ESRF	**Experiment title:** XRD study of ultrathin graphene oxide membranes in solutions with different size of ions	**Experiment number**: HC/3837
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Shifts: 6	**Local contact(s)**: Carlotta Giacobbe, giacobbe@esrf.fr	*Received at ESRF:*

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Report:

The purpose of project was to make X-ray diffraction study of Graphite Oxide membranes (mGO) swelling (intercalation of solvent between graphene oxide layers) in liquid aqueous solutions of organic dyes. Our goal was to study thin mGO in situ intercalated of ions with different radii. Graphite oxide membranes synthetised by Hummers' method (30 nm thick) were loaded into glass capilleries with solutions of organic dyes (concentration 200 $mg \cdot l^{-1}$), sealed and XRD was recorded at room temperature. Dyes with hydrated radii bigger than 4,5 Å were used: rosebengal, methylene blue, crystal violet, brilliant blue.

One of the promising fields of mGO applications is nanofiltration. As was reported previously[1-2] that permeation of big molecules (hydrated radius bugger than 4,5 Å) through mGO did not occur. As can be seen in Figure 1, swelled structures are similar in inter-layer distance provided by d(001) to the GO swelling in pure water. Moreover, we observed discoloration for some of the dye solutions after some time. It can be suggested that adsorption of polar organic dyes on the polar GO surface could be responsible for lack of permeation through GO membranes.

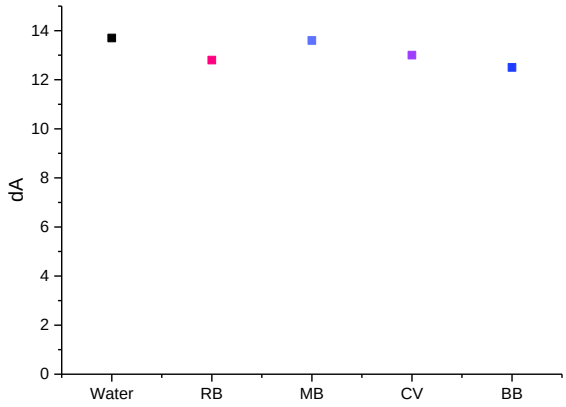

Figure 1. Interplanar distances of thin mGO in different dye solutions in comparison with value in water: RB – rosebengal, MB – methylene blue, CV – crystal violet, BB – brilliant blue.

Therefore, we performed additional set of experiments aimed on study of mGO swelling in several alcohols, from methanol to octanol. It was reported previously, that swelling in GO and GO structures such as membranes takes time to 5 minutes. We decided to monitor swelling of large flakes membrane made by Hummers' graphite oxide with alcohols. Results for system mGO - pentanol-1 are presented in figure 2. We performed our study during 24 hours. XRD patterns were recorded using as-prepared samples, after 4 h, after 7,3 h. and after 23 h. It is found that swelling of GO-based membranes takes time and considering only samples of GO freshly loaded into solvent will not provide correct value of inter-alyer distance for swelled structure. This result could shed the light on the disputes about different interlayer distances in GO materials. Slow kinetics of GO membrane swelling is in sharp contrast with rapid swelling of precursor graphite oxide powders.

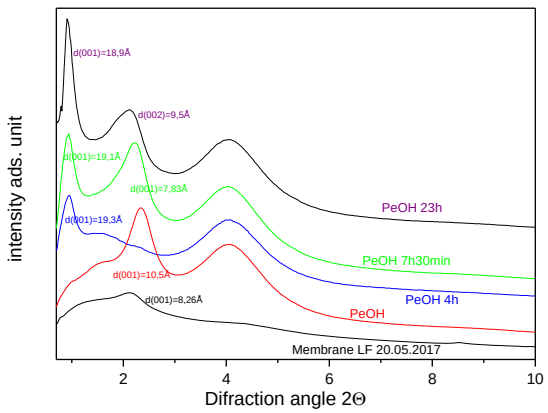

Figure 2. XRD pattern of large flake mGO immersed in pentanol-1. Black curve – mGO without solvent, red curve – as-prepared mGO, blue curve – after swelled 4h, green curve – after 7,5 hours, violet– after 23h.

Moreover some additional temperature-dependent experiments with thin mGO immersed in acetonitrile. As compared with GO powder, mGO did not change interplanar distance with temperature. As could be assumed, compact membrane structure could not allow expansion.

References

1. Joshi, et al, , *Science* **2014,** *343* (6172), 752-754
2. Yang, Q.et al, , *Nature Materials* **2017,** *16* (12), 1198-1200.
3. Barroso-Bujans F. et al. *Phys. Chem.* **2017**, *19* (28), 18366–18371.