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# Preparation of Graphene Oxide (GO) incorporated-Polyvinylidene Fluoride (PVDF) Nanofiltration Membrane with Alkaline Post-Treatment for Textile Wastewater Treatment

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**ABSTRACT**

The purpose of this research is to study the potential of polyvinylidene fluoride (PVDF) polymer incorporated with graphene oxide (GO), following with the alkaline etching post-treatment process for dye waste water treatment. Its anti-oxidation properties of PVDF, have led to its choice as a host polymer due to its high thermal stability, great organic selectivity, and excellent chemical and mechanical resistance. In addition, the post-treatment with a NaOH solutions of varied concentration ranging from 0 M to 0.2 M for 30 minutes was conducted in alter the morphology of the fabricated membrane with the aim to increase the perm-selectivity of the membranes. Besides, the fabricated membranes were further characterized in terms of the chemical and physical properties using Fourier-Transform Infrared Spectroscopy (FTIR), Contact Angle (CA), Ultraviolet Visible spectroscopy (UV-Vis), Atomic Microscopy (AFM) and Scanning Electron Microscopy (SEM). The experimental results showed that the post-treatment has decreased the membrane flux of dye wastewater. Based on the obtained result, as the concentration of NaOH solution increased, the permeability increased. While the overall dye rejection of the membrane remained of above 90 %.

*Keywords*: Polyvinylidene Fluoride (PVDF), Graphene Oxdie, Alkaline Post-Treatment with Sodium Hydroxide (NaOH) solution, Textile Wastewater

## 1.0 INTRODUCTION

Dye wastewater poses a significant environmental threat due to its harmful impact on aquatic ecosystems and human health. To address this issue, membrane technology has emerged as a promising solution for efficient dye removal from wastewater [1]. Various membrane-based techniques such as reverse osmosis, nanofiltration, ultrafiltration, and hybrid treatment systems have been developed to tackle the challenges associated with dye-containing effluents from industries like textiles. These membrane technologies offer benefits such as high removal efficiency, cost-effectiveness, eco-friendliness, and the potential for water reclamation [2, 3]. By utilizing membrane filtration methods, including nanotechnology, the textile industry can effectively treat dye wastewater, minimize environmental pollution, and contribute to sustainable water management practices [4]. Main benefit of using membrane technology as a method of water treatment in textile industry, is that it produces higher quality of clean water while utilizing less chemicals compared to other methods [5, 6]. By implementing an alkaline etching treatment in

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polymer-based membrane (PVDF) can potentially improve the pore size of the treated membrane [8]. Recent works had shown that alkaline etching of PVDF membrane reported declination of mechanical and thermal stability of PVDF membrane [7]. That said, exposure to alkaline solution prove to increase pore size of polymer membrane through exposure to 0.01 M and 0.2 M for 30 minutes, 60 minutes and 90 minutes [9]. Additionally, the use of graphene oxide (GO) in PVDF polymer-based membrane also can induce high hydrophilicity characteristic and water flux. Thus, improved the permeability and antifouling properties of the membrane used. By implementing an alkaline etching treatment in polymer-based membrane (PVDF) can potentially improve the pore size of the treated membrane. Recent works have shown that alkaline etching of PVDF membrane reported declination of mechanical and thermal stability of PVDF membrane. Besides, exposure to alkaline solution prove to increase pore size of polymer membrane through exposure to 0.01 M and 0.2 M for 30 minutes, 60 minutes and 90 minutes [9, 10]. Hence, this study aims to increase the separation performance of PVDF membrane by adding the graphene oxide (GO) nanoparticles in PVDF polymer-based membrane. Furthermore, the alkaline post-treatment process is also conducted in order to study the morphological changes in the PVDF membrane and also the final performance of PVDF membranes for the dye wastewater treatment.

## 2.0 METHODS

### 2.1 Materials

N-Methyl-2-Pyrrolidone (NMP) and Methylene Blue (MB) were purchased from Merck. Polyvinylidene fluoride (PVDF) polymer was obtained from VDF (Kynar, 760). Graphene Oxide (GO), Polyvinylppyrrolidone (PVP) and sodium hydroxide (NaOH) were supplied from Sigma Aldrich. All of the materials in this work are of analytical grade and used as received.

### 2.2 Fabrication of PVDF Flat Sheet Membranes

Asymmetric PVDF membranes were prepared via nonsolvent-induced phase separation (NIPS) technique using dope formulations as shown in Table 1. In order to increase the porosity of the PVDF membrane, 1 wt.% of PVP was firstly added to the NMP solvent, followed by the addition of 22 wt.% of PVDF polymer. The polymer dope solution was continuously stirred until all the polymer were completely dissolved [10]. The membrane was then cast on a glass plate and was kept for 30 s at ambient temperature before immersing into a water coagulation bath at room temperature. The obtained PVDF membranes were thoroughly washed with de-ionized (DI) water to remove the residual solvent. The PVDF membranes were then stored in DI water at a temperature of 5°C prior to use. It is necessary to note that NF-1 membrane indicates that 1 wt.% of GO was added to the polymer solution during the preparation of composite PVDF membrane.

**Table 1** Dope formulation used to prepare the PVDF membranes

| Membranes | PVDF (wt%) | GO (wt%) | PVP (wt%) | NMP (wt%) |
|---|---|---|---|---|
| NF-0 | 22 | 0 | 1 | 77 |
| NF-1 | 22 | 1 | 1 | 76 |

### 2.3 Alkaline Solution Post-Treatment using Sodium Hydroxide (NaOH)

To prepare a NaOH solution with a concentration 0.01 M, add 0.8 g of NaOH pellets into 2 L of water. To prepare 0.2 M concentration of NaOH solution, add 16 g of NaOH diluted with 2 L of water. After both concentration of a solution prepared, the NF-0 and NF-1 membrane submerge in alkaline solution of 0.01 M and 0.2 M with NF-0, NaOH 0M and NF-1, NaOH 0 M as control membrane. Both NF-0 and NF-1 submerged into the alkaline solution of 0.01 M and 0.2 M of NaOH for 30 minutes. Then, let the membrane dry off for 24 hours before characterization.

**Table 2** Post-treatment process using alkaline etching with varied concentration of NaOH solutions

| Membranes | Graphene Oxide (g) | Concentration of NaOH (M) |
|---|---|---|
| NF-0, 0 M | 0 | 0 |
| NF-1, 0 M | 1 | 0 |
| NF-0, 0.01 M | 0 | 0.01 |
| NF-1, 0.01 M | 1 | 0.01 |
| NF-0, 0.2 M | 0 | 0.2 |
| NF-1, 0.2 M | 1 | 0.2 |

### 2.4 Membrane Characterizations

The chemical structure of the fabricated membranes was evaluated using FTIR spectrometers FTLA2000 (ABB, Switzerland) equipped with an attenuated total reflection (ATR). A total of 128 scans were measured for each sample. The water contact angle was measured using VCA Optima-AST to characterize the hydrophilicity of the membrane. The morphological properties of the membrane was characterized using scanning electron microscopy (SEM), Hitachi. Atomic force microscopy (AFM) (Park System E100, Korea) was also used to analyze the surface roughness of the PVDF membranes.

### 2.5 Nanofiltration Performance

The flux and dye rejection of fabricated PVDF membranes were evaluated using a cross-flow nanofiltration system. The membranes were initially compacted at a trans-membrane pressure of 0.7 MPa with DI water for approximately 1 hour. The active membrane area was 42 $cm^2$. The NF experiments were then performed using 50 ppm of methylene blue dye solution at an operating pressure of 0.6 MPa and a temperature of 25 °C, respectively. The membrane water flux (F) was calculated using the following equation:

$$F = \frac{V}{t \times A} \quad (1)$$

where, V is the permeate volume (L), A is the membrane area ($m^2$) and t is the experimental time to obtain V (h).

The ultraviolet-visible spectrophotometer (UV-Vis) is used to determine the amount of colour in the feed and permeate solutions at a wavelength of 664 nm. The membrane dye rejection was then calculated using the following equation:

$$R(\%) = (1 - \frac{C_p}{C_f}) \times 100 \quad (2)$$

where, Cp is the permeate concentration (ppm) and Cf is the feed concentration (ppm), respectively.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy is an analytical method that is used to identify the chemical composition of the membranes. Figure 1 show the ATR-FTIR spectra of nanofiltration PVDF membranes. Typical bands of PVDF polymer were observed at 1175 $cm^{-1}$, 1430 $cm^{-1}$, 1405 $cm^{-1}$, 1276 $cm^{-1}$ and 840 $cm^{-1}$, respectively.

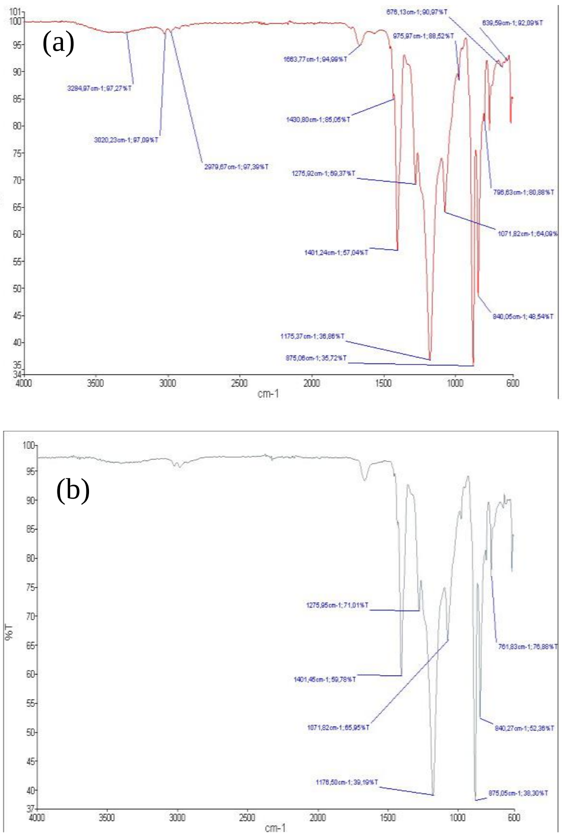


**Figure 1** ATR-FTIR spectra of (a) NF-1, 0.02 M membrane, and (b) NF-a, 0.01 M membrane

### 3.2 Scanning Electron Microscopy (SEM)

Figure 2 shows the SEM images from the top surfaces of each membrane with and without graphene oxide (GO). The surface of the membrane is observe using SEM and examine at a magnification of 1000x. As can be seen from the Figure 2, there were no significant differences on the membrane top surfaces among all the fabricated membrane with and without the alkaline post-treatment process [11]

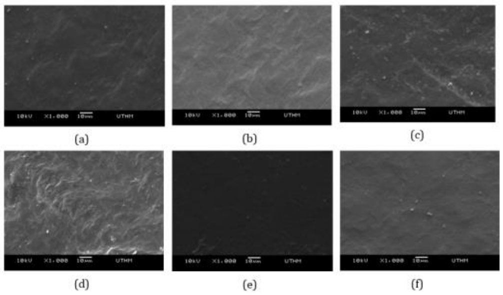


**Figure 2** SEM images of (a) NF-0; (b) NF-1, 0 M; (c) NF-0, 0.01 M; (d) NF-1. 0.01 M; (e) NF-0. 0.2 M; (f) NF-1, 0.2 M at magnification of 1000x

### 3.3 Atomic Force Microscopy (AFM)

Figure 3 shows the topographic images taken from the AFM for all the fabricated membranes. Based on the figure, both NF-0, 0.2 M and NF-1, 0.2M membranes exhibits the highest mean surface roughness (Ra) value when compared to other PVDF membranes with the Ra value of 47.606 nm and 58.898 nm respectively. While the lowest value of Ra among all the composite membrane is the NF-0, 0.01 M and NF-1, 0.01 M. The result indicates that the alkaline post-treatment process altered the morphology of both pristine and composite PVDF membranes [12, 13].

After the post-treatment the surface of the membrane become smoother and thus less rough compared to membrane NF-0, 0 M and NF-1, 0 M. However, as the concentration of NaOH solution increase, the surface roughness of the membrane also increases. The surface roughness of the membrane also influences the selectivity and permeability of the composite membrane, where the higher the roughness, the lower the permeate flux. In contrast the higher the surface roughness, the higher the selectivity of the membrane as seen in the results in the permeate flux and dye rejection [13, 14].

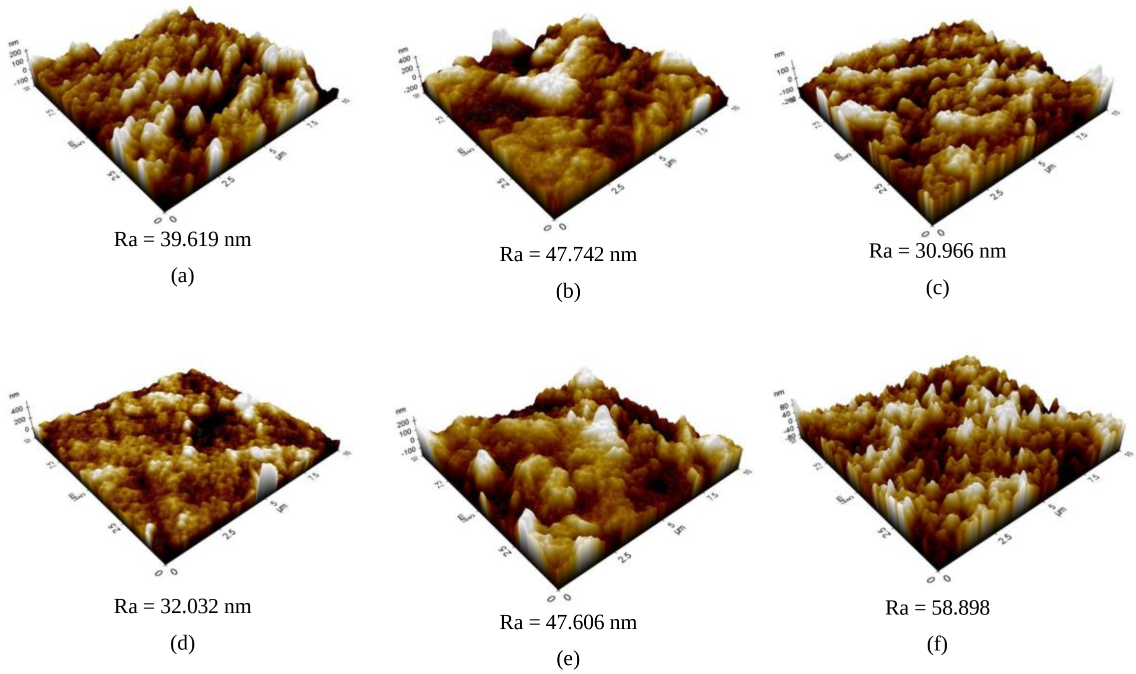


**Figure 3** (a) NF-0, 0 M; (b) NF-1, 0 M; (c) NF-0, 0.01 M; (d) NF-1, 0.01 M; (e) NF-0, 0.2 M; (f) NF-1, 0.2 M

### 3.5 Contact Angle

Figure 4 below shows the contact angle value of each fabricated PVDF membrane after treated at varied concentration of NaOH solution. As can be seen from the Figure 4, PVDF membranes that incorporated with the GO nanoparticles exhibited a slightly lower contact angle value when compared to the unmodified PVDF membranes. This is mainly attributed to the hydroxyl (-OH) and carboxylic acid (-COOH) functional groups present in the GO nanoparticles. When both modified (NF-1) and unmodified (NF-0) PVDF membranes were post-treated with the 0.01 M NaOH solution, the contact angle value for both NF-0 and NF-1 membranes were gradually increased. However, when the concentration of NaOH solution is increased up to 0.2 M, both NF-0 and NF-1 membranes showed decreasing in contact angle value.

### 3.6 Permeate Flux

Figure 5 shows the water flux of all the fabricated membranes when tested using dye waste water. For dye wastewater flux, the trend shows that membrane that has not been post-treated with alkaline solution has the highest flux where, NF-0, 0M membrane and NF-1, 0M membrane has a water flux of 68.18 L/m$^3$h and 90.91 L/m$^3$h, respectively. However, when the NF-0 and NF-1 membranes were post-treated with 0.01 M NaOH solution, the water flux of the membranes decreased which probably due to the increased in hydrophobicity of the membranes. Nevertheless, the water flux of NF-0 and NF-1 membranes were slightly increased when treated with 0.2 M of NaOH solution for 30 minutes.

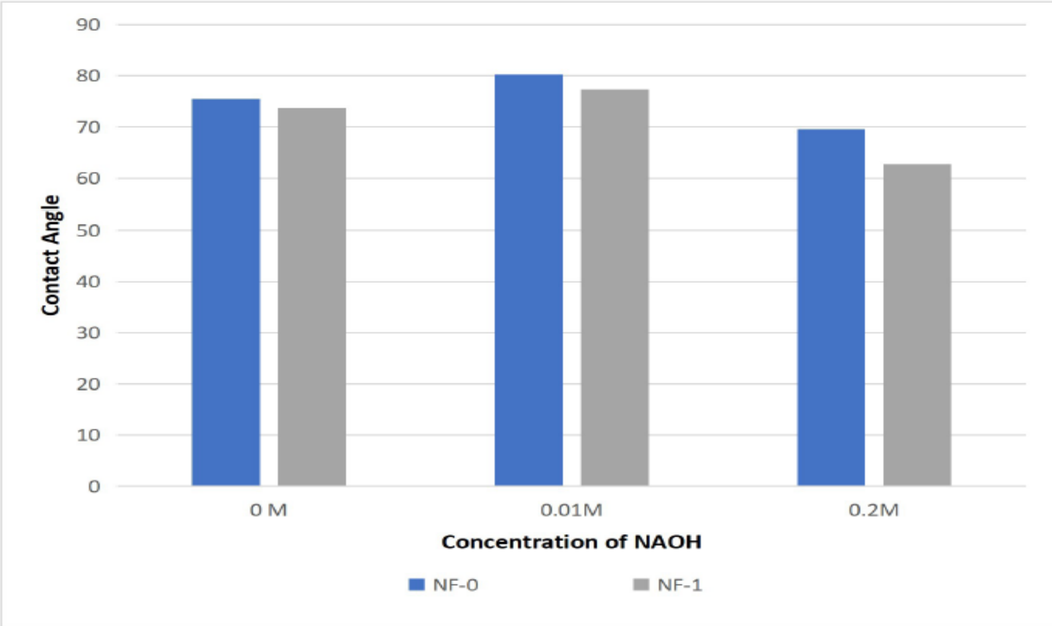


**Figure 4** Contact angle value of NF- 0 and NF-1 membranes treated at varied concentrations of NaOH solution

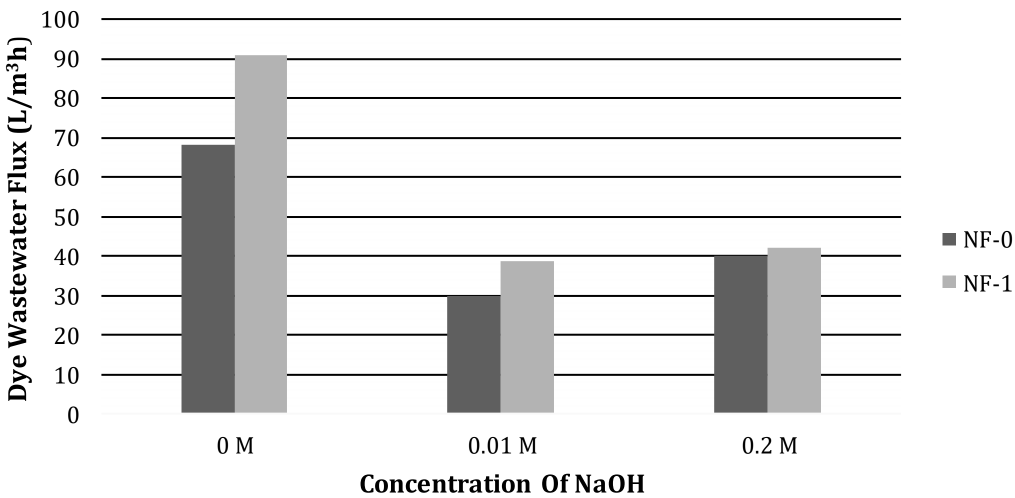


**Figure 5** Permeate flux of NF- 0 and NF-1 membranes treated at varied concentrations of NaOH solution

### 3.7 Dye Rejection

Figure 6 shows the dye rejection of all the fabricated membranes. Based on the obtained results, membrane that has the highest dye rejection is NF-0, 0.01 M membrane with the value of 97.67 % which has been post-treated with 0.01 M concentration of NaOH solution [15]. And the lowest dye rejection value among all the membrane is the NF-0 membrane which has been post treated with 0.2 M of NaOH solution with dye rejection value of 93.37 %. All the membrane that incorporated with 1 g of GO has the consistent and higher range of dye rejection value with membrane NF-1, 0 M, NF-1, 0.01 M and NF-0, 0.2 M has the dye rejection percentage 97.13 %, 96.42% and 96.24 %.

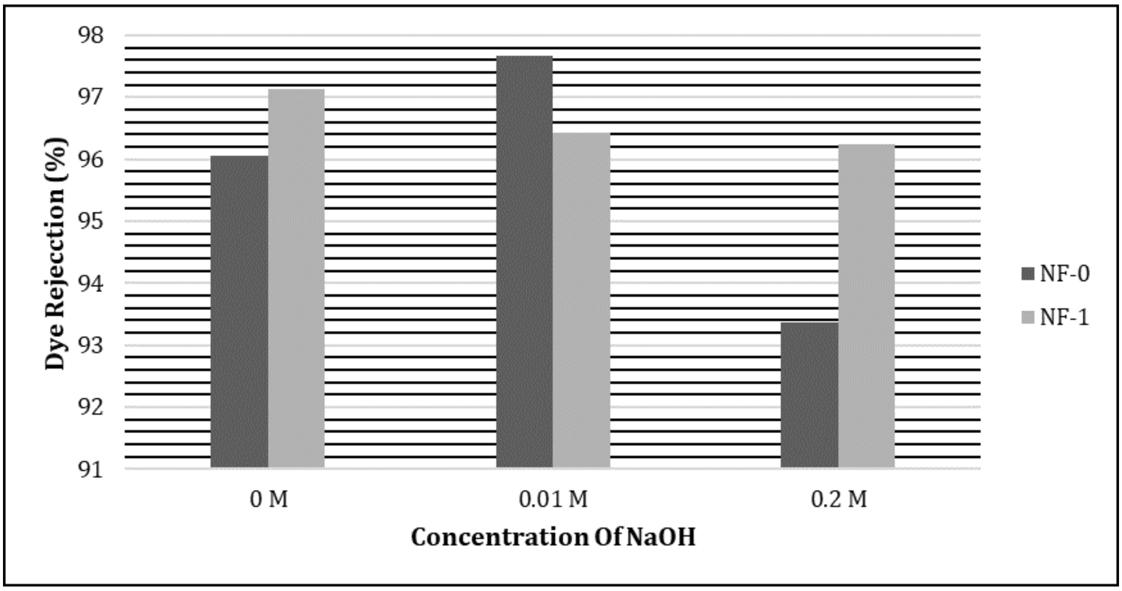


**Figure 6** Dye rejections of NF- 0 and NF-1 membranes treated at varied concentrations of NaOH solution

## 4.0 CONCLUSION

In this study, unmodified and modified PVDF membranes were prepared by incorporating GO nanoparticles to the polymer matrices followed by the post-treatment using alkaline solution prepared at varied concentrations. The post-treatments were successfully conducted using NaOH solution with concentration of 0.01 M and 0.2 M at room temperature for 30 minute treatment time. The surface roughness of both unmodified and modified PVDF membranes dramatically increased after the alkaline post-treatment using 0.2 M NaOH solution. Furthermore, the mild alkaline post-treatment (0.01 M NaOH solution) has resulted in an increase value of dye rejection up to 97.67%. However, further increase in NaOH concentration has resulted in declining both water flux and dye rejections. This study showed that the morphology of the unmodified and modified PVDF membranes were altered when post-treated with alkaline solution. Nevertheless, a remarkable decrease has been observed for membrane water flux when the PVDF membranes were treated with a various concentration of alkaline solutions.

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## CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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