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Effect of Hydrochloric Acid Concentration and Immersion Duration on Porous Paper Formation

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Abstract: Paper, consisting of intertwining cellulose fibers, possesses a porous nature that allows liquids to penetrate and stay within its structure. This natural porosity is vital for paper's ability to absorb substances, forming the foundation of porous paper. Porous paper, which has many interconnected void spaces, is essential for breathability, filtration, and absorption in various industries, including printing, biomedical applications, sensors, and filtration. This study explores the effects of varying concentrations of hydrochloric acid (HCl) and immersion times on the fabrication of porous paper, aiming to identify optimal conditions for achieving desired porosity levels. The experimental setup involved immersing paper samples in HCl solutions with concentrations ranging from 0.1 to 0.5 M, with immersion times ranging from 30 to 180 seconds for each concentration level. The paper samples were then assessed for surface characteristics, porosity, and absorption capabilities. The results demonstrate that higher concentrations of HCl and longer immersion times generally cause the paper's porosity to increase. However, it is noted that excessive acid concentration or prolonged immersion can compromise paper structure. The study identifies specific HCl concentrations and immersion times that optimize porosity while maintaining structural strength, which is critical for applications requiring controlled release, absorption, and filtration.

Keywords: concentration, hydrochloride acid, immersion time, porous paper

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1. INTRODUCTION

Porous paper is characterized by its intricate network of cellulose fibers and interconnected void spaces. It plays a crucial role in various industrial applications due to its high absorption capacity, filtration efficiency, and breathability [1]. The porosity of paper is a key determinant of its performance and suitability for specific uses like humidity sensors, making it essential to understand the factors that influence porosity during the production of porous paper. Some applications include humidity sensors, electronics and energy storage, sound absorption, absorbent packaging, and so on [2].

The production of porous paper involves a series of steps, with chemical treatments playing a significant role in modulating its porosity. This process enables manufacturers to finely adjust the porosity of the paper by modifying factors like concentration, treatment duration, and the choice of chemical [3]. This allows manufacturers to match the paper's porosity with precise specifications tailored for various applications. Hydrochloric acid (HCl) is commonly used as a chemical agent to induce porosity in a paper by selectively degrading cellulose fibers and creating void spaces within the matrix [4].

As reported in [5], the paper immersed in a 0.2 M HCl solution for 80 seconds undergoes modification, forming a porous paper. The concentration of HCl used during the treatment process and the immersion time of paper samples in the acid solution may be the key process parameters that directly influence the porous paper's resulting porosity, structure, and performance characteristics. Understanding the intricate relationship between HCl concentration, immersion time, and porosity is essential for optimizing the production process and tailoring porous paper properties to meet specific industrial requirements.

This study investigates the effect of different concentrations of HCl and immersion times on producing porous paper. The main objective is to identify the optimal HCl concentration and immersion time combination that yields the desired porosity level while maintaining the paper's mechanical strength and other essential properties.

This research provides comprehensive insights into HCl treatment's porosity-enhancing effects through a systematic experimental approach wherein paper samples are treated with varying HCl concentrations and immersion times. The findings of this study will not only contribute to advancing our understanding of porous paper production and have practical implications for industries relying on porous materials for diverse applications.

2. METHODOLOGY

In this work, the immersion setup shown in Figure 1 is used. Immersing paper with acid like HCl can selectively break down cellulose fibers, creating pores and increasing porosity [4].

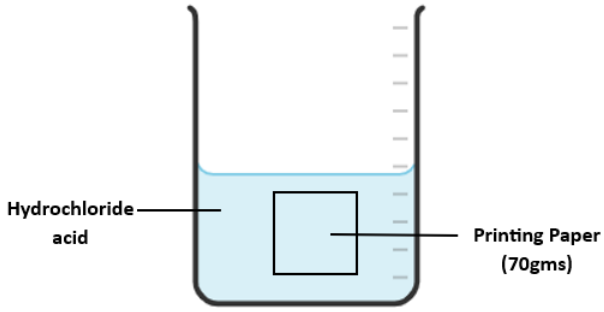


Figure 1. Immersion setup

The samples of printing paper (IK Yellow, 70gsm) were immersed in HCl solution for 30s to 180s at room temperature before rinsing with deionized water. Then, they will be kept drying at room temperature for 1 day or heated by oven at 100°C for 5 minutes before characterization takes place. The effect of drying conditions, immersion time, and different concentrations were observed in this study. The paper will be cut into dimensions ranging from 2 cm to 5 cm. The samples were weighed before and after the experiment. For each experiment condition, two replicate samples have been prepared.

The examination of the samples involved the use of Scanning Electron Microscopes (SEM), Energy-dispersive X-ray spectroscopy (EDX), Atomic Force Microscopy (AFM), and the calculation of porosity. SEM (HITACHI TM3000, Japan) produces high-resolution images of a sample's surface by scanning it with a focused electron beam. At the same time, EDX is paired with SEM to determine the elemental composition of the sample being imaged [6]. AFM (SII NanoTechnology Inc., SPI3800N, Japan) generates images of a sample's surface at high resolutions by scanning a sharp probe over the surface [7]. Determining the porosity of the paper samples provides numerical data on the level of pore formation caused by the HCl solution. Porosity is typically calculated as the ratio of void volume to total volume, expressed as a percentage, which can be calculated by applying the following equation by considering the density of cellulose as 1.5 g/cm^3 [5]:

$$\text{Porosity (\%)} = \left(1 - \frac{Psample}{1.5}\right) \times 100 \qquad (1)$$

where $Psample$ (g/cm^3) is the density of the sample. The $Psample$ can be determined from the mass of the sample after the experiment divided by the volume of the sample.

3. RESULTS AND DISCUSSION

3.1 Effect of Drying Condition

To determine the modification of porous paper by HCl solutions, a comparison is conducted between two drying conditions, drying at room temperature and drying in an oven at 100°C. This comparison aims to evaluate the impact of drying environments on HCl-treated porous paper samples. The SEM-EDX results for drying in the room temperature and drying in heat conditions are shown in Figure 2.

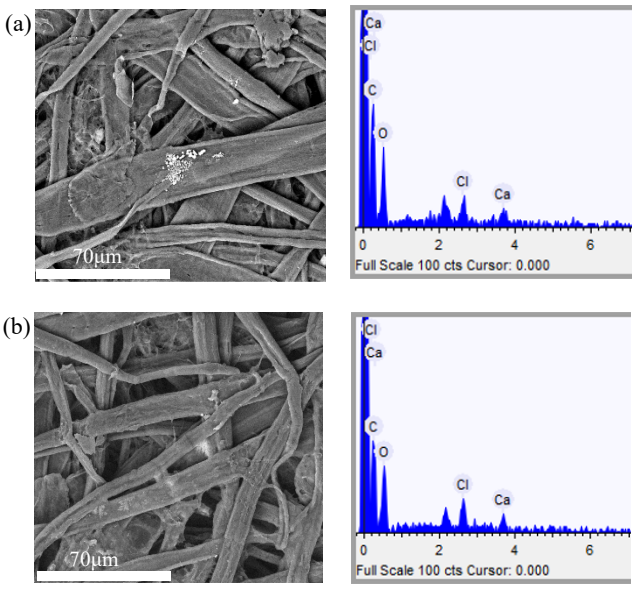


Figure 2. SEM and EDX of the samples (a) room temperature (b) heat condition

Based on the observation of SEM images from both room temperature and heat conditions, small white spots were observed between cellulose fibers. These white spots indicate the presence of material deposits or changes in the structure of the paper, potentially resulting from the HCl immersion and subsequent drying processes. This observation was further supported by EDX analysis, which revealed specific elemental compositions in the samples. Specifically, the room-temperature sample exhibited 8% calcium (Ca) and 10% chlorine (Cl), while the heat-treated sample showed 8% Ca and 12% Cl. Ca and Cl elements from the HCl solution have reacted with the cellulose fibers, shown in Equation (2), leading to the formation of these white spots. The percentage of Ca remains consistent between both samples, but the heat-treated sample shows a higher percentage of Cl compared to the room-temperature sample. According to Equation (2), a higher percentage of Cl indicates that more reactions happened [8].

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \qquad (2)$$

The porosity of samples is observed to support the SEM-EDX results further. The porosity of the paper samples was observed and plotted against the concentration of HCl solution used during immersion. As shown in Figure 3, it was observed that as the concentration of HCl solution increased, the percentage of porosity in the paper samples also increased. When comparing the drying conditions, it was noted that samples dried with heat consistently exhibited higher porosity percentages compared to those dried at room temperature. The heat-dried samples consistently show better results in terms of porosity across varying HCl concentrations, as depicted in Figure 3.

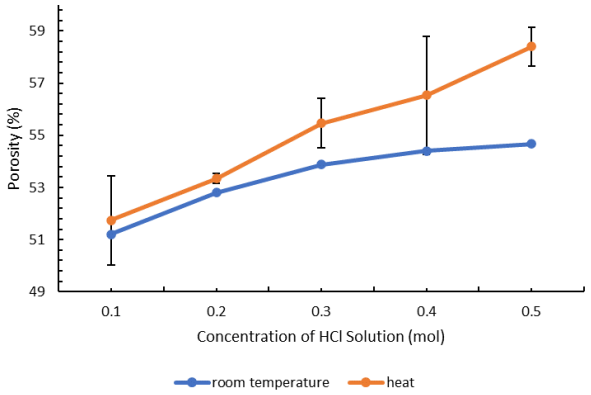


Figure 3. Porosity level at different concentrations of HCl solution

These findings suggest that both the concentration of HCl solution and the drying conditions play significant roles in determining the porosity of porous paper. The superior porosity observed in heat-dried samples indicates the effectiveness of heat in enhancing pore formation and structural modifications induced by the HCl treatment. These insights are crucial for optimizing the production process of porous paper, as they highlight the importance of selecting appropriate HCl concentrations and drying methods to achieve desired porosity levels for specific applications.

3.2 Effect of Immersion Time in Different Concentrations

Based on the findings in section 3.1, the sample dried with heat better than at room temperature. To further analyze the relationship between the effect of immersion time in different concentrations of HCl on the porous paper, the experiment focuses on HCl solutions with concentrations of 0.1 M to 0.5 M, with immersion times set at the 30s, 60s, 120s, and 180s were conducted. Figure 4 shows the relationship between the percentage of porosity with immersion time in different concentrations of HCl solution.

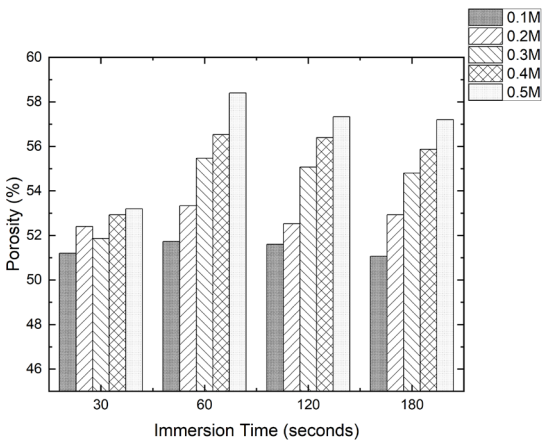


Figure 4. Porosity level with different immersion time

The data from Figure 4 indicates that porosity increases in correlation with the concentration of HCl solution. Higher concentrations of HCl lead to a greater extent of the paper's structure modification, resulting in increased porosity due to enhanced pore formation or structural changes induced by the immersion. For a 30-second immersion time, the percentage of porosity did not show significant changes across different concentrations of HCl solution. The 60s immersion time resulted in a higher porosity value than others. This suggests that longer immersion times allow for more thorough penetration of HCl into the paper matrix, leading to greater pore formation and increased porosity. However, it is notable that porosity decreases for immersion times of 120s and 180s, despite the initial trend of increasing porosity with higher concentrations of HCl solution and longer immersion times [5]. This observation suggests there may be a threshold or optimal immersion time beyond which further treatment leads to diminishing returns or even detrimental effects on porosity. Balancing the duration of HCl treatment with the desired level of porosity and structure is crucial for achieving optimal results in porous paper production.

To further support the results for the percentage of porosity, SEM images of untreated paper, 0.1 M and 0.5 M of HCl, with 30s to 60s immersion time, have been compared. The higher and lower concentrations of HCl solution were chosen to allow for a comprehensive analysis of the effects of immersion time on paper properties. The SEM images for untreated paper and paper immersed in different concentrations and at different times are shown in Figure 5 and Table 1, respectively. The comparison between untreated paper and paper immersed in HCl solutions revealed decreased white spots on HCl-treated paper. This decrease in white spots proves that HCl can modify the paper structure and properties. As an acidic solution, HCl can interact with the paper matrix's cellulose fibers. This interaction can lead to chemical modifications such as hydrolysis, which breaks down cellulose chains and creates void spaces or alterations in fiber morphology [3].

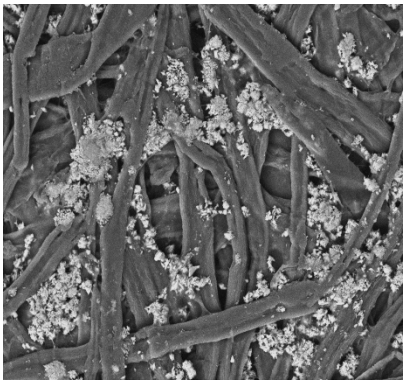


Figure 5. SEM image for untreated paper

Table 1. SEM images for samples with different HCl concentration and immersion time

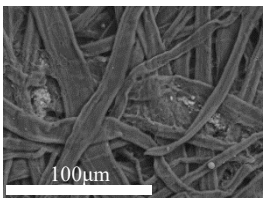
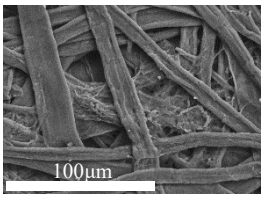
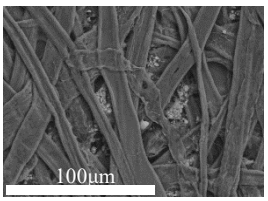
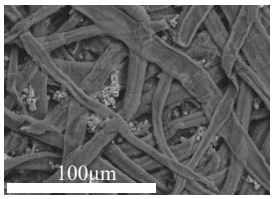
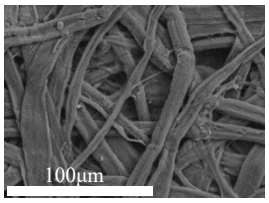
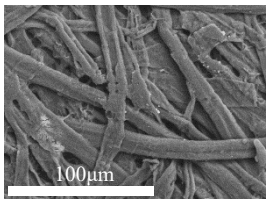
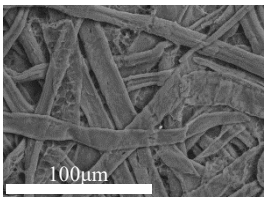
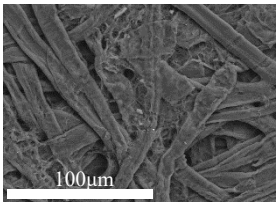
Concentration of HCl	Immersion Time (s)			
	30	60	120	180
0.1 M				
0.5 M				

Table 2. EDX spectrum for samples with different HCl concentrations and immersion times

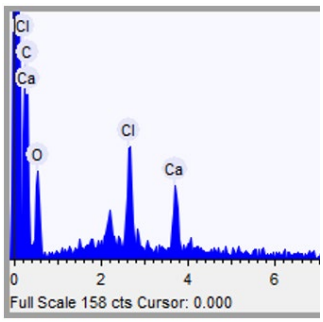
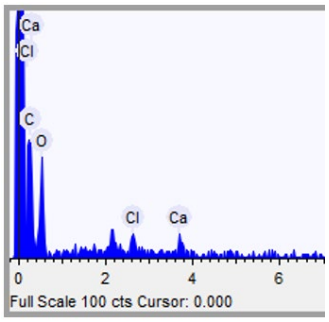
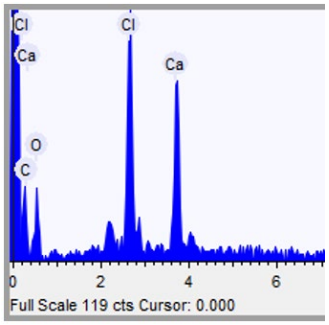
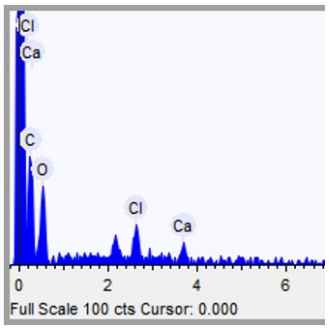
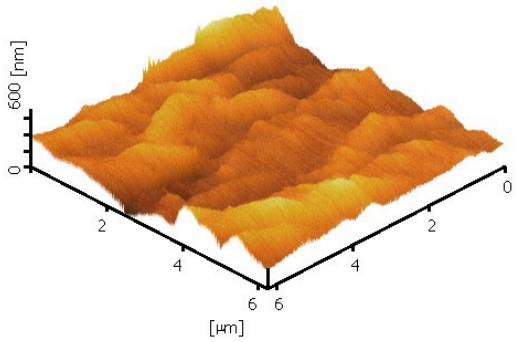
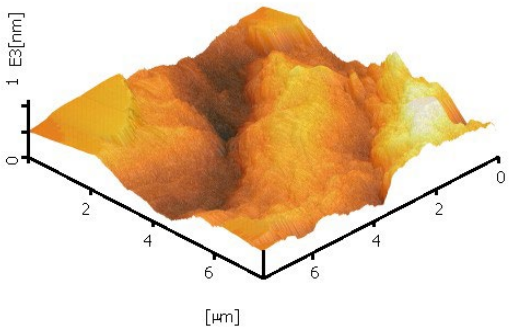
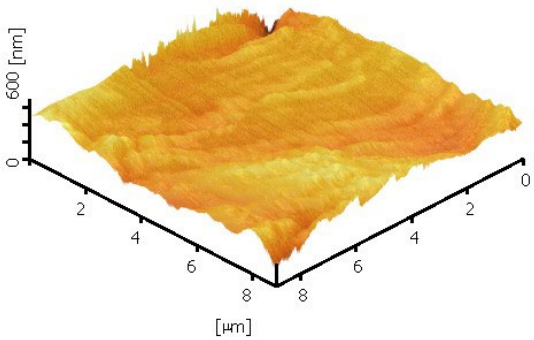
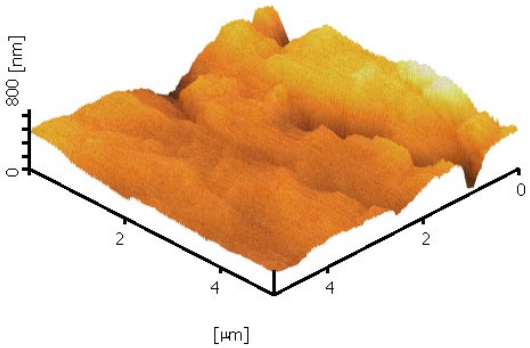
Concentration of HCl	Immersion Time (s)			
	30		60	
0.1 M		Element / % Ca 9.9 Cl 11		Element / % Ca 9.1 Cl 8.1
0.5 M		Element / % Ca 27 Cl 27		Element / % Ca 8.1 Cl 12.5

Table 3. AFM 3D images for 0.5M of HCl solution with different immersion times

Immersion Time (s)	
30	60
RMS = 420 nm 	RMS = 449.5 nm 
120	180
RMS = 409.8 nm 	RMS = 220 nm 

The comparison between different concentrations of HCl reveals a concentration-dependent effect on paper modification, shown in Table 1. Higher concentrations of HCl result in more pronounced changes in the paper structure, as evidenced by fewer white spots in samples treated with 0.5 M HCl compared to 0.1 M HCl [5]. Furthermore, immersion time plays a crucial role in the extent of paper modification during HCl immersion [10]. When comparing the different immersion times in the HCl solution, the paper immersed in the 60s shows fewer white spots than the 30s. This means that longer immersion times allow for a more thorough penetration of HCl into the paper matrix, leading to deeper and more comprehensive structural changes. However, SEM images of paper immersed for 120s and 180s showed more white spots compared to 30s and 60s immersion times. This observation contrasts with the trend observed with the 60s immersion, indicating that excessively long immersion times may lead to over-modification or detrimental effects on the paper structure [11]. The increase in white spots suggests potential damage or excessive degradation of cellulose fibers due to prolonged exposure to HCl, leading to non-uniform or undesirable structural changes.

To further investigate the SEM results, EDX results, which are shown in Table 2 for 30s and 60s, are supported. For 30s, 0.1 M of HCl sample has 9.9% Ca and 11% Cl while 0.5 M has 27% for both Ca and Cl. These results indicate significant Ca and Cl content differences between the two HCl concentrations for the 30s immersion time. The higher concentration of HCl resulted in substantially higher calcium and chlorine levels in the treated paper. For 60s, 0.1 M of HCl sample has 9.1% Ca and 8.1% Cl, while 0.5 M has 8.1% Ca and 12.5% Cl. Interestingly, the lower concentration of HCl (0.1 M) resulted in slightly higher Ca content but lower Cl content than the higher concentration (0.5 M) for the same immersion time. Therefore, based on SEM-EDX results, 60s immersion time and 0.5 M of HCl are chosen because the SEM image shows the lowest white spots, and the percentage of Cl is higher for the other sample.

Table 3 shows the AFM 3D images and surface roughness for samples immersed in 0.5 M of HCl with different immersion times. Based on Table 3, the sample from immersion of 60s in 0.5 M concentration of HCl sample achieved the highest value of root mean square (RMS). The higher RMS value indicates a rougher surface, meaning more significant height deviations across the surface [12]. This can increase porosity because more spaces or voids exist between the surface features [13]. Conversely, a lower RMS value indicates a smoother surface with smaller height deviations.

The surface roughness of the sensor's active area can influence its interaction with humidity. In the context of porous paper, surface roughness affects the formation and characteristics of pores. A rough surface can promote the creation of smaller pores and enhance the overall porosity of the paper [14]. This increased porosity benefits applications such as humidity sensors, where moisture absorption and diffusion are essential for sensor performance. Ensuring the sensing surface is smooth prevents unwanted adsorption or contamination that could affect sensor accuracy. Additionally, RMS values might impact the sensor's response time, stability, and overall performance. Therefore, the immersion time of 60s with a 0.5 M HCl concentration is chosen based on the AFM testing results.

4. CONCLUSION

In conclusion, the tests comparing drying conditions at room temperature and heated at 100°C revealed that heat drying led to higher porosity than room temperature drying. Subsequently, SEM-EDX and RMS testing were conducted further to test the effect of immersion time on the paper. These analyses showed that the sample immersed in 0.5 M of HCl solution for 60 seconds exhibited the highest RMS values, indicating a rougher surface and greater porosity. This combination of immersion time and HCl concentration was optimal for creating a highly porous structure while maintaining the structure of the paper. The increased porosity is particularly beneficial for applications where higher surface area and porosity enhance moisture absorption and diffusion. These characteristics are essential for achieving high sensitivity, fast response times, and reliable performance in humidity sensing.

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