

Filtration of Nanoparticles with Dimethyldioctadecylammonium Bromide Treated Microporous Polypropylene Filters

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Microporous polypropylene membrane filters are modified with a cationic surfactant, dimethyldioctadecylammonium bromide (DDAB), to create a charged surface. Negatively charged nanoparticles can then be filtered by utilizing the electrostatic interaction between the charged particles and the polar heads of the surfactants adsorbed on the filters. The study focuses on particle adsorption and particle filtration. Particle adsorption studies have shown that particle adsorption can be increased significantly with this treatment due to Coulombic attraction. Filtration results for 60 nm negatively charged particles (carboxylate modified copolymer) filtered through DDAB treated filters show a significant increase in particle capture efficiency. Capture efficiency is dependent on the pH of the suspension due to competitive adsorption between the hydroxide ions and the negatively charged nanoparticles. As the mean pore diameter increases, capture efficiency decreases due to the increase in distance between the particles and the charged filter surface. Filtration efficiency can be increased from 10% to 95% by surface modification of the filters.

Introduction

The removal of particulate contaminants is very important in many industries, such as water reclamation facilities, potable water treatment, microelectronics, and pharmaceutical industries. Filtration of particulate contaminants is dependent on several factors including particle size and physicochemical properties of the particles and the collectors or filter media. Large particles can be filtered by entrapment mechanism. As the size of the particle decreases, however, particle removal becomes more difficult and thus the interaction between the particles and the collectors must be increased to enhance filtration efficiency.

Deposition of submicron particles onto collectors has captured the interest of many investigators over the years.^{1–12} The main focus of these researches has been on the interactions between the particles and the collectors. The dominant factor in submicron particle adhesion/deposition are the surface interaction forces and Brownian motion.^{6,9,12} Onorato and Tien⁶ have found that favorable interactions between particles and the collector can significantly increase particle deposition. They reported a 10-fold increase in the deposition of negatively charged particles on a positively charged collector as compared to

a negatively charged collector. Chang and Vigneswaran¹² have shown that, by decreasing the electrostatic repulsion between the particle and the filter surface, particle attachment can be greatly enhanced. Harley¹³ et al. studied the adsorption of small particles onto larger particles of opposite charge. Their results support the implication that long-range interactions play an important role in the amount of particles adsorbed and the rate of adsorption.

In the present study, we focus on the electrostatic attraction between the particles and the fibers of microporous polypropylene filters. We provide a unique method to lower the energy barrier between the particles and the filter surface and thus increase the deposition of these particles on the surface of the filter. Polypropylene is commonly used to make prefilters and filters because it is extremely inexpensive and very inert. Because most natural materials are negatively charged,¹⁴ we modify the microporous polypropylene filter with a monomolecular layer of cationic surfactant to give it a positive charge. We then study the adsorption of negatively charged particles on the filters and also study the filtration efficiency of these surface modified filters (Figure 1). This approach is useful not only for removing bacteria, viruses, or nanoparticles in waste water treatment, but can be equally useful in resource recovery processes.

Experimental Section

Filter Treatment. Filters used in these experiments are melt-blown microporous polypropylene disk filters with a diameter of 25 mm (Millipore, MA). The average pore sizes are 0.6 (AN06), 1.25 (AN12), 2.5 (AN25), 5.0 (AN50), and 10.0 μm (AN1H). These filters were treated with a two-tailed water-insoluble cationic surfactant, dimethyldioctadecylammonium bromide (DDAB), by first dissolving the surfactant in methanol and then soaking the filters in the methanol solution (4 mL per filter) for 3 h. After the 3-h treatment, the filters were vacuum dried overnight. Before use for filtration experiments, the filters were flushed with 30 mL of distilled water to remove excess and/or loose surfactants from the filter surface. The average pore diameters were supplied by the manufacturer. Dimeth-

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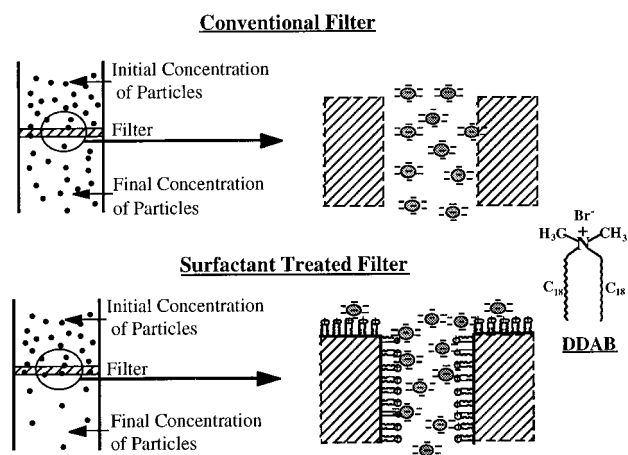


Figure 1. Schematic illustrating particle capture in conventional filter and filter coated with a monomolecular layer of surfactant.

ylldioctadecylammonium bromide was purchased from Sigma Chemical Company (St. Louis, MO) and used without further purification.

Nanoparticles. The nanoparticles were purchased from Bangs Labs, Inc. (Carmel, IN). The negatively charged particles, P(S/A/V-COOH), are composed of polystyrene, an acrylic polymer (unspecified), a vinyl group (unspecified polymerizable group), and a functional carboxylate group. The surface charge densities of the negatively charged 60 ± 3.6 and 197 nm (no standard deviation given) particles are 365 and 141 $\mu\text{equiv/g}$, respectively. The positively charged particles are quaternary ammonium modified polystyrene particles (P(S/Quat Ammonium)) with an average diameter of 200 nm and a surface charge density of 121 $\mu\text{equiv/g}$. Particle concentrations (weight percent solids) are measured by UV absorbance with a Hewlett Packard 8453 UV/vis spectrophotometer at a wavelength of 255 nm.

Qualitative Comparison of Coating. Qualitative comparison of the degree of DDAB coating on the filters was done through contact angle measurements. AN06 (0.6 μm) filters were treated with different concentrations of DDAB according to the procedure mentioned above. After the filters were rinsed with 30 mL of distilled water, they were cut into four strips. The strips were then submerged onto a rectangular piece of poly(methyl methacrylate) (4 mm in thickness) in a 50 mL beaker (Pyrex No. 1000) containing 20 mL of distilled water (Figure 2). A drop, approximately 1.5 μL , of 1,1,2,2-tetrabromoethane was placed on top of the filter with a microsyringe. After the droplet was allowed to spread on the filter for 1.5 min, the contact angle of the droplet was measured with a contact angle goniometer. Six readings at different locations on the filter surface were taken with each of the filters to get an average contact angle value. The zeta potentials of the filters were measured with the Brookhaven BI-EKA Electrokinetic Analyzer on loan for equipment evaluation (Brookhaven Instruments Corporation, New York).

Particle Adsorption Procedure. For particle adsorption experiments, the filters, both untreated and treated AN06, were rinsed with 30 mL of deionized distilled water. Each filter was then soaked in 25 mL of a particle suspension containing 0.012 wt % solids (2.8×10^{10} particles/mL) of 197 nm P(S/A/V-COOH) or 200 nm P(S/Quat Ammonium) for 30 min. The filter was then removed from the suspension and rinsed in 100 mL of distilled water and then vacuum dried overnight before it was coated with gold for scanning electron microscopy (SEM). SEM pictures were taken with a Hitachi S4000 field emission scanning electron microscope (Tokyo, Japan). Particle analysis was performed on a Macintosh computer using the public domain NIH Image program (developed at the U.S. National Institutes of Health and available on the Internet at <http://rsb.info.nih.gov/nih-image/>).

Filtration Apparatus. Filtration was accomplished by using a stainless steel filter holder, a 12 -mL glass syringe, and a syringe pump with variable speed control (Dual Infusion/Withdrawal Pump, Model 944, Harvard Apparatus Co., Millis, MA). For each experiment, 10 mL of particle suspension was filtered through

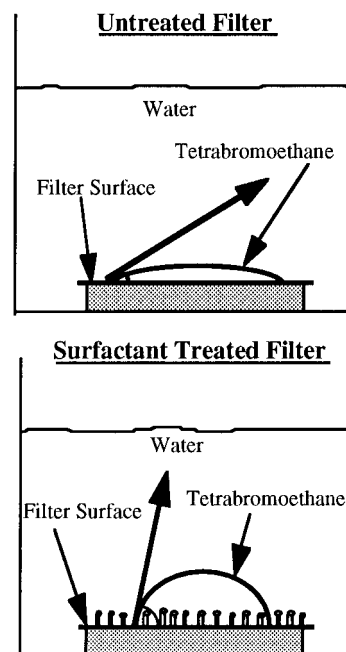


Figure 2. Schematic illustrating contacting angle measurement for the microporous filters.

each filter at a constant flow rate of 9 mL/min. The filtrate was collected in a 11 -mL glass vial and then transferred to a UV/vis cell for concentration measurement.

Results and Discussion

Adsorption and Desorption of Surfactant from Filters. Microporous polypropylene filters are coated with a monomolecular layer of dimethyldioctadecylammonium bromide (DDAB) to give them a positively charged surface. DDAB is chosen because of the two hydrocarbon chains that can hydrophobically bond to the surface of the polypropylene and make this surfactant insoluble in water. Contact angle is used as a measure of the amount of DDAB adsorption at the surface of the filters. For smooth, nonporous planar solids, contact angle measurements can be easily accomplished by placing a droplet of liquid such as carbon tetrachloride on the surface of the substrate and measuring the angle by using a microscope fitted with a goniometer eyepiece. For the polypropylene filters, however, contact angle measurement is a little more difficult. First, carbon tetrachloride could not be used because it is too hydrophobic and immediately gets absorbed into the fibers upon contact. The liquid that is suitable for this material is 1,1,2,2-tetrabromoethane. Second, the surface of the microporous filter is not smooth. Surface roughness can increase or decrease the contact angle. For wetting surfaces, $\theta < 90^\circ$, surface roughness reduces the contact angle, but increases it for nonwetting surfaces.¹⁵ For this reason, an average of six readings at different locations on the filter surface and the standard deviations are reported in Figure 3. Because 1,1,2,2-tetrabromoethane is used instead of water, high contact angle is an indication that the surface is hydrophilic. Conversely, low contact angle means that the surface is hydrophobic. The average contact angle for the untreated filters is approximately 25° . The 5 mM DDAB solution treated filters have the lowest contact angles among the treated filters, and the 10 mM DDAB treated filters have the highest contact angles (Figure 3). Since the standard deviations of these measurement are very large, it was concluded that the difference in 10 and 20 mM DDAB

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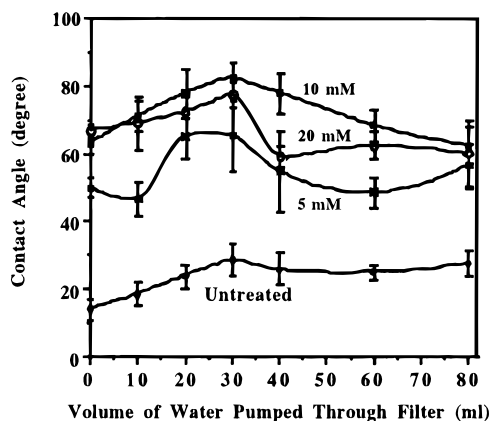


Figure 3. Qualitative comparison of the degree of coating and stability of coating by using contact angle measurements for both surfactant treated and untreated AN06 (0.6 μm) filters.

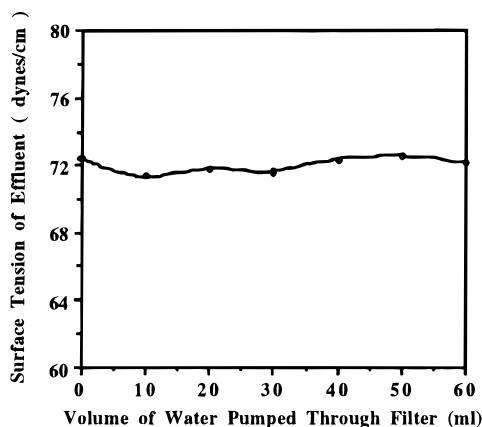


Figure 4. Surface tension of rinse water (rinse effluent) after it has been pumped through a 10 mM DDAB treated AN06 filter.

treated filters was not very significant. Therefore, the 10 mM treatment was chosen as the standard method of treatment for the filters.

The adsorption strength of the cationic surfactant was tested by flushing the treated filters with different amounts of water and then measuring the contact angles. The amount of water pumped through the filters does not have a significant effect on the contact angle, which indicates that the surfactant is not desorbing. The effluents were collected for surface tension measurements (Figure 4). The results indicate that the surfactant is not desorbing as detected by surface tension measurements. From previous experiments, we have shown that 2.5×10^{-5} mol/L surfactant in water decreased the surface tension of water from 72.4 to 43.9 dyn/cm. Therefore, surface tension method should be able to detect DDAB in the range of micromoles per liter of water.

Particle Adsorption on Filter Surface. Since both the filters and the particles are nonconductive, they need to be coated with gold before scanning electron micrographs can be taken. Due to the limitation of the method and availability of the particles, we were confined to study the adsorption of particles of larger sizes (197 and 200 nm) than those used in the actual filtration experiments (60 nm). The zeta potential of the untreated filters indicates that the filters are slightly negatively charged (Figure 5). Scanning electron micrographs of the untreated and 10 mM DDAB treated AN06 filters are shown in Figure 6. These filters are made by a melt-blown process and are fibrous. In the next couple of figures, the surface of the filters looks smooth because of the high magnification (we are actually looking at small segments of

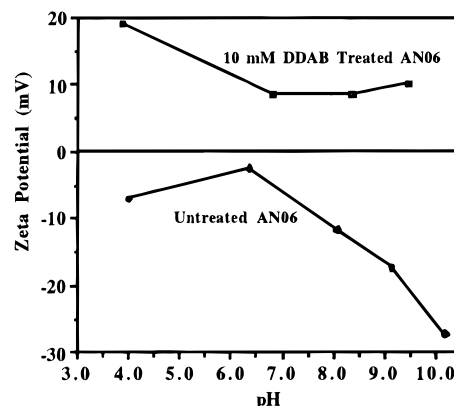


Figure 5. Zeta potential of untreated and 10 mM DDAB treated filters (AN06) as measured by streaming potential.

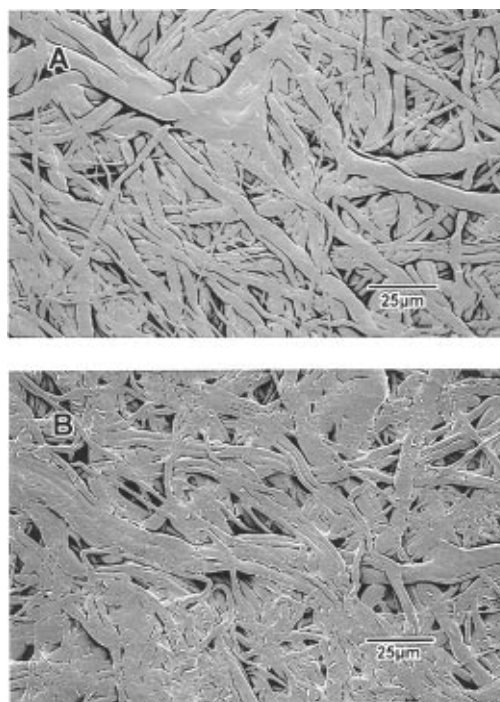


Figure 6. Scanning electron micrographs of (A) untreated AN06 filter and (B) 10 mM DDAB treated AN06 filter after it has been rinsed with 30 mL of deionized, distilled water.

individual fibers). Since the untreated filters are slightly negatively charged, it is expected that negatively charged particles will not adsorb on the surface due to the electrostatic repulsion but positively charged particles will adsorb due to the electrostatic attraction. Experimental results are in agreement with this prediction (Figure 7A,B). Only a few negatively charged particles are attached to the surface of the untreated filter whereas quite a few more positively charged particles are attached. The zeta potentials of the surfactant treated filters exhibit a positive charge for the whole pH range (Figure 5). In this case, a negligible number of the positively charged particles adsorb on the surface. The negatively charged particles, however, are overwhelmingly attracted to the surface (Figure 7C,D).

Particle adsorption is also a function of the suspension concentration. By increasing the suspension concentration, more particles will diffuse to the surface of the filter and adsorb on the surface. Effects of concentrations from 0.020 to 0.050 wt % solids are shown in Figure 8, which illustrates that the number of particles adsorbed on the filter surface increases with their concentration in the aqueous phase.

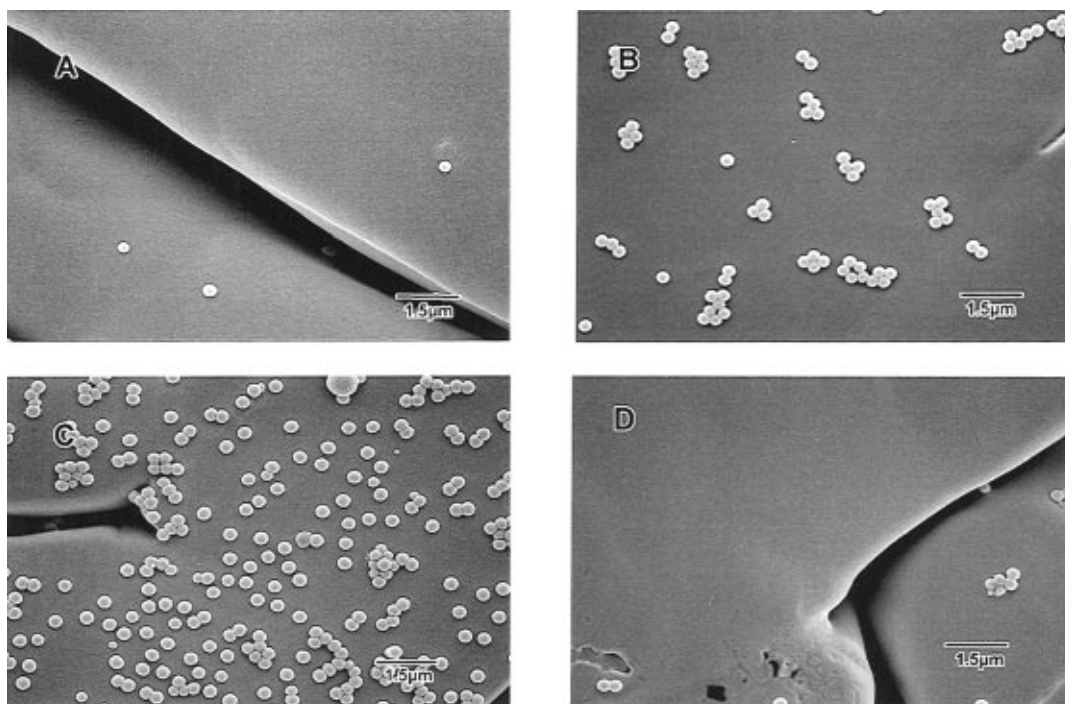


Figure 7. Particle adsorption on AN06 filter surfaces at pH 4.0 and 0.012 wt % solids particle concentration: (A) untreated filter and 197 nm negatively charged particles; (B) untreated filter and 200 nm positively charged particles; (C) 10 mM DDAB treated filter and negatively charged particles; (D) 10 mM DDAB treated filter and 200 nm positively charged particles.

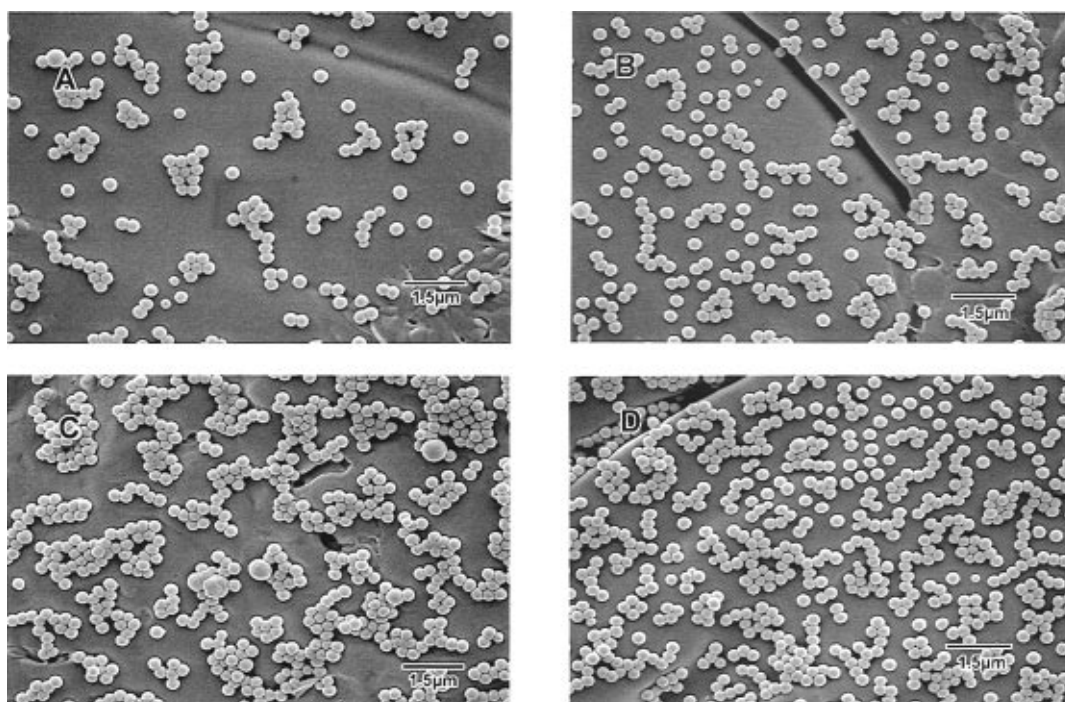


Figure 8. Effect of suspension concentration on particle adsorption on 10 mM DDAB treated AN06 filters at pH 4.0: (A) 0.020 wt % solids; (B) 0.030 wt % solids; (C) 0.040 wt % solids; (D) 0.050 wt % solids.

Filtration Efficiency of DDAB Treated Filters. Filtration efficiency or percent removal is significantly enhanced with DDAB treatment. Each of the data points plotted in Figure 9 is an average of two runs. For the untreated filters, the filtration efficiency ranges from 5% to 10%, but after the filters were treated with 10 mM DDAB, filtration efficiency increased to 50% or 60% for the lower initial concentration range. The increase in capture efficiency is mainly due to the electrostatic attraction between the negatively charged particles and the positively charged polar head of the surfactant molecules on the filter surface. Since the average pore

size is $0.6 \mu\text{m}$, the increase in capture efficiency is partly due to the smaller pore size in certain regions of the filters due to surfactant adsorption in clusters. However, by examining the results for the filtration at pH 10.0, it is evident that the increase due to entrapment is not very significant since the filtration efficiencies of the treated and untreated filters are very similar. If entrapment is the main mechanism, then filtration efficiency should not be dependent on the pH of the suspension unless pH-induced flocculation is occurring. However, if pH-induced flocculation is taking place, then the capture efficiency of the untreated filters should increase as pH is lowered.

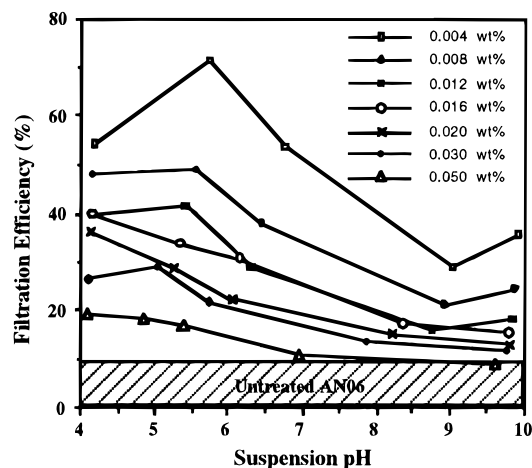


Figure 9. Capture efficiency of 10 mM DDAB treated AN06 (0.6 μm) filters at various initial concentrations of 60 nm P(S/A/V-COOH) and different suspension pH values.

This was not observed experimentally. In addition, quasi-elastic light scattering measurements showed that the average particle size did not increase with decreasing suspension pH, indicating an absence of flocculation at lower pH.

Since the particles are more negatively charged at higher pH values due to a higher degree of ionization, higher filtration efficiency is expected at the higher pH range. However, the results show the opposite trend. Capture efficiency is higher at the lower pH range. This trend could be due to one of the following two effects: either the surfactant is desorbing at the higher pH range or competitive ion adsorption is taking place.

To determine if the surfactant is desorbing, the treated filters were flushed with pH 10.0 solution. The effluents were collected for surface tension measurements. If the DDAB is desorbing, then the surface tension of the effluents should be lower than that of the pure water due to the surfactants at the surface. Results indicate that there was no change in surface tension of the effluents. Further proof that the surfactants are not desorbing is offered by contact angle measurements. Even with 200 mL of pH 10.0 solution flush, the average contact angle of the surface, 70.7 ± 12.7 deg, remains approximately the same as that for those that were flushed with 30 mL distilled water. Finally, the filters were rinsed with 30 mL of pH 10.0 solution, followed by 20 mL of distilled water, and then used to filter particles at pH 4.0. Results, as shown in Figure 10, indicate that the filters are just as effective as those that were rinsed with distilled water, which is another indication that the surfactant is not desorbing at the higher pH values.

Since the surfactants are not desorbing, the only other explanation is that the hydroxide ions are competing with the negatively charged particles for the positively charged surfactant sites. At pH 10.0, for example, because of the high number of hydroxide ions and because of their higher mobility due to their smaller size, they can diffuse to the surface of the filter much faster than the large negatively charged particles. The adsorption of the hydroxide ions shields the charge of the surfactants from the particles, and therefore, the particles are not adsorbing to the surface of the filters (Figure 11).

Effect of Ionic Strength. As seen from the results of the filtration experiments, increasing the hydroxide concentration (increasing pH) has a detrimental effect on particle adsorption. By increasing the ionic strength, particle capture efficiency is expected to decrease due to the ions interacting with the surfactant molecules on the

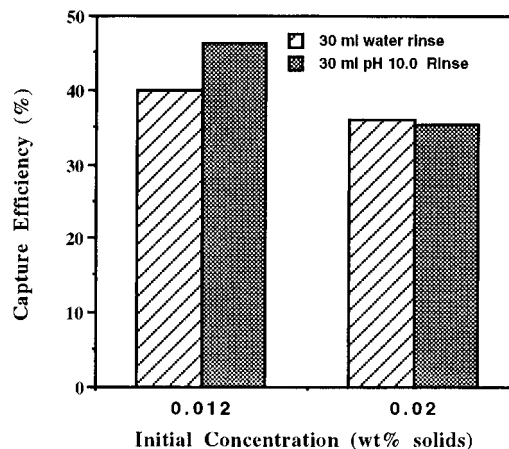


Figure 10. Comparison of capture efficiency of water rinsed vs pH 10.0 solution rinsed 10 mM treated AN06 filters for 60 nm P(S/A/V-COOH) at pH 4.0 and initial particle concentration of 0.012 wt % solids.

filter surface. Salt concentrations higher than 0.10 mol/L were not used because higher concentrations would cause particle aggregation due to compression of the electrical double layer. Results for several salts are shown in Figure 12. Sodium chloride and potassium sulfate have a small effect on filtration efficiency. Potassium nitrate has the largest effect on filtration efficiency. Potassium sulfate and potassium nitrate have been shown to decrease the surface charge (zeta potential) of quaternary ammonium modified surfaces.¹⁶ None of these salts, however, has the same effect as hydroxide ions. Hydroxide ions have a much higher affinity for surface adsorption than these salts. It has been reported that hydroxide ions have a higher surface adsorption affinity than the chloride ions on poly(ether ether ketone) surfaces.¹⁷

Effect of Pore Diameter. The capture efficiency of filters with different mean pore diameters was also studied. The suspension pH of 4.0 was chosen for this study because the highest capture efficiency is observed at this pH value, and therefore, changes will be more pronounced. Both untreated filters and surfactant treated filters show a sharp decrease in filtration efficiency as the pore diameter of the filters increases (Figure 13). However, for the 10 mM DDAB treated filters, the capture efficiency remains much higher than for the untreated filters. The decrease in capture efficiency as pore diameter increases is expected because filtration of these nanoparticles is diffusion controlled. The electrostatic attraction between the particles and filter surface is only effective within a certain distance. If the particles and surface are too far apart, each will not feel the presence of the other. When the pore sizes are too large, the particles do not have enough time to diffuse to the surface and no interaction takes place. Thus, the particles will pass straight through the filters.

Effects of Multiple Layers of Filters. The polypropylene filters used for these experiments are very thin (150 μm). For this type of filter to be effective in any application, multiple layers of filters must be used. With just four thin layers of filters, more than 95% of the particles can be removed from the solution. As the number of layers of filters increases, the incremental increase in capture efficiency levels off. In other words, by doubling the number of filters, the capture efficiency is not doubled,

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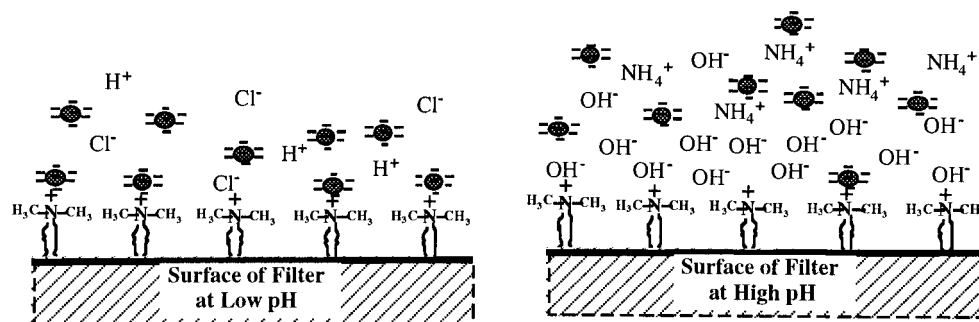


Figure 11. Schematic illustration of the mechanism of competitive adsorption at low and high suspension pH values.

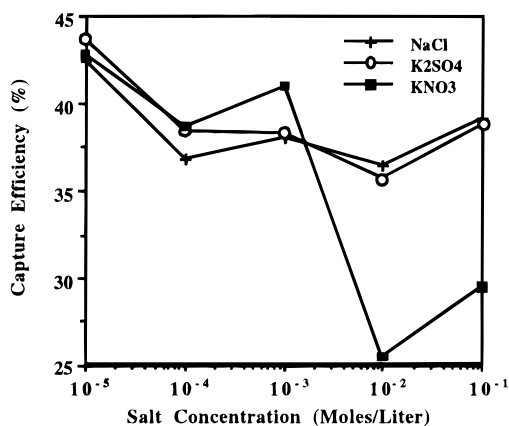


Figure 12. Effect of salt concentration of different salts on filtration efficiency of 60 nm P(S/A/V-COOH) particles at pH 4.0 and initial concentration of 0.012 wt % solids.

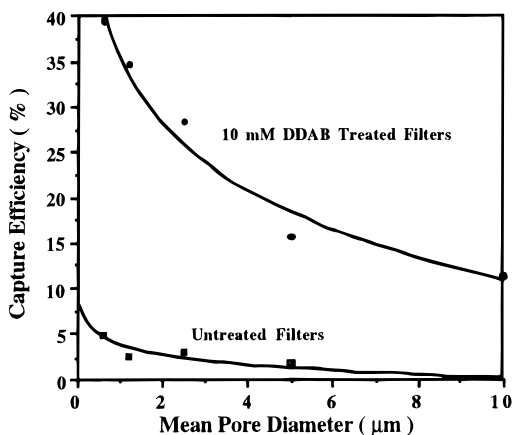


Figure 13. Effect of mean pore diameter on filtration efficiency of filters for 60 nm P(S/A/V-COOH) particles at pH 4.0 and initial concentration of 0.012 wt % solids.

and the increase with each additional filter gets smaller and smaller. In packed bed filtration (column filtration), the capture efficiency is given by the following equation:

$$\eta = \frac{c_{in} - c_{out}}{c_{in}} = 1 - e^{-\lambda L}$$

where η is the capture efficiency, λ is the filter coefficient, and L is the bed length or in this case, the number of filters. The treated filter data in Figure 14 fit this equation perfectly. Using the above equation, the filter coefficient is calculated to be 0.65/unit filter. Pressure drop is an important parameter in any filter design. The pressure drop for water is lower for the surfactant treated filters than for the untreated filters (Figure 15). The surfactant treatment makes the filters more wettable with water.

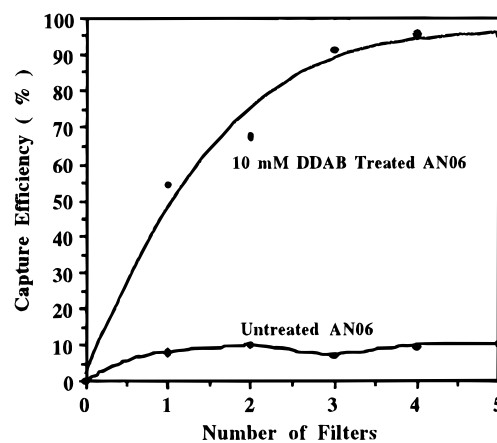


Figure 14. Effect of multiple layers of AN06 filters on capture efficiency at pH 4.0 and initial particle concentration of 0.012 wt % solids.

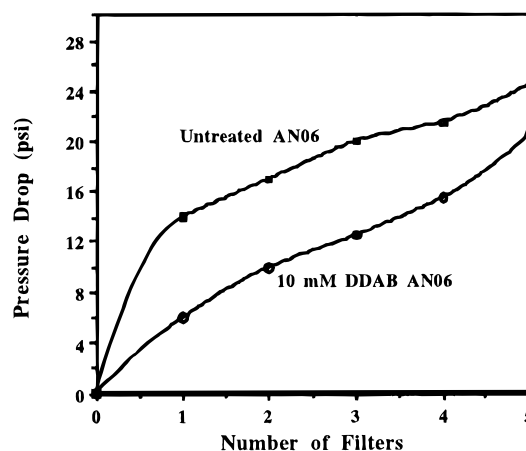


Figure 15. Pressure drop as a function of the number of filter for the untreated and treated AN06 filters.

Therefore, for the same pressure drop, more throughput can be obtained with the treated filters.

Conclusions

Due to their large pore sizes, conventional filters cannot be used to filter submicron particles, nanoparticles, or biological particles such as bacteria or viruses. These filters must be modified to enhance the interaction between the filter and the particles. In this investigation, polypropylene membrane filters were modified with a two-tailed cationic surfactant to create a positively charged surface. Negatively charged particles can then be filtered by using electrostatic interaction between the charged particles and the polar heads of the surfactants adsorbed on the filters. Particle adsorption studies have shown that particle adsorption can be increased significantly with this treat-

ment. Filtration results for 60 nm negatively charged particles (carboxylate modified copolymer) filtered through DDAB treated microporous polypropylene filters show a 4–5-fold increase in particle capture efficiency. Capture efficiency decreases as the pH of the suspension increases due to competitive adsorption between the hydroxide ions and the negatively charged nanoparticles. As the mean pore diameter increases, capture efficiency decreases due to the increase in the distance between the particles and the oppositely charged filter surface. Multiple layers of filters can boost the capture efficiency up to 95% with only four layers of filters. Thus, the results of this study clearly establish the importance of surface modification of filters to enhance filtration efficiency by enhancing the

attractive Coulombic interaction between the particles and the filter surface.

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