Influence of swelling and penetrants' adsorption on the performance of graphene oxide membranes

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Graphene oxide (GO) membranes exhibit unique properties in nanofiltration and reverse osmosis processes. Their performance and rejection characteristics are influenced by the interlayer distance, which is governed by two competing factors: GO swelling in liquid phases [1] and penetrant adsorption [2]. The latter can reduce flux by decreasing the interlayer distance or reducing the available interlayer volume for permeate transport. GO membranes show high rejection rates for both anionic and cationic dyes [3], with permeance values ranging from 5 to 15 l/(m²·bar·h) for water or alcohol solutions. The near-complete rejection of dyes is attributed to size exclusion, as methylene blue (MB) ions are considered larger than the interlayer spaces in GO. In this study, we investigate the filtration characteristics of GO membranes for separating cationic (Methylene blue, MB) and anionic (Methyl orange, MO) dyes. During filtration, we observed that the permeate flux remained constant or slightly increased for MO solutions, while MO rejection decreased from 100% to 85%. In contrast, for the cationic MB dye, a significant and irreversible decrease in permeate flux occurred, with rejection remaining around 100% (Figure 1). To understand this effect, we conducted an adsorption study of the dyes on graphene oxide. Negatively charged MO molecules adsorb weakly onto graphene oxide, with an adsorption capacity of around 50-70 mg/g(GO). However, for the positively charged MB, the adsorption capacity is much higher, reaching 600 mg/g (GO). To study real filtration conditions, these experiments were carried out in aqueous dye solutions during the *in situ* experiment using the Grazing-Incident Wide-Angle X-Ray Scattering (GIWAXS) technique (P03 beamline, synchrotron PETRA III, DESY). The interlayer distance *d* of GO membranes after filtering a certain volume of dye solution was analyzed (Figure 2). Parameter *d* in a 10 mM NaCl solution was measured to be 12.9 Å. After filtering a small volume of dye solution, the *d*-spacing decreased to 11.7 Å, with further filtration causing significant shrinkage to 10.4 Å. For negatively charged MO molecules, which do not adsorb between GO nanoflakes, the interlayer space decreased slightly from 12.9 Å to 12.4 Å, likely due to the compaction of the GO structure under external pressure. The reduction in permeate flux during MB filtration can be explained by two effects: (i) the adsorption of MB molecules in the interlayer space and (ii) the resulting shrinkage of the interlayer distance, both of which significantly reduce the available volume for water transport. Therefore, MB and other anionic dyes are not suitable for testing size exclusion effects in GO membrane permeation, as sorption effects can lead to high rejection rates of anionic dyes.

References

[1] A.A. Eliseev et al. Nano Lett. 23 (2023) 9719–9725
[2] L. Chen et al. Nature. 550 (2017) 380–383
[3] L. Chen et al. Chem. Eng. J. 347 (2018) 12–18.

Figures

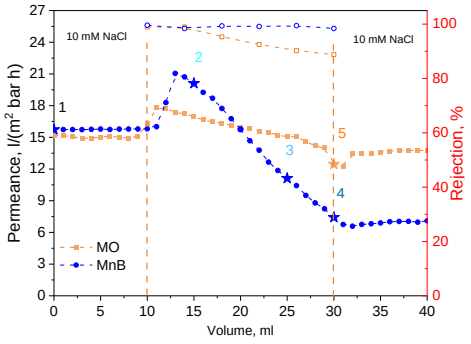

Figure 1. Dependence of GO permeance and rejection during dye solutions filtration

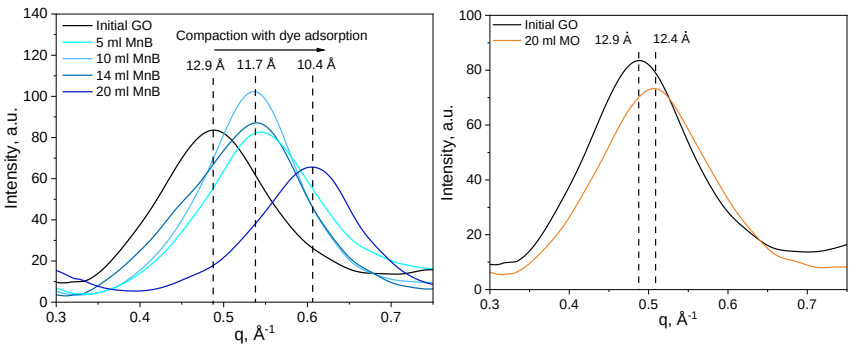

Figure 2. GIWAXS patterns for membranes after dyes filtration. Numbers correspond to the volume indicated on figure 1