17th International Conference on Inorganic Membranes
New Frontiers for Inorganic Membranes
July 1 - 5, 2024
Oceania Convention Center - Florianópolis - Brasil

Concentration and Purification of Graphene Dispersions Using Ceramic Microfiltration Membrane

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Abstract

Downstream purification of graphene is crucial for large-scale production. The concentration of graphene in the dispersions produced as well as the content of impurities or by-products of the process are important requirements for industrial applications[1,2]. Typical purification techniques include centrifugation, filtration, solvent exchange, precipitation, decantation, and salting out [2-5], however, these methods have limitations primarily associated with their impracticality for large-scale graphene production. For example, centrifugation requires prolonged high-speed spinning, which leads to substantial energy consumption [2-4]. Research is underway to overcome these challenges [1,3]. Membrane-based methods have the advantage of easy scalability and allow for the integration of purification and concentration steps to control the quality of the product. However, membrane fouling by the deposition of a graphene suspension on the membrane surface is a major problem that limits the process performance, which demands high shear rates to minimize the concentration polarization effect. Periodical membrane cleaning by applying extreme pH conditions or high temperatures is usually required to prolong membrane lifetime. These conditions make inorganic membranes a natural choice for graphene purification. In this study, an inorganic membrane was applied to purify and concentrate graphene dispersions. The conditions to remove impurities by diafiltration and concentrate the graphene dispersion using ceramic microfiltration (MF) were evaluated. Experimental batch data were used to design and construct an automated pilot unit.

The experiments with industrial graphene dispersions were conducted in a bench-scale microfiltration setup equipped with a ceramic microfiltration membrane supplied by Likuid Nanotek with a nominal pore size of 0.1 µm. The membrane consists of zirconium oxide with a TiO_2 intermediate layer arranged on a TiO_2/Al_2O_3 support. The membrane module configuration had 19 cylindrical channels of $3.0x10^{-3}$ m diameter, corresponding to a $1.9x10^{-3}$ m^2 of membrane area. Graphene dispersions containing 0.79, 0.25, and 0.15% w/w were used. Additionally, each dispersion contained 0.056% w/w of the additive utilized in the production process. The permeate flux was calculated using a data acquisition system that continuously stored the permeate mass measured using a semi-analytical balance.

Diafiltration was initially applied to remove impurities and the additive present in the graphene dispersion, and distilled water was gradually added to the feed stream during the test, corresponding to the volume of the permeate collected. During the diafiltration the additive concentration was monitored using UV-Vis spectroscopy util reaches an acceptable concentration value. Fig. 1a shows the permeation flux behavior during the diafiltration experiments conducted with a 0.79 g/L graphene dispersion and a tangential velocity of 0.15 m/s. Periodical backwashing of the membrane was performed for 15 s after 15 min of filtration, but without significant improvement.

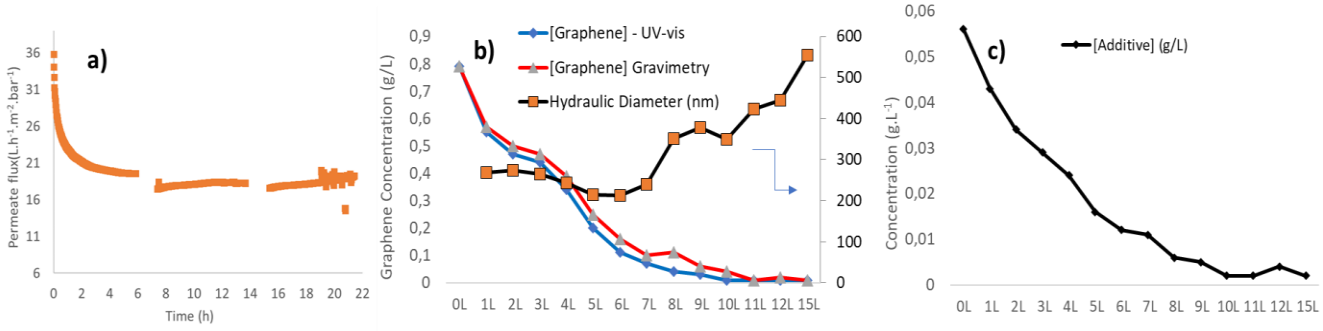

Figure 1 – Diafiltration of graphene dispersion.

Despite a significant drop in the permeate flux observed in the first few hours of operation (approximately 2 h), the permeate flux stabilized at 18 $L.h^{-1}.\ m^{-2}$.(Fig. 1a). This result indicates the fast formation of a filtration cake, which was stabilized by the tangential flux. Diafiltration was conducted until the permeated volume reached 15 times the initial

feed volume. The removal of the additive is shown in Fig. 1C, which shows a continuous decrease in the additive concentration, reaching a removal rate of 96.4%. However, a gradual reduction in solid concentration over time was also observed (Fig. 1.b), as measured using UV-Vis spectroscopy and gravimetry. This result may be attributed to the formation of graphene aggregates caused by the destabilization of the dispersion during additive removal, as confirmed by the increase in the hydrodynamic volume of the graphene particles (Fig. 1b) determined by dynamic light scattering. Additionally, visual observations revealed that graphene particles adhered to the feed tank wall during the diafiltration experiments. Therefore, to avoid those effects it was concluded that concentration of graphene suspension should be conducted without previous diafiltration.

The concentration test was performed without the addition of distilled water, whereas the concentrate stream was circulated to the graphene feed tank. A tangential velocity of approximately 3 $m.s^{-1}$ was used to achieve better hydrodynamic and filtration conditions. Fig. 2 shows the degree of concentration and permeate flux over time.

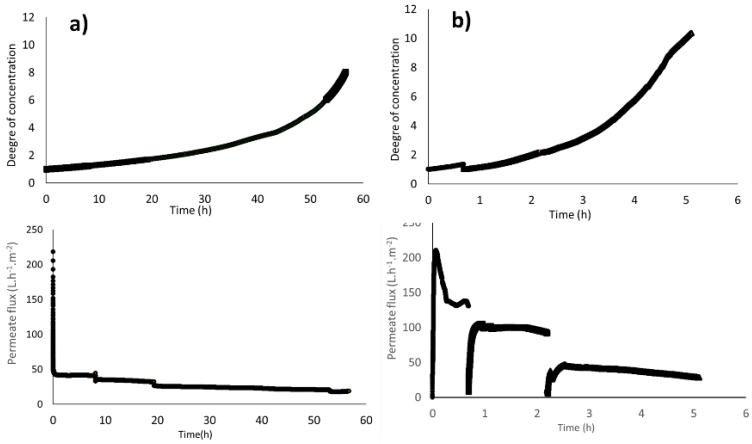

Figure 2 – Concentration of graphene dispersion.

The graphene dispersion with 0.79 %w/w was concentrated for 58 h, reaching a concentration factor of 8 (Fig. 1a). During this experiment, despite the increasing graphene concentration, the permeation flux remained constant at approximately 20 L/h.m², indicating that flow velocity is an important process parameter. Using a larger membrane area (0.0358 m²), it was possible to achieve a concentration factor of 10 with a stabilized permeation flux of 34 L/h.m² after only 5 h of operation(Fig. 2b), indicating the possibility of process optimization for large-volume processing of graphene dispersions. Similar results were obtained for 0.15 %w/w and 0.27 %w/w graphene dispersions, i.e., concentration factor approximately 8 and permeation fluxes of 84 and 66 L/h. m².bar-1, respectively. The higher permeation fluxes were attributed to the lower graphene concentration in the original dispersions.

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