. Bands at 2900 and 2800 cm⁻¹ were assigned to the N-H²⁺ in the –C₆H₄NH²⁺C₆H₄⁻ group and a C-H stretching of an aromatic ring [11,16]. The C=C stretching vibration of an aromatic ring presented at 1520–1576 cm⁻¹ in a quinoid ring [16] and at 1438–1490, 1670 cm⁻¹ in a benzenoid ring [17,18]. The band at 1243–1233 cm⁻¹ can be attributed to the C-N stretching of a secondary aromatic amine, and the one at 890–885 cm⁻¹ to an out-of-the-plane for a 1,4-disubstituted aromatic ring (para-coupling) [19]. This para-coupling indicated the presence of a substituted head-to-tail coupling throughout polymerization [17].

The presence of polyaniline was confirmed by the presence of major bands at around 3300, 1500, and 1400 cm⁻¹, representing N-H stretching, the C=C stretching of a quinoid ring, and the C=C stretching of a benzenoid ring. Furthermore, emeraldine salt was obtained, which had a peak at around 3300–3200 cm⁻¹, which represented the N-H stretching of secondary amines in emeraldine salt [19].

![Fourier transform infrared spectra of the prepared polyaniline.](image_url)

Figure 1. Fourier transform infrared spectra of the prepared polyaniline.

In Figure 2a, we have shown the nitrogen adsorption-desorption isotherm of polyaniline, which indicated its texture. The shape of the adsorption isotherm of polyaniline was type IV, which suggested a mesoporous structure [12]. The mesoporous structure was confirmed by the presence of hysteresis
loops at a high relative pressure [14], of ca. 0.6–1 P/Po for an aniline concentration of 0.04 M and ca. 0.8–1 P/Po for an aniline concentration of 0.4–0.1 M. Varying aniline concentrations caused variation of N\textsubscript{2} adsorption capacity. At an aniline concentration of 0.04–0.3 M, there was a decreasing N\textsubscript{2} adsorption capacity, while there was a high capacity at an aniline concentration of 0.4 M. Based on N\textsubscript{2} adsorption and hysteresis loops, gas adsorption and desorption at an aniline concentration of 0.04–0.3 M corresponded to reduction pore [12]. Increasing aniline concentration from 0.04–0.3 M led to a decrease in average pore size from 14.26–10.46 nm. Pore size increased by 1.86 nm when aniline concentration was 0.4 M.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(a) Nitrogen adsorption-desorption isotherm, (b) average pore size, (c) cumulative pore area, (d) cumulative pore volume of the prepared polyaniline with different concentration of aniline.}
\end{figure}

In Figures 2c and 2d, we have shown the pore distribution of polyaniline at various aniline concentrations. At an aniline concentration of 0.04 M, polyaniline had fine pores indicated by the presence of a high cumulative pore area, high cumulative pore volume, and low average pore diameter. Therefore, polyaniline formed at an aniline concentration of 0.04 M had fine pores with a low average diameter and high pore distribution. At an aniline concentration of 0.3 M, polyaniline had a low pore...
distribution with dispersed, average diameter pores. Consequently, this polyaniline had a low surface area.

In Figure 3, we have shown the surface area of polyaniline at increasing aniline concentrations from 0.04–0.3 M. Polyaniline formed at a 0.3 M concentration of aniline had the lowest specific surface area (13.63 m$^2$/g). In contrast, when aniline concentration increased to 0.4 M, the specific surface area of polyaniline increased to 24.27 m$^2$/g. This result can be explained by the structure and pores of polyaniline. As higher pore distributions correspond with high surface areas, variation in the concentration of aniline created significant variation in surface area. At a high aniline concentration (0.4 M), high surface area occurred due to the high production of oligomer [20]. Therefore, high aniline concentrations cause the elongation of polymer chains, which increase the surface area of a polymer.

![Figure 3. Specific surface area of polyaniline.](image)

4. Conclusion
The surface area of polyaniline varied significantly at different concentrations of aniline. Low aniline concentrations, such as 0.04 M, formed polyaniline with a high surface area and pores with a low average diameter that were highly distributed. Of all concentrations tested, polyaniline obtained at a 0.04 M concentration of aniline had the highest surface area (61.88 m$^2$/g), and polyaniline obtained at a 0.3 M concentration of aniline had the lowest surface area (13.63 m$^2$/g).

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