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THE EFFECTS OF TRIBUTYL PHOSPHATE
ON A POLYMERIC ULTRAFILTER(U)

SUMMARY

The purpose of this project was to determine the effects that tributyl phosphate (TBP) would have on a polysulfone crossflow ultrafilter. Aqueous simulant solutions containing TBP (100 or 1000 mg/L) and Fe(III), Si(IV), Al(III), and NaNO₃ were examined. Results obtained from simulant solutions containing 100 mg/L TBP were virtually identical to those obtained in the absence of TBP. However, a solution containing higher concentrations of TBP (1000 mg/L) very rapidly reduced the permeate flow rate to nearly zero. Chemical cleaning was successful in restoring initial flow rates. Permeate flux was plotted as a function of transmembrane pressure for clean water before and after the filter had been exposed to TBP. Also, the axial pressure drop was plotted as a function of the Reynolds numbers. Linear correlation of these data suggested that the filter did not swell or become distorted. Therefore, it was concluded that TBP does not have a permanent effect on this polysulfone ultrafilter.

INTRODUCTION

Crossflow Filtration is a relatively new technique which can be used in certain applications in place of dead-end filtration. It is a process by which the solution to be filtered is passed through a tube which has a thin membrane on the tube walls. This membrane contains small holes or "pores" which allow clean water (permeate) to pass but retain the solids (concentrate). The permeate is forced through these pores due to a pressure difference. The concentrated solution continues to flow down the length of the tube and exits at the end of the tube (Figure 1). In normal filter operation, a thin layer of solids builds up on the membrane surface at first, causing an initial decrease in permeate flow rate. This thin layer of solids is called the gel layer or polarization layer. However, after this layer has been created, the permeate flow rate reaches an equilibrium value. Additional solids are swept away from the membrane due to the high velocity of the concentrate solution through the tube. The thickness of this layer is related to the composition and velocity of the solution. The advantage of crossflow filtration over

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dead-end filtration is the continuous removal of the solids from the surface of the filter. This yields a thin gel layer which has a small resistance to flow.

Ultrafiltration involves filters that have pore sizes from 0.002 to 0.2 microns in diameter. Often, ultrafilters are categorized as nominal molecular weight cutoff range instead of pore size. Ultrafilters can remove particles as small as viruses and albumin protein. The pore sizes included in microfiltration overlap those of ultrafiltration. Microfiltration pore sizes are from .05 to 2 microns in diameter. Microfilters can remove materials such as paint pigment and tobacco smoke. A filter can be made from various substances, including ceramics, sintered metal, and polymers. An advantage of the ceramic or sintered metal filters is that they can be backpulsed, which helps prevent excessive clogging. Backpulsing is a process in which the flow of the solution is momentarily reversed to remove the gel layer. In the polymeric filters, clogging can be a more serious problem because backpulsing is not normally an option. This pluggage can result from a number of factors, ranging from bacteria to certain chemicals.

Tributyl Phosphate (TBP) is an organic chemical which has been reported to be a plasticizer.¹ This plasticizing property of TBP may cause swelling or weakening of polymers used in ultrafilters. Since the effects of TBP on polymeric filters have not been researched a great deal, it was of interest to determine if aqueous solutions containing TBP have an adverse effect on a polymer filter. The experiment was conducted by contacting aqueous solutions containing TBP with the filter. The fluid dynamic properties of the filter observed after contact with TBP were then compared with those observed before.

EXPERIMENTAL

The filter used for all the tests was a hollow fiber cartridge ultrafilter (HF 1.0-43-PM500, Romicon, Inc.). The filter fibers and filter housing are composed of polysulfone. A diagram of the filtration apparatus is shown in Figure 2. The nominal molecular weight cut off was 500,000 A.M.U. The pore size of this type of filter is approximately .03 microns. The normal flux rate was determined by measuring the velocity at different transmembrane pressures (7.5 - 17.5 psi) with deionized (d.i.) water. This procedure was repeated each time after the filter was cleaned to ensure that it was performing normally. The flow rates were determined by measuring the time to collect 1000 mL of permeate and concentrate. These rates were then divided by the surface area of the filter, which was 929 cm², to obtain the flux measurements. In cases in which the permeate velocity was very low, smaller amounts were collected in order to obtain accurate readings in a reasonable amount of time. After determining the normal flux measurements for the filter with d.i. water, the filter was tested with a simulant. The inlet feed pressure was 20 psi, and the outlet concentrate pressure was 10 psi creating an axial pressure drop of 10 psi. The permeate pressure was 0 psi, creating an average transmembrane pressure of 15 psi. These conditions were maintained throughout the rest of the tests. The feed tank was an agitated 170-L stainless steel tank. The

pressure was provided by a variable speed MICROPUMP. The pump, filter, and tank were connected with rigid polyethylene tubing.

The inorganic simulant contained the following reagent grade chemicals: 1500 mg/L NaNO_3 , 5.7 mg/L Fe(III) [added as $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Baker)], 5.0 mg/L Si(IV) [added as Na_2SiO_3 (NOAH)], 2.7 mg/L Al(III) [added as $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Mallinckrodt)]. These reagents were dissolved in 8 L of 5 wt.% HNO_3 (Fisher) and stirred overnight. All solutions were prepared with water from a Millipore deionizing unit and determined to have a conductivity $>16 \text{ Mohm} \cdot \text{cm}$. The solutions were diluted to 170 L and neutralized with 8.0 M NaOH (Mallinckrodt) to $\text{pH} = 7.5 (\pm 0.5)$. Filtration began approximately 10 minutes after neutralization. The simulant solution was run through the filter for 28 hours while velocity measurements and feed and permeate samples were collected periodically. Temperature and pH were recorded at these same times. The pH was kept at approximately 7.5 (± 0.5) by addition of 0.1 M NaOH . To clean the filter, a 0.2% oxalic acid solution followed by a 0.2% sodium hydroxide solution were recirculated through the filter for two hours each. The filter and tubing were rinsed after each chemical cycle with 8 L of d.i. water.

An inorganic simulant (Fe(III) , Si(IV) , and Al(III)) solution was prepared as described above. Every attempt was made to reproduce the conditions of the preparation identically. Tributyl phosphate (TBP) [$(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_3\text{P(O)}$ (Aldrich, 99+%)] was added to obtain a final concentration of 100 mg/L. This solution was recirculated for 8 hours. The filter was then rinsed and cleaned as in the previous trial. The flux on d.i. water determined that the filter was clean and restored to original condition.

A fresh container (170 L) of inorganic simulant was prepared. tributyl phosphate was added to obtain a final concentration of 1000 mg/L. This solution was recirculated through the filter. The experiment was suspended after only 5 hours because the filter fouled so quickly. Again, the filter was cleaned with acid and base and tested with d.i. water to make sure the cleaning had been successful.

A 1000 mg/L solution of TBP in d.i. water (no inorganic simulant) was tested on the Romicon filter unit. This simulant was prepared by adding 170 g TBP to 170 L of d.i. water and agitating vigorously for 18 hours. This test also was shut down after 5 hours of operation because it fouled so badly. After this last test, d.i. water was used to rinse the filter and this returned the flux to normal. This test was repeated and the results were identical within experimental error.

The turbidity of the feed and permeate samples from all four different experiments was measured and recorded. Turbidity is a method of measuring the "cloudiness" of a solution. In each case, the instrument was checked for accuracy with standards.

The viscosity of the feed that contained the TBP was also measured. The sample size used for all the measurements was 7.1 mL, and the temperature of the liquid was 25 °C. The amount of

time a substance took to pass through the viscometer was measured three times and averaged. The known viscosity for water at 25 degrees Celsius is 0.8904 centipoise. To obtain the kinematic viscosity (ν), this number was divided by the density of water (0.99707 g/mL). The result was 0.8930 centistokes, which was then divided by the average time water took to flow through the viscometer (294.7 s). This number (0.003030 centistokes/sec) became the viscometer constant (C). Viscosity for the feed samples was found using the following equation:

$$\nu = C \cdot t \cdot d$$

Where t is the average time (seconds), and d is density (g/cm^3).

The Reynolds (Re) number (the ratio of inertial forces to viscous forces²) was calculated as a function of pressure drop before, during, and after exposure to TBP using the following equation: $\text{Re} = Dv/\nu$. The diameter (D) of the tube was 0.043 inches. The average velocity (v) was calculated ($v = v_f + v_c/2$).

RESULTS

The Fe(III), Si(IV), and Al(III) ions are initially dissolved in the simulant solution below pH = 2. As NaOH is added, the solutions gradually turn cloudy brown due to the precipitation of the metal hydroxides. At the operating pH, the iron hydroxide, aluminum hydroxide, and silicate are quite insoluble and coprecipitate to form a fluffy solid which settles on extended standing. The solubility of TBP is reported to be approximately 400 mg/L.³ Due to the difficulty in dissolving the TBP, the TBP was added to the d.i. water and vigorously agitated for 16 hours prior to addition of the inorganic chemicals. The TBP-containing solutions had precipitates which were markedly lighter in color and less viscous. With the high concentration of TBP, there was clearly a suspension of fine droplets of TBP in solution. These droplets did not coalesce into a separate phase after standing for 24 hours.

Permeate flux was plotted as a function of transmembrane pressure for d.i. water from the inorganic simulant test (Figure 3). The correlation between the data points in Figure 3 was 0.978. This high correlation coefficient demonstrated that the filter was performing linearly with respect to pressure. Nonlinear behavior would have suggested that the filter was swelling, or the membrane being compressed, with increasing pressure. Normally, the line extrapolated to near the origin will have a slightly positive x-axis intercept. This is because some pressure is necessary to overcome the membrane resistance and initiate permeate flow.⁴ The results observed here show a positive y-axis intercept very close to the origin (0.0005). Therefore, a positive x-axis intercept would be within experimental error.

The simulant containing Fe(III), Si(IV), and Al(III) decreased the permeate flow of the filter slightly, as expected (Figure 4). The flux dropped approximately thirty percent in the first seven hours and then leveled out. This flux drop is consistent with formation of a gel layer on the membrane. The reason for the increase in d.i. water flux in Figure 4 is an increase in temperature. The solution rose from an initial temperature of 24.5°C to 27.0°C. Experiments have demonstrated that the permeate flow rate

increases by 3% for each degree Celsius rise in temperature.⁵ The results of the turbidity measurements on the simulant test samples showed that the feed was 1.3 NTU and the permeate <0.1 NTU. Therefore, the filter was removing most of the solids from the solution.

Addition of 100 mg/L of TBP to the inorganic simulant resulted in an initial flux which was approximately ten percent lower than on simulant alone. However, after six hours of operation the fluxes were almost identical. A plot of the flux as a function of time is shown in Figure 4.

In contrast to the results found in the experiment containing 100 mg/L of TBP, when 1000 mg/L of TBP was added to the simulant, the filter fouled very quickly. The initial flux was roughly ten percent of the inorganic simulant flux, and in two hours the flux was essentially zero. Similarly, the filter performance was poor with a solution of d.i. water and 1000 mg/L of TBP (no added Fe(III), Si(IV), Al(III), or NaNO₃) as presented in Figure 5. It is proposed that in both of these experiments containing 1000 mg/L of TBP, the suspended TBP droplets physically plug the filter pores.

The filter was cleaned and checked for performance between each experiment. The d.i. water flux remained normal after the filter had been cleaned, despite being exposed to TBP for a total of approximately 23 hours (Figure 6). Also, the axial pressure drop did not change when pressure was plotted against the Reynolds number for points before, during, and after the filter was exposed to TBP (Figure 7). These two results suggest that swelling of the membrane did not take place, and the TBP did not affect the polysulfone ultrafiltration unit permanently.

Table 1 contains results of the turbidity determination of the samples taken from the four tests. Samples of the feed solution and permeate solution were collected immediately after startup. Subsequent samples were then collected at 1 hour intervals for each experiment. There is virtually no difference in the turbidity results between those of the inorganic simulant solution and those of the inorganic simulant with 100 mg/L of TBP. The TBP is probably completely dissolved in this case. In the tests containing 1000 mg/L of TBP, the turbidity of the feed samples is much higher. There is probably a suspension of TBP in the water, which makes the solution turbid. The solubility limit of TBP in water is about 400 mg/L.³ Although the permeate flow rate was lower with the addition of 1000 mg/L of TBP, the turbidity still measured <0.1 NTU, indicating that the filter removed the suspended solids and suspended droplets of TBP.

The viscosities of the feed samples were very close to each other and also to water. Viscosity results are reported in Table 2. It does not appear that the filter fouling could be due to changes in the viscosity of the solutions.

CONCLUSIONS

At a concentration below the solubility limit (100 mg/L), Tributyl Phosphate did not affect the performance of the polymeric ultrafilter. Permeate flow rate after six hours was the same as it had been for the simulant containing only inorganics. With 1000 mg/L of TBP added to the aqueous simulant, the filter fouled immediately and flux was reduced to <0.1 cm/sec within two hours.

Similar results have been observed⁶ with tributyl phosphate solutions in a Norton Ceraflo filter (0.2 micron). When 1000 mg/L of TBP and Fe(III), Si(IV), and Al(III) simulant was filtered through a Norton Ceraflo filter unit, the filter fouled very badly. Therefore, suspensions of TBP can obviously have an effect on different types of filters and is not limited to the polymeric filter alone.

No permanent loss of integrity of the filter occurred under the conditions studied, as measured by the d.i. water flux. The filter had been exposed to TBP-containing solutions for a total of approximately 23 hours. After cleaning, the d.i. water flux was essentially unchanged as a result of these experiments. The preliminary results presented here suggest that longer-term exposure experiments are needed to determine the effects of TBP after weeks or months of operation.

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FIGURE 1.
Cross-flow vs. Dead-end Filtration

Figure 2
POLYMER ULTRAFILTER UNIT

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Figure 3.
DI Water Correlation

Figure 4.
Filter Performance with Simulant
and TBP Solutions

Figure 6.
Filter Performance on DI Water
Before and After TBP

Figure 7.
Pressure Drop as a function
of Reynolds Number

Table 1

<u>Solution</u>	<u>Sample</u>	<u>Turbidity (NTU)</u>
Inorganic	Feed 1	1.4
Simulant	Feed 2	1.3
"	Feed 3	1.3
"	Feed 4	1.3
"	Feed 5	1.5
"	Feed 6	1.5
"	Permeate 1	<0.1
"	Permeate 2	<0.1
"	Permeate 3	<0.1
"	Permeate 4	<0.1
"	Permeate 5	<0.1
"	Permeate 6	<0.1
100 ppm TBP + Simulant	Feed 1	1.2
"	Feed 2	1.2
"	Feed 3	1.2
"	Feed 4	1.3
"	Feed 5	1.3
"	Feed 6	1.4
"	Permeate 1	<0.1
"	Permeate 2	<0.1
"	Permeate 3	<0.1
"	Permeate 4	<0.1
"	Permeate 5	<0.1
"	Permeate 6	<0.1
1000 ppm TBP+ Simulant	Feed 1	43.0
"	Feed 2	45.0
"	Feed 3	45.0
"	Permeate 1	<0.1
"	Permeate 2	<0.1
1000 ppm TBP	Feed 1	47.0
"	Feed 2	51.0
"	Feed 3	55.0
"	Feed 4	56.0
"	Permeate 1	<0.1
"	Permeate 2	<0.1

Table 2

<u>Sample</u>	<u>Viscosity</u> <u>(centipoise)</u>
d.i. H ₂ O	0.8904
1000 ppm TBP + simulant	0.8933
1000 ppm TBP	0.8972

Additional Slides

C.A. Stewart

Filtration Spectrum

THE EFFECTS OF TRIBUTYL PHOSPHATE ON A POLYMERIC ULTRAFILTER

Charlene Stewart

Summary:

- **Inorganics cause minimal fouling**
- **Dissolved TBP causes minimal fouling**
- **Insoluble TBP causes excessive fouling**
- **TBP does not permanently affect polymer**

Objectives:

- **Determine performance of filter on simulated waste streams**
- **Determine if TBP plasticizes the polymer**

Methodology:

- Challenge the filter to various concentrations and conditions
- Simulate wastewater using Fe, Si, Al, NaNO_3 , and TBP ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$) $_3\text{P}(\text{O})$
- Study filter characteristics by examining the fluid dynamics

Conclusions:

- **NaNO₃, Fe, Si, and Al Simulant-
30% fouling**
- **Simulant plus 100 ppm TBP-30% fouling**
- **Simulant plus 1000 ppm TBP-100%
fouling**
- **1000 ppm TBP-100 % fouling**
- **TBP does not permanently affect
filter after 23 hours exposure**

Regular Simulant vs. 1000 ppm TBP Simulant

TBP Experiment-6/20/90

Norton Filter Performance with TBP

END

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