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Ultraviolet-Visible Spectroscopy of Dyes

UV-vis spectroscopy was used to measure the absorbance of each dye tested at specified concentrations. The absorbance was shown to be linearly dependent upon the concentrations for the ranges used. **Figure 1** illustrates the UV-vis spectrum of the permeate and the feed solution. The rejection can be easily calculated via the equation,

$$R = \left[\left(1 - \frac{Abs.Permeate}{Abs.Feed}\right) \times 100\%\right].$$

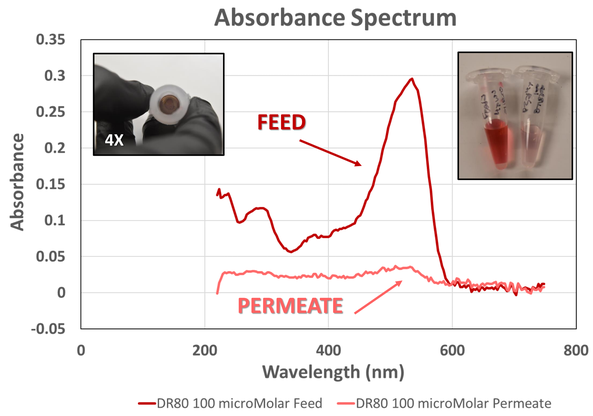


Figure 1 – Shows the absorbance spectrum for Direct Red 80 (DR80) at a concentration of 100 µM when going from high to low concentration. The inset on the left shows what the 4X looks like in the filter housing and the right inset shows the comparison between the feed and permeate in the absorbance plot.

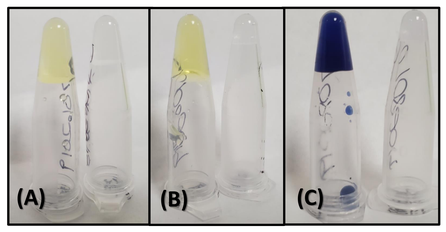


Figure 2 (A-C) to the left shows the near 100% rejection for DY26, DY8, and DB14 for a commercial filter functionalized with 15 layers of USANPs. Left vial is the feed, right vial is the permeate.

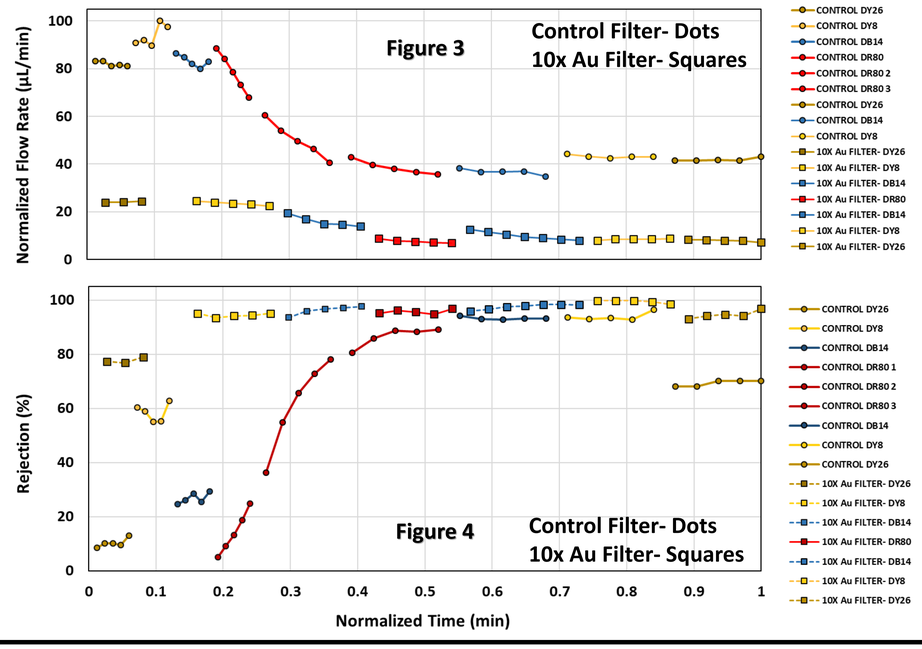
The results of **Figures 3 & 4** suggest that the Direct Red 80 becomes permanently attached to the polycarbonate (PC) filter reducing the flowrate while adding surface charge to the membrane to increase rejection of negatively charged pollutants. To confirm this behavior, rejection of three molecular dyes was performed as a function their molecular charge, concentration, and the number of USANP monolayers applied to the PC filter. Experiments started with the lowest concentration of dye, and the lowest number of USANP monolayers, performing tests up to the highest concentration, and then back down. A 0-layer control, 4-layer, and 8-layer experiment have been completed. The 0-layer control and 8-layer experiments are shown in **Figure 5.** The 4-layer filter behaves similarly to the 0-layer control.

Rejection of Negatively Charged Pollutants

Can commercially available filtration membranes be easily functionalized in such a way to enhance the removal of charged contaminants in water treatment processes? The experimental observations presented in **Figures 1-5** appear to suggest such functionalization goals are possible. The literature demonstrates there have been two pioneering works that demonstrated that Ultrathin Self-Assembled Nanoparticle (USANP) membranes (composed of ~5 nm diameter metallic gold nanoparticles surrounded by organic ligands) when applied to commercial membranes displayed charge sensitive rejection to molecular dyes and also have the ability to charge modify the openings in commercial filters **[1] [2]**. The rejection mechanisms in these works were proposed to be either size dependent or charged based. Recent experimental results shown in **Figures 3 & 4** demonstrate that the supporting filter for these USANP membranes can be functionalized solely with highly charged molecular dye Direct Red 80 using no USANP membranes. After the control sample is functionalized with Direct Red 80 alone, average rejection for tested molecular dyes at a concentration of 145 µM increased from 31.8 % to 85.6 % even without the addition of a USANP layer. This indicates that dyes themselves are capable of functionalizing the commercial membranes, providing an additional method to enhanced rejection of charged contaminants. Many new questions now exist. For example, look at Direct Yellow 8 (DY8) prior to the functionalization of the control filter in **Figure 3**, why does it have a strikingly large rejection compared to Direct Yellow 26 and Direct Blue 14? Why is the rejection for Direct Yellow 26 lower than Direct Yellow 8 post functionalization with Direct 80?

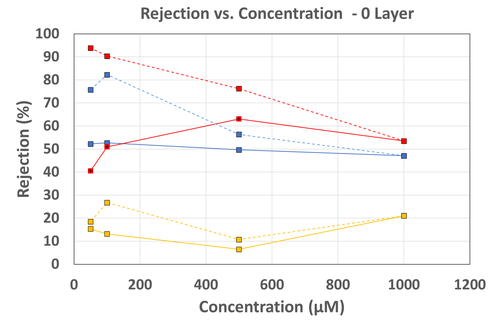
Rejection and Flow Rates of Charged Molecular Dyes

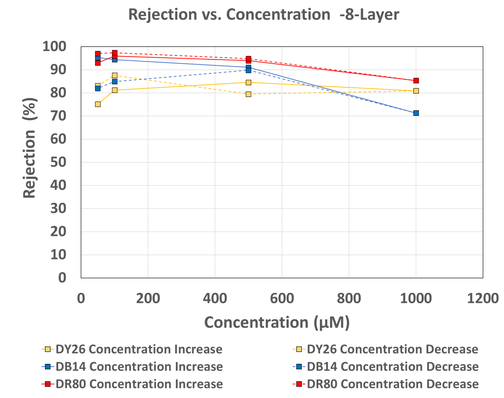
Figure 3 shows that the initial flow rates for DY26, DY8, and DB14 in the control filter were much higher than the 10-layer USANP filter; however, **Figure 4** shows the rejection values for the control filter were much less than they were for the 10-layer USANP filter. The flow rate data in **Figure 3** also shows that once the Direct Red 80 dye is pulled through the filter, the flowrate drastically decreases and the rejection drastically increases as shown in **Figure 4**. This modification by the Direct Red 80 seems to be permeant as the rejection for DY26, DY8, and DB14 then remains at high rejection, nearly equal to that of the 10-layer USANP filter (the exception being DY26). A 15-layer USANP filter, not functionalized with Direct Red 80, gave almost 100% rejection for immediate tests of DY26, DY8, and DB14 as shown in **Figure 2 (A-C).**



Concentration & Hysteretic Rejection

Figure 5 below shows the hysteretic behavior in the rejection as a function of concentration. This behavior suggests that the molecular dyes themselves are attaching the PC filter as the rejection in most cases is higher when going down in concentration (dashed lines) from a higher saturated concentration test (increasing concentration, solid line). This makes sense intuitively. The rejection of negatively charged dye molecules should increase if they see a more negatively charged pore structure on the filter. Overall, this hysteretic effect is more noticeable when fewer USANP layers are used.





Conclusions and Future Work

This work suggests that commercial filters can be functionalized with self-assembled gold nanoparticles monolayers and charged molecular dyes. Future work will look at the effects of combining both types of functionalization to explore enhanced rejection of charged pollutants from water. Future work will consist of testing the conductivity rejection of specific ions that are dissociated in aqueous solution and exploring how the rejection is dependent upon pH and terminal groups and/or structure of the charged pollutants. Systematic data sets are needed to compare the observed behavior to rejection theories in the literature.

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