Nanoparticle rejection by microfiltration and ultrafiltration membranes

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Background

Separating engineered nanoparticles (NPs) from aqueous matrices is useful in various ways. 1) NPs can be removed from wastewaters to reduce environmental exposure in receiving waters. 2) NPs can be concentrated to improve detection and quantification in drinking water, wastewater, blood, urine, breast milk, etc. 3) NPs can be separated from processing chemicals for purification during NP production. 4) NP catalysts can be held in suspension and removed from the desired product stream. For all of these applications, membranes can potentially provide the needed separation.

Objective

This study seeks to measure the extent to which microfiltration (MF) and ultrafiltration (UF) membranes are capable of removing engineered NPs, especially those that have organic functional groups and are smaller than the membrane pores. It builds on previous work with colloid-membrane systems [1-3], but compares several NPs of similar size and different material.

Materials and Methods

We used negatively and positively charged functionalized NPs: silver [Ag(-)], titanium dioxide [TiO_2(-) and TiO_2(+)] and gold [Au(-) and Au(+)] (all from Vive Nano, Toronto, ON, Canada). NPs had mean diameters between 2 and 9 nm. MF experiments were performed with 25-mm diameter syringe filters or a 45-mm dead-end cell pressurized with N_2. UF experiments were performed in the same cell or with centrifugal filtration devices (Amicon Ultra, Millipore). MF membrane materials are as noted in figure captions. All UF membranes had regenerated cellulose active layers (PLC, Millipore). NPs were suspended in 18 MΩ water buffered with 1 mM HCO_3. NP concentrations were measured by ICP-OES after acidifying the samples with 3% HNO_3 (for Ag and TiO_2) or 3% HCl + 1% HNO_3 (for Au).

Results

See figures. The overall result was that positively charged NPs were better rejected than negatively charged NPs, but charge alone was not a sufficient predictor of rejection.

Conclusions

Functionalized NPs interact with membrane surfaces to cause greater rejection than predicted by pore size alone. Even some negatively charged NPs were rejected by negatively charged membranes with pores larger than the NP. In general these small NPs will be better rejected than would be expected by comparing membrane pore size with NP size.

One useful outcome was the development of a protocol for characterizing NPs based on rejection and recovery in centrifugal UF devices (Figure 6). This could allow a determination of which NPs would be most readily transported in environmental or engineered systems, even those not using membranes. In this study, Ag(-) was the least rejected and most easily recovered (had the least membrane adsorption affinity) so it would be the most easily transported.

References

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(2) Schafer, A.I.; Schwicker, U.; Fischer, M.M.; Fane, A.G.; Waite, T. D. Microfiltration of colloids and natural organic matter. *Journal of Membrane Science.* 2000 171(2): 151-172.

(3) Kim, S.; Marion, M.; Jeong, B.; Hoek, E. Crossflow membrane filtration of interacting nanoparticle suspensions. *Journal of Membrane Science.* 2006 284(1-2):361-372.
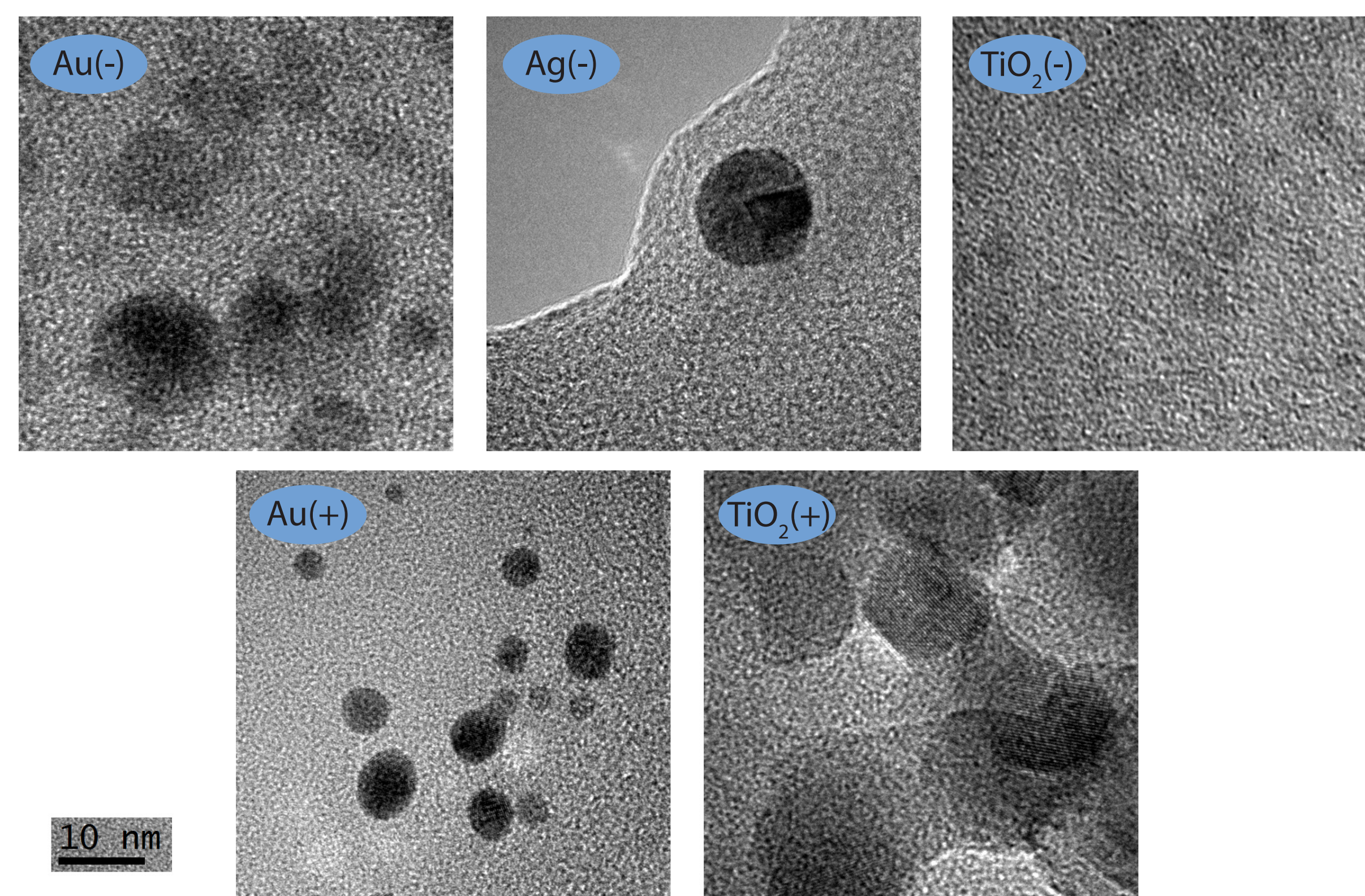
Figure 1. TEM images of functionalized NPs. Particle sizes measured by dynamic light scattering (DLS) were between 2 and 9-nm for all NPs.

Figure 2. NPs used here (from Vive Nano) were created and thereby functionalized with (a) an acrylate polymer to yield a negatively charged surface or (b) a quaternary ammonium polymer to yield a positively charged surface.

Figure 3. Rejection for NP suspensions passed ten times through syringe filters (0.22 µm pore size) made of five different polymeric materials. Au(-) was rejected much more readily than the other two negatively charged NPs despite their similar surface functionality. Positively charged NPs were rejected almost completely owing to strong NP-membrane electrostatic interactions . Rejection occurred even though all NPs were smaller than the membrane pores. Control samples were passed through the filtration device with no membrane present.
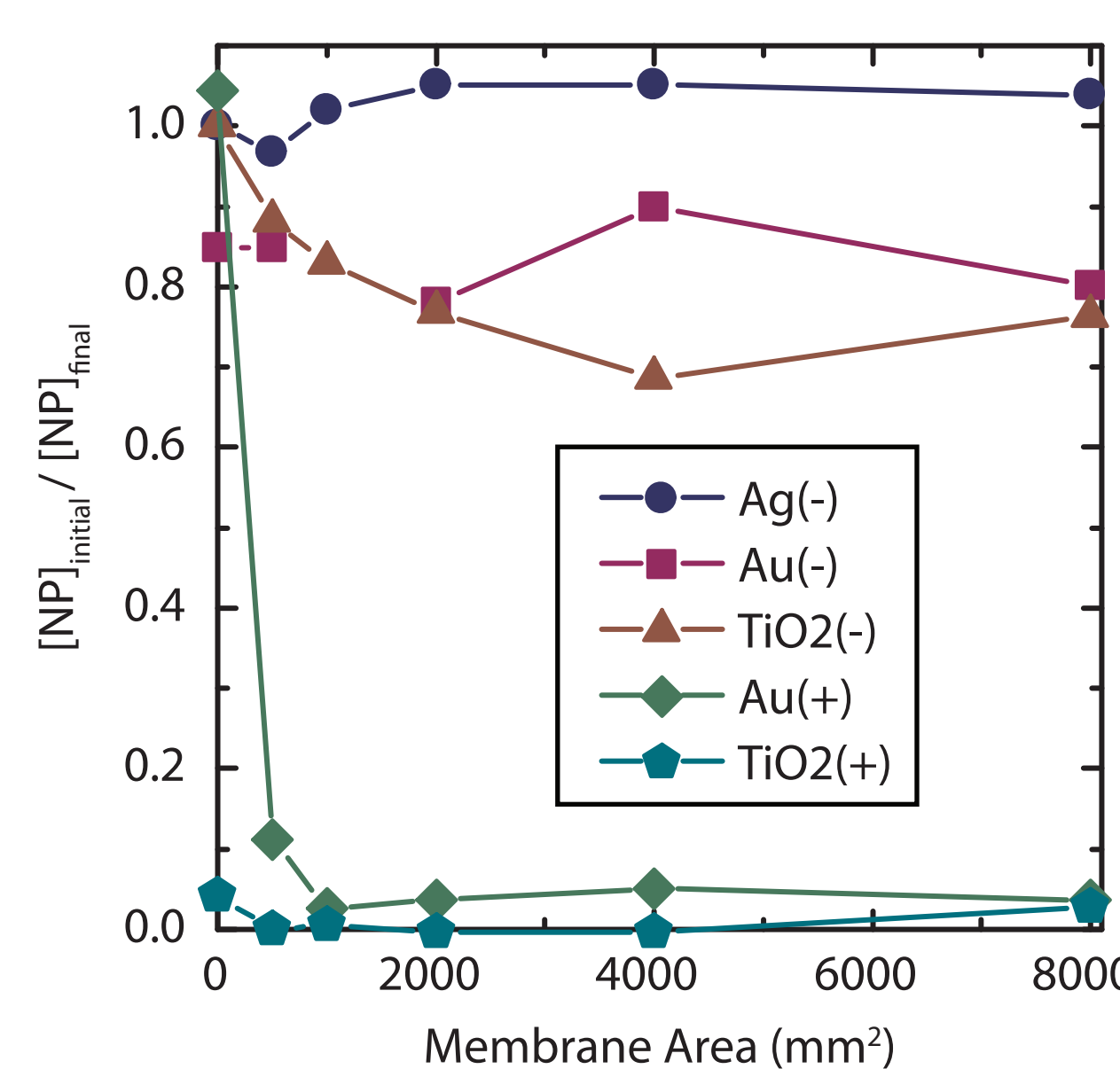

Figure 4. Adsorption experiments with NPs and 0.1-µm PVDF membranes (24-hour contact time) help elucidate mechanisms of rejection. Adsorption was an important mechanism for positively charged NPs and a somewhat significant mechanism for Au(-) and TiO_2(-). Adsorption was not important for Ag(-); sieving (size exclusion) would be the main mechanism for Ag(-) rejection.
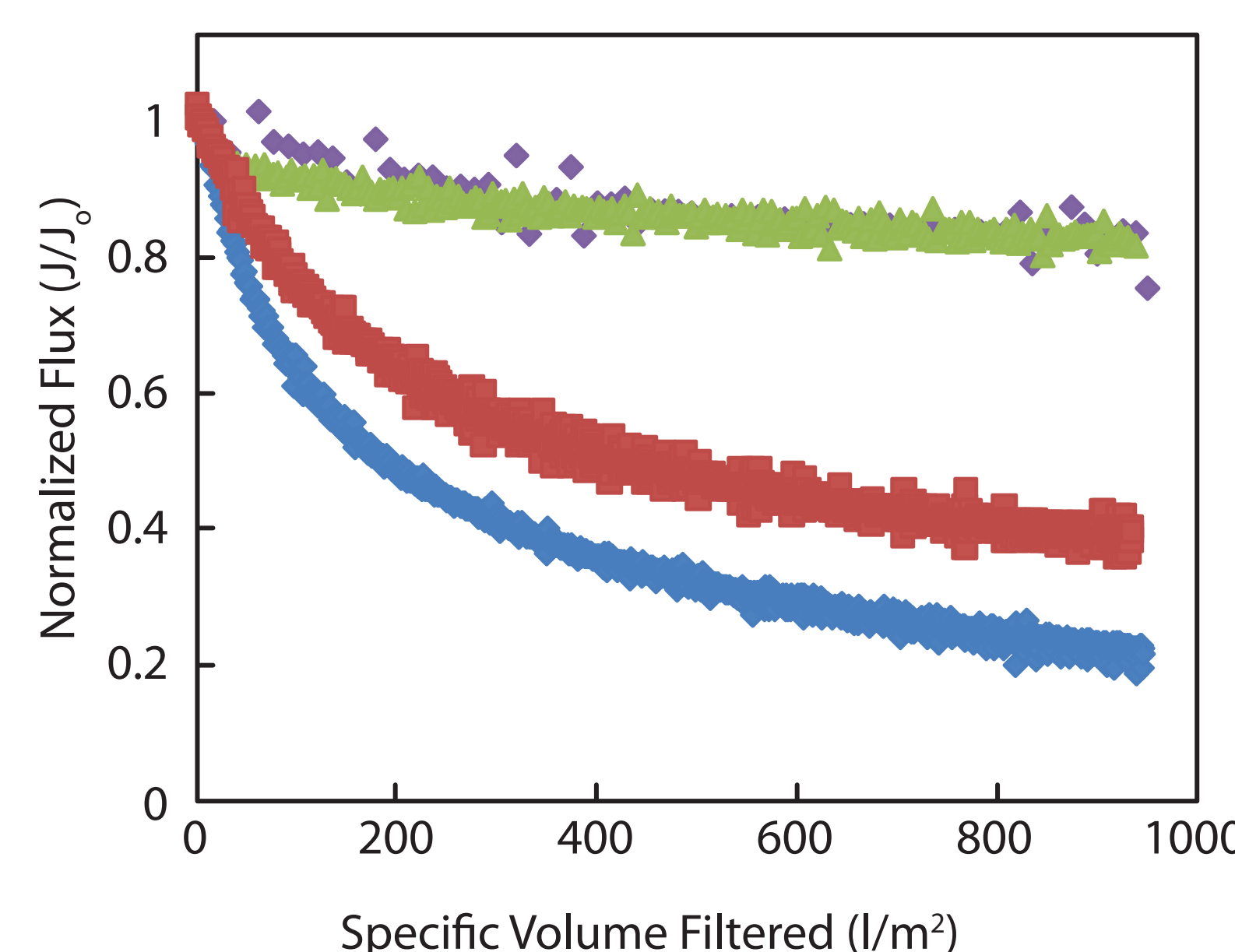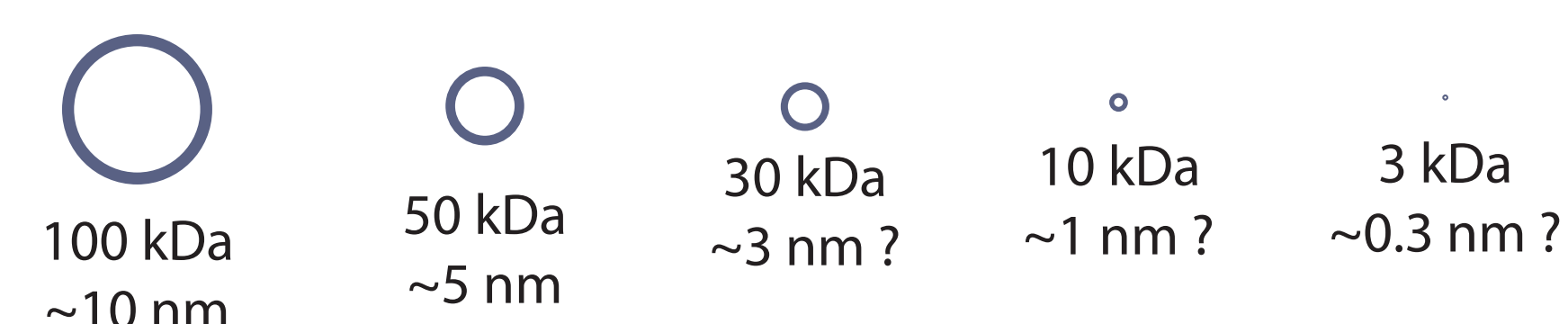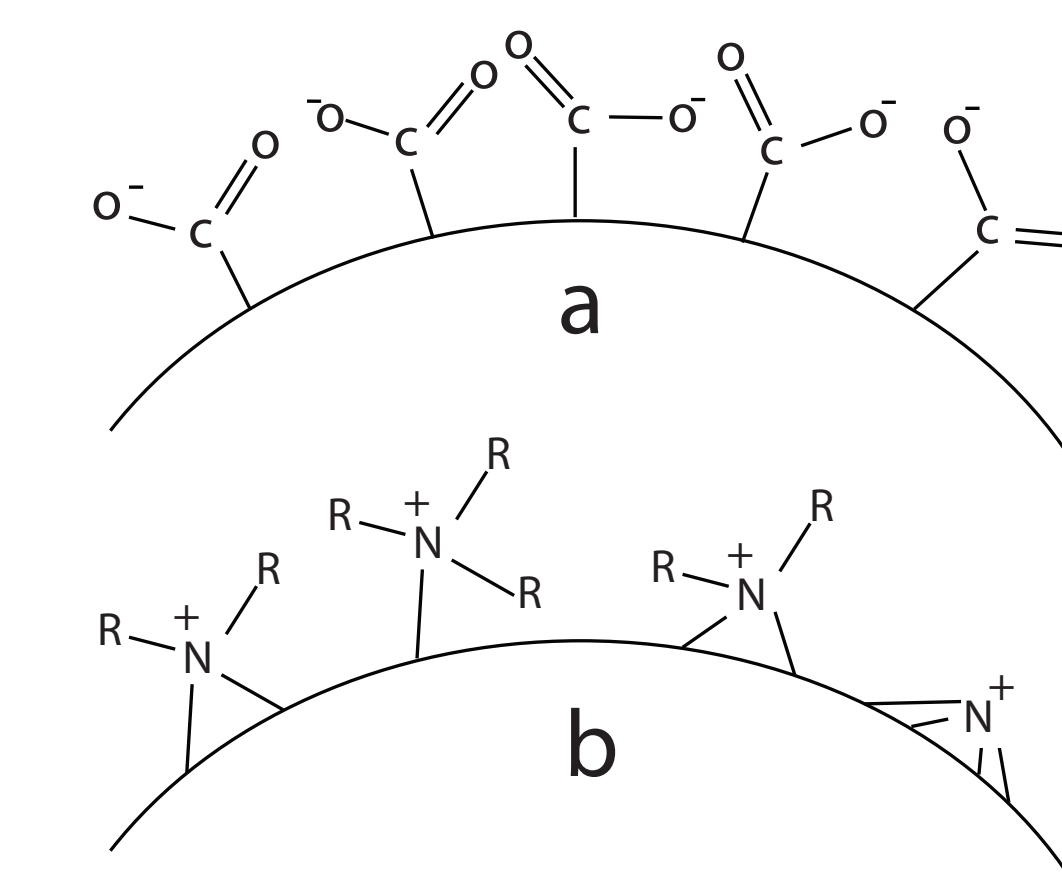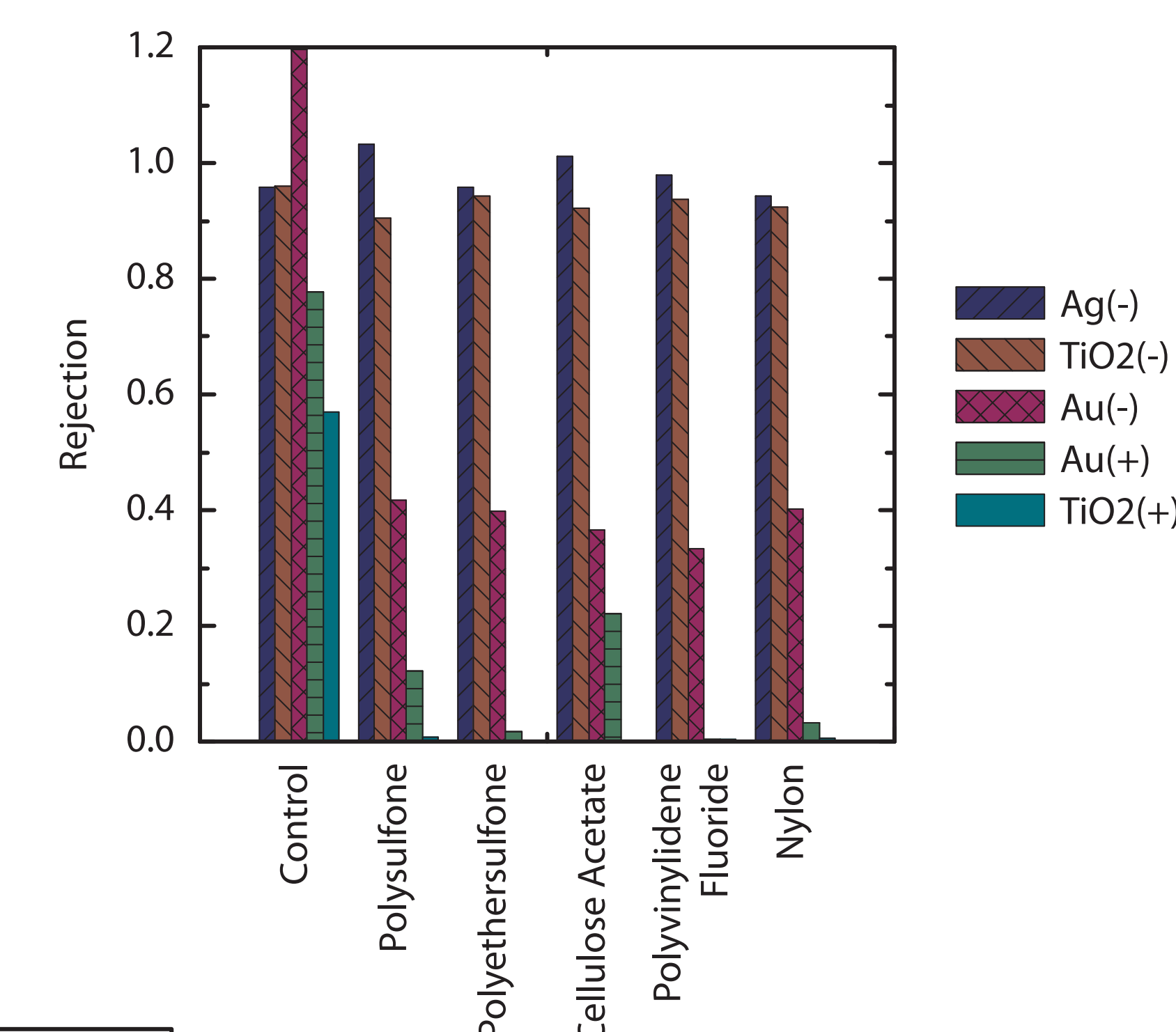

Figure 5. Flux measurements for a 390-ppb suspension of Ag(-) on several membrane pore sizes. Even though Ag(-) was poorly rejected by 0.22 cellulose acetate and 0.1-µm PVDF membranes, over long filtration times it did build up and cause some flux decline. We hypothesize that greater flux decline was observed in 100-kDa membranes than 30-kDa because Ag(-) penetrated and blocked the 100-kDa pores (which were roughly the same size as the NPs) while Ag(-) was less able to enter the 30-kDa pores.
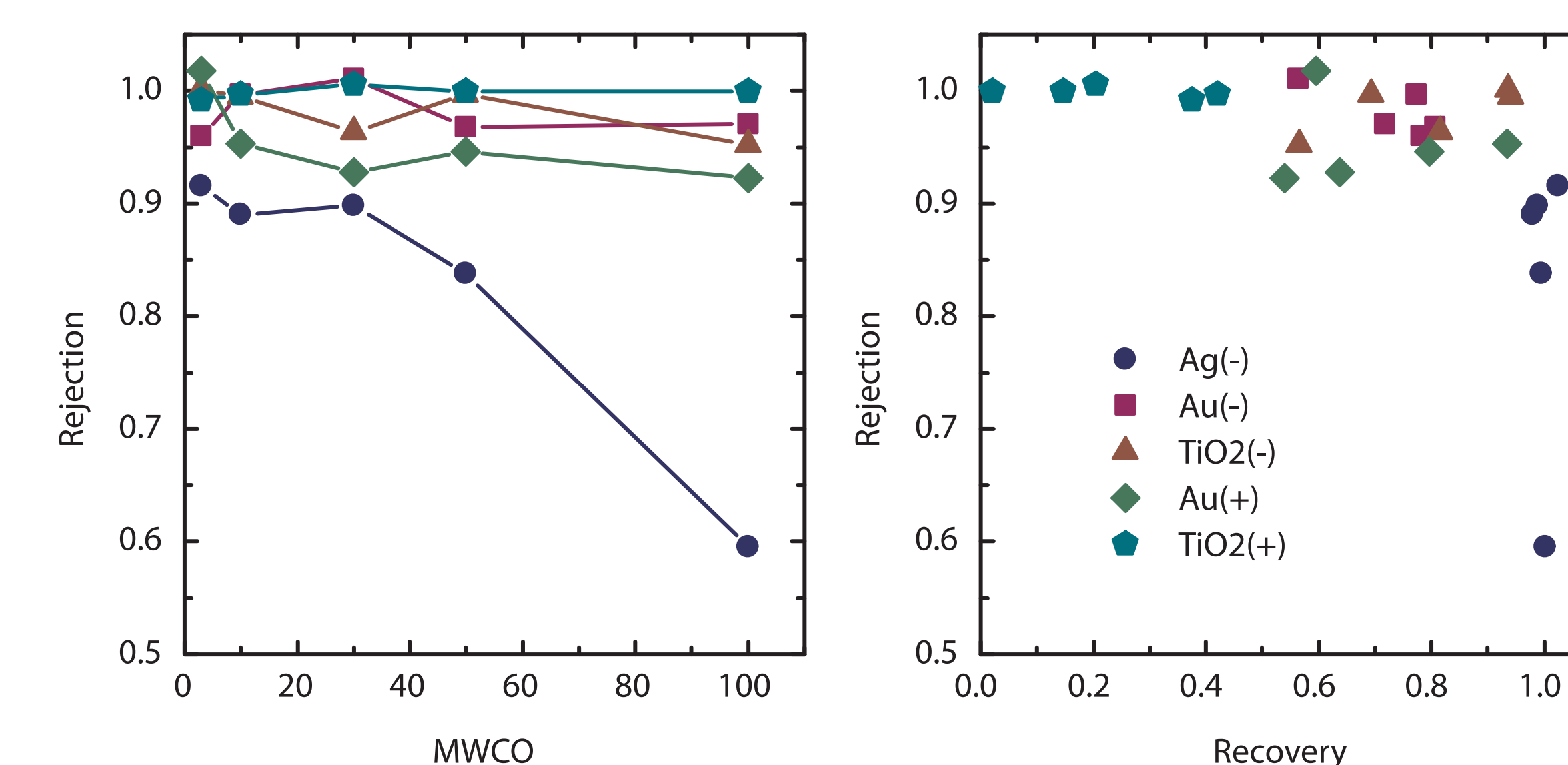

Figure 6. Experiments using centrifugal filter devices (Amicon Ultra, Millipore) provided a unique method for characterizing NPs. Not only could rejection be measured, but recovery on NPs from the concentrate side of the membrane was facilitated. A plot of rejection vs. recovery gave fairly tight groupings where NP types were easily distinguished. NPs that were strongly attracted to the membrane showed high rejection and poor recovery. Weakly attracted (or repelled) NPs that were small enough to pass through the membranes lay in the low-rejection, high-recovery region. Such a procedure could give a simple way to determine which NPs (or NPs functionalized by adsorbed material in environmental matrices) would most readily transport in the environment.

Figure 7. In a perfect world the 9-nm spherical NP depicted at left would easily pass through the 0.22 and 0.1-µm MF membranes and the 100 kDa UF membrane whose circular-cross-section pores are depicted below. Tighter UF membranes would easily reject such an NP by size exclusion. However, real-world interactions between functionalized NP and membrane surfaces, as well as non-ideal pores, mean that even "large" holes can trap nano-sized materials.

0.22 µm ~220 nm

0.1 µm ~100 nm

100 kDa ~10 nm

50 kDa ~5 nm

30 kDa ~3 nm ?

10 kDa ~1 nm ?

3 kDa ~0.3 nm ?

Note: the relationship between UF membrane molecular weight cutoff (MWCO) and pore size (nm) is not strictly defined. Values used here are from http://www.pall.com/laboratory_7046.asp but 30, 10, and 3-kDa pore sizes are not listed. See also Ren et. al, *Journal of Membrane Science, 279* (2006) 558–569, and references therein for more information.

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