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Ultrafiltration membranes from novel low-fouling copolymers for RO pretreatment applications (Part II)

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ABSTRACT

New approaches to improve the anti-fouling characteristics of existing UF membranes based on polyethersulfone (PESU) have been investigated and reported in our previous paper. By incorporating either very hydrophilic polymers or anti-adhesive copolymers in the dope formulation, novel Multibore® fibers were spun by means of the well-known non-solvent induced phase separation (NIPS) process. These membranes were validated in multiple lab scale pilot trials for various applications, namely surface and waste water purification as well as seawater desalination pre-treatment. This current work focuses on an additive approach based on a novel amphiphilic copolymer of polysulfone, polyethylenoxide and polysiloxane, leading to a membrane surface with alternating hydrophilic and hydrophobic groups. Full scale modules with 60–70 m^2 of surface area have been operated at a variety of sites for a total of over 2 years. For each application, a significantly reduced fouling propensity was achieved compared to the reference modules, leading to a number of benefits. These include the possibility of running the plant at higher fluxes, reducing the energy requirements of the membrane plant, reducing the number of chemical cleans, or improving the overall recovery of the membrane plant. Other advantages which were observed are the ease of cleaning, especially after specific fouling incidents had occurred, either through the intake of unwanted substances in the feed, or after upsets in the regular cleaning sequences. This study shows that it is possible to improve membrane surfaces so that cleaning processes become much more effective, without sacrificing on chemical stability or rejection performance.

Keywords: Copolymer; Fouling; Membrane modification; Ultrafiltration; Seawater

1. Introduction

Ultrafiltration (UF) for water treatment has grown in significance over the past 30 years, and is now the method of choice for many applications [1,2]. These include the direct treatment of surface water to produce drinking water, the treatment of wastewater for reuse or the pretreatment of reverse osmosis (RO) membranes for use in desalination of seawater. Due to this commoditization of UF, membrane suppliers have to constantly improve their membrane, module, systems and operating modes. One of the most interesting topics both in academic as well as industrial research deals with the reduction of fouling phenomena [3–6]. Many researches focus on increasing the hydrophilicity of the membrane which should reduce the adsorptive forces with mainly organic fouling. This can be done by creating copolymers between the base membrane material and a hydrophilic component, like PESU and polyethylene oxide

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(PEO) [7–9]. Another option is to sulfonate the backbone of the polyethersulfone [10–12]. An alternative approach discussed in the literature is based on groups having low interaction with organic molecules. This leads to antiadhesive properties which might also positively influence the fouling performance [13–15].

The development of novel UF membranes from low fouling copolymers has been described in the first part of this work [16], which focused mainly on the synthesis of these copolymers and how they could be incorporated in the resulting membrane. As initial proof of the low fouling characteristics, some pilot results were shown, albeit with small laboratory scale modules of around 0.3 m^2 of membrane surface area. One of the reported copolymers made of polysulfone (PSU), PEO and polysiloxane (PSilox), the polysulfone-polyethylene oxide-polysiloxane (PSU-PEO-PSilox), has proven particularly beneficial for the purpose of producing low-adhesion membranes. In this paper the main focus is on the results obtained in fullscale pilot units where this novel copolymer was used as an additive in the dope formulation. Pilot results are shown for the main applications of UF in water filtration: surface water, seawater and tertiary waste water pre-treatment.

The benefit of a membrane surface exhibiting low-adhesion is dependent on the wishes and necessities of an end-customer. In many cases there will be a focus mainly on the costs of the produced water. In this case, it mostly makes sense to try to increase the output of the membrane plant as far as possible, so in this case the emphasis will be on an increase in flux. In other cases there might be severe restrictions on the use of cleaning chemicals, so that reductions in the frequency of chemical cleans are of utmost importance. Another factor which a customer could want to bear in mind is the ecological footprint of his plant. In this case, the minimization of chemical cleanings has to be done hand in hand with keeping the driving force, the transmembrane pressure (TMP), as low as possible in order to save on energy. This paper shows that the low-adhesion benefits can be translated into the type of benefit which the end user needs from their membrane plant.

2. Materials and methods

The standard inge GmbH membranes, called Multibore®, are made of PESU and are produced via a NIPS technique, in which the nascent fiber comes in contact with a non-solvent for the PESU. An important characteristic is the rejection ability of the membrane for pathogens such as bacteria and viruses. This membrane is classified as an UF membrane as it has a rejection in excess of 99.99% of viruses (proven by means of the MS2 phage surrogate). In order to further improve the membrane in challenging feed waters with higher organic loading, an additive approach has proven to be very successful. This paper specifically focuses on the PSU-PEO-PSilox additive or copolymer.

As can be seen from Fig 1 that the PSU-PEO-PSilox copolymer consists of a backbone of PSU material which is very compatible with PESU which is the main material of most in-out membranes. This material compatibility is vital in order to prevent the PSU-PEO-PSilox copolymer from leaching out of the membrane during its filtration duties. The further components of this molecule comprise the very hydrophilic PEO alternating with the more hydrophobic PSilox.

For the purpose of the piloting requirements, the Multibore® membrane is used as the reference membrane. In order to obtain PSU-PEO-PSilox additive containing membranes with nearly identical performance characteristics to the reference membrane, some membrane spinning parameters were adjusted such as dope composition, dope and coagulation temperature and lumen fluid composition. The new membranes were spun incorporating the PSU-PEO-PSilox additive in a concentration under 1% of the total dope formulation, in which PESU is the main component. Further additives were polyvinylpyrrolidone (PVP) K90 as well as glycerin. The PVP was added in order to increase the dope viscosity, and to help with obtaining the correct pore size and pore structure.

All studies detailed in this paper were conducted with pilot units equipped with 2 fullscale modules (inge® dizzer® XL series type) running in parallel and completely independently. One module (Reference module) contains the standard Multibore® membrane while the second module is filled with the PSU-PEO-PSilox membrane (Siloxane module). Both modules on the same pilot had the same effective surface area but depending on the pilot, the surface area of each individual module varied: 60 m^2 (1.5 m module length) or 70 m^2 (1.7 m module length).

In order to see the behavior of the novel membrane when faced with various types of naturally fouling ingredients, three different types of water were treated and are compared: sea water, surface-reservoir water, tertiary wastewater. The sea water pilot was situated on the northern Mediterranean coast of Spain. The surface water piloting has been conducted at a large reservoir in Luxembourg. The third pilot was operated on a municipal wastewater treatment plant in Germany.

All pilots are run close to real dead-end application conditions. The flux, ranging from 60 to 140 l/(m^2 h) is maintained at a fixed level, and the TMP is allowed to increase. At fixed intervals, typically every 30–60 min, a backwash (BW) is initiated with a flux of 230 l/(m^2 h). Once or twice a day a chemically enhanced backwash (CEB) is used in order to ensure long-term stable operation. The first step of the CEB consists of a pH increase to around 12 by means of caustic soda (NaOH). This removes the organic materials which have adsorbed on the membrane. The cleaning effect can be enhanced by the addition of sodium hypochlorite (NaOCl at 20–100 ppm free chlorine, Cl_2). In case of sea water, the pH is not allowed to go higher than 9.5–10, in order to prevent the magnesium (Mg) and calcium (Ca)

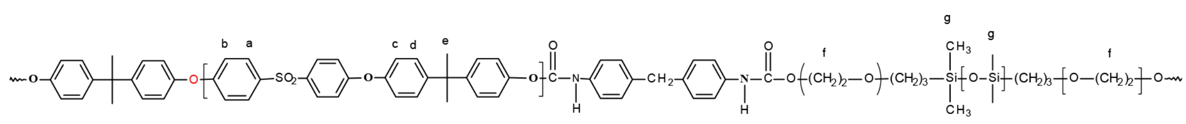

Fig. 1. Molecular structure of PSU-PEO-PSilox copolymer.

to precipitate. The high pH clean is followed by a low pH clean with sulfuric acid (H_2SO_4) at a pH around 2. This low pH removes the build-up of inorganic materials and prevents long term scale building. In all pilot units, an additional CEB is initiated as soon as the maximum TMP value is reached (set point between 0.8–1.0 bar).

All pilot units had the benefit of remote control with continuous data acquisition, which meant that plant monitoring and adjustments to the operation could be done from other locations.

3. Results and discussion

3.1. Membranes

Thanks to the adjustment of the spinning parameters, the main characteristics of the resulting hollow fiber membrane are indistinguishable from the reference membrane regarding the commonly used characterization methods (Table 1). The comparison shows typical data related to the membrane's pore size, pore size distribution and porosity in terms of molecular weight cut-off (MWCO), pure water permeability (PWP) and MS-2 phage rejection. Other data are presented here which relate to the mechanical stability of the 2 different membranes. Burst and collapse pressures are important parameters which give an indication which single pressure shocks can be handled by the membranes in case of sudden plant malfunctions. Further interesting data are delivered by using a Tensometer which pulls a single piece of hollow fiber membrane with a constant speed of 300 mm/min in a longitudinal direction. The force and the resulting extension on the membrane is measured up to the point where the membrane breaks.

Analysis methods determining surface characteristics which are influenced by chemical changes can differentiate between the 2 different membranes [1]. To facilitate its implementation, the measurement of the contact angle was not performed on hollow fibers but on flat sheet membranes produced with the same concentration in polymers and additives. Compared to the reference membrane material with a contact angle of around 60–70 degree, the membrane based on PSU-PEO-PSilox is showing a more hydrophobic character with a contact angle of 80–100 degree. As demonstrated by Krüger et al. [16], the PSU remains largely in the membrane matrix due to its compatibility with PESU, while on the other hand, the PEO and the PSilox tend to migrate to the membranes surface. The PEO increases the hydrophilicity and reduces significantly the contact angle, but the PSilox has the opposite effect. As the measured contact angle of the siloxane membrane is higher, it can be concluded that the hydrophobic character of the PSilox overpowers the PEO.

Table 1
Characteristics of a reference Multibore® membrane and a PSU-PEO-PSilox containing membrane

Characteristics	Standard membrane	PSU PEO PSilox cont. membrane
MWCO, kDa	80 ± 20	90 ± 15
PWP, l/(m² h bar)	1000 ± 150	1100 ± 150
Burst pressure, bar	> 12	> 12
MS2 rejection, log	> 5	> 5
Collapse pressure, bar	> 12	> 12
Force, N	31 ± 4	32 ± 4
Elongation, %	60 ± 10	63 ± 10
Contact angle*, °	60 – 70	80 – 100

3.2. Pilot results

Long term piloting was performed at various sites on different water types: tertiary wastewater, surface water and seawater. This paper presents results of three sites representative of each water type. Some water quality data for the 3 sites are shown in Table 2.

For each water type, a comparison was made between the Reference module and the Siloxane module running in parallel. In the initial phases of the pilot studies, the flux of both modules was maintained at identical value so as to compare the evolution of the TMP as well as permeability. After observing that the permeability of the Siloxane membrane was higher than the reference membrane, the fluxes between the 2 modules was differentiated in order to find the potential for flux increase for the Siloxane membrane.

The aim of these pilot studies was to try and run the membranes close to their limits, to see where these limits lie and to observe differences in the cleaning effect between the two different membrane chemistries. Conversely it was not the intention to show a long term stable performance. The paper does not present all data of the longterm operation but only representative and characteristic periods where both membranes are operated either under the same flux or identical TMPs.

Table 2
Water quality data from 3 piloting sites

	Tertiary wastewater	Seawater	Surface water
Temperature, °C	8.0–20.0	13–19	3.8–11.3
pH	6.9–7.6	8.2	6.9–7.4
Conductivity, µS/cm	470–1390	56000	140–151
Turbidity, NTU/TE/F	0.9–14.9	0.1–1.0	3.8–11.3
Hardness, mmol/L	1.8–3.4	–	0.1–0.3
Total organic carbon (TOC), mg/L	–	0.7–1.0	1.7–3.0
Diss. organic carbon (DOC), mg/L	5.3–9.0	–	–
Sulfate (SO_4^{2-}), mg/L	32	3307	10.3–11.1
Chloride (Cl^-), mg/L	–	21793	14.5–17.3
Iron (Fe), mg/L	0.02–0.2	–	65–140
Calcium (Ca^{2+}), mg/L	75.0–95.0	449	10.0–11.7
Magnesium (Mg^{2+}), mg/L	11.0–26.0	1378	4.2–5.0
Total suspended solids (TSS), mg/L	8.0–50.0	1	–

3.2.1. Treatment of secondary municipal waste water

The waste water treatment plant treats a mixture of municipal as well as industrial wastewater and has a capacity of around 90,000 people equivalent. The influence of industrial water has a significant effect on the composition and treatability of the wastewater. Polyaluminiumchloride (PAC) was dosed at a concentration of 3 ppm Al. The pilot plant has been in operation for a total of 4 mo. During the initial period, the Reference module was run at the same flux as the Siloxane module. As shown in Fig. 2. under the same flux, the permeability of the Siloxane membrane is always approximately 30% higher than the Reference membrane permeability.

After the initial period during which fluxes were identical, the flux of the Siloxane membrane was increased to a point where the TMP was similar to the Reference module. Under these conditions, the Siloxane module can operate at a flux 17% higher than the Reference module, 70 l/(m^2 h) compared to 60 l/(m^2 h). This flux difference was maintained throughout the duration of the pilot study. As shown in Fig. 3, even with the higher flux, the permeability level of the Siloxane module remains higher than the Reference module.

For the duration of the full pilot run, the TMP during BW was monitored. One can note that the TMP of the Siloxane module is always lower than the Reference module (Fig. 4). This confirms that the Siloxane membrane presents a lower fouling behavior. During the filtration process material retained by the membrane (larger than the pore size of around 20 nm) needs to be rinsed out as well as possible by the BW. If the adhesive forces between this material and the membrane are lower due to the Siloxane additive, than the BW needs less power in order to loosen the interaction and transport it out of the capillaries.

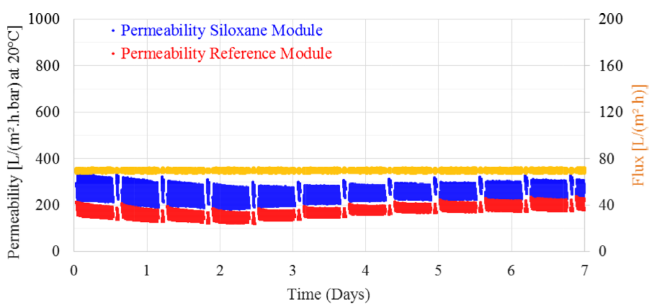

Fig. 2. Wastewater – Permeability comparison – Modules operated under identical flux.

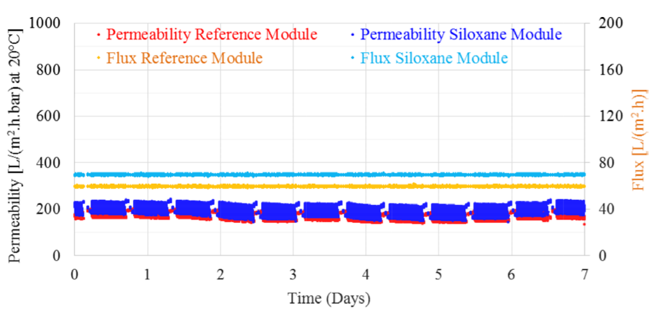

Fig. 3. Wastewater – Permeability comparison – Modules operated under different flux.

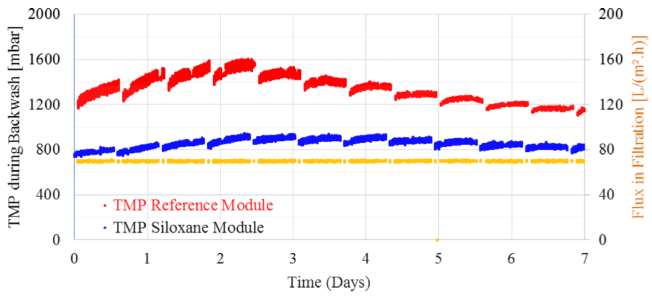

Fig. 4. Wastewater – TMP comparison during backwash – Modules operated under identical flux.

During the 4 month period, one can conclude that the Siloxane module always maintained higher permeability levels compared to the Reference module.

3.2.2. Seawater

The seawater intake for this pilot plant is situated on the northern Spanish Mediterranean coast. The water quality data show very low turbidity and TSS in combination with relatively low organic contents (Table 2). During the entire 6 mo of pilot operation, no coagulants/flocculants were dosed. Fig. 5 shows the permeability of both the reference module and the Siloxane module during the initial phase when both modules were operated under the same and constant flux. As for the test on wastewater, the permeability of the Siloxane module is clearly higher than the Reference module by approximately 60%.

Thanks to the low turbidity (< 1 NTU) and low TOC (< 1 mg/L) of the feed water, fluxes were increased after the initial period to relatively high levels for both the Reference module and the Siloxane module, respectively 120–130 l/(m^2 h) and 140–150 l/(m^2 h). Once again, the Siloxane module shows a constantly higher permeability than the Reference module (Fig. 6.) even operated at 20% higher flux. The TMP of the Siloxane module also remains lower than for the reference module.

As for the pilot test on wastewater, the TMP during BW (Fig. 7) of the Siloxane module is lower compared to the Reference module.

As already observed on wastewater, when operated under identical fluxes, the Siloxane membranes filter seawater under lower TMP's and higher permeability's than the Reference module. This results in lower energy consumption thus lower running costs.

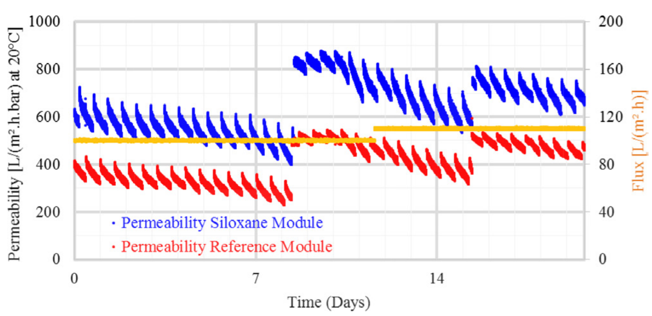

Fig. 5. Seawater – Permeability comparison – Modules operated under identical flux1a.

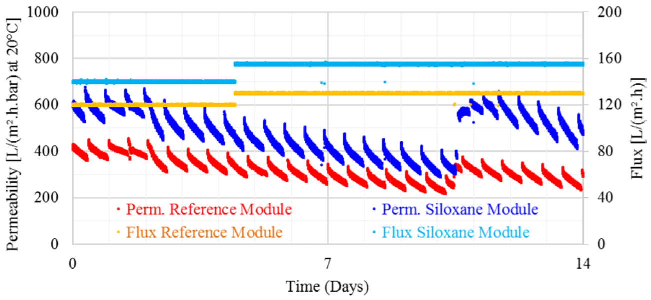

Fig. 6. Seawater – Permeability comparison – Modules operated under different flux.

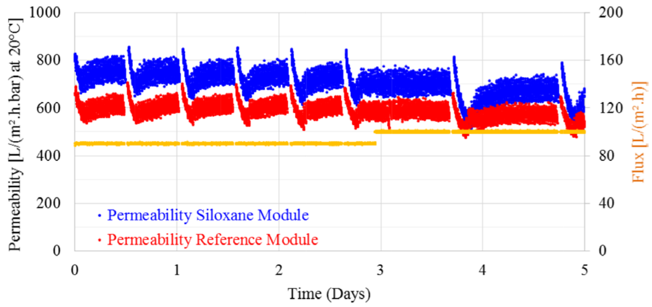

Fig. 8. Surface water – Permeability comparison – Modules operated under identical flux.

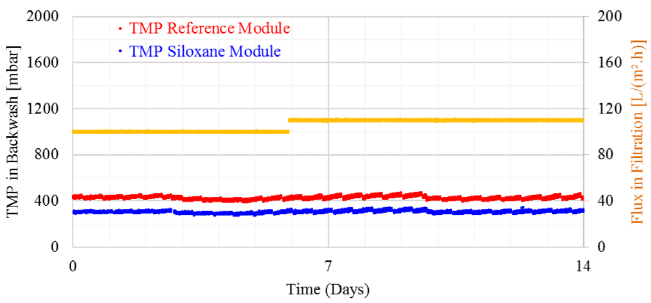

Fig. 7. Seawater – TMP comparison during backwash – Modules operated under identical flux.

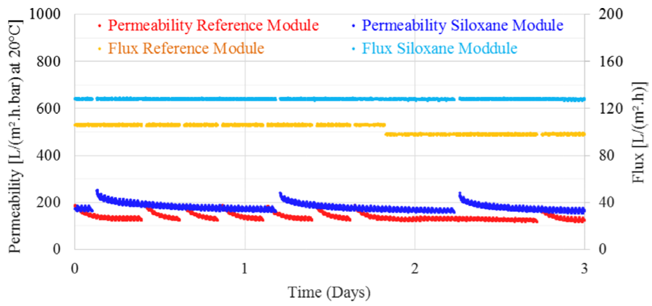

Fig. 9. Surface water – Permeability comparison – Modules operated under different flux.

3.2.3. Surface water

As shown in Table 2, the water quality of this large reservoir in Luxembourg is strongly variable due to the influence of temperature and rain fall. To cope with this highly variable water quality, and per inge® experience, ferric chloride ($FeCl_3$) was dosed at a concentration of 3 ppm Fe upstream of the membranes.

As for the previous two pilot studies, the Siloxane module operates at 30–40% higher permeability than the Reference module when run under the same flux (Fig. 8).

After the previous initial period, the flux of the Siloxane module was increased to 130 l/(m^2 h) and the flux of the Reference module to 110 l/(m^2 h) as shown in Fig. 9. After some days of operation with 20% higher flux for the Siloxane module, the TMP of the Reference module exceeded the pre-set high-level trigger point, after which an automatic CEB was executed. To further continue the comparison of both modules, the flux for the Reference was reduced to 100 l/(m^2 h). Once again, even if operated at a flux 30 % higher and similar TMP and CEB frequency, the permeability of the Siloxane module is slightly higher than the Reference module.

As for both previous tests, the Siloxane module is less affected by fouling than the Reference module.

3.3. Discussion

Even though the long-term fouling behavior of the PSU-PEO-PSilox was clearly superior to the Reference membrane, the TMP increase in each filtration cycle is similar in both membrane types. This is caused by the specific type of membrane filtration, dead-end filtration, where all solutes including molecules and particles which can cause membrane fouling enter the capillaries and are prevented from leaving the enclosed system until a BW takes place. One can observe that the PSU-PEO-PSilox additive based membrane allows operation at lower TMP or higher permeabilities whatsoever is the type of water. One can assume and conclude that this is linked to the reduction in the adhesion characteristics of foulants (mainly organics) to the membrane surface. When the interaction forces between the solutes and the membrane's surface are weaker, then the cleaning effect of the BW or chemical cleans improves. This translates into a higher efficiency BW, and the membrane starts with a higher permeability in the next filtration cycle. The permeability after BW remains higher over longer periods of time so that the long-term or irreversible types of fouling take longer to build-up. This keeps the TMP at lower levels, saving energy and reducing the reliance on chemical cleaning.

As measured by contact angle [8], the PSU-PEO-PSilox membrane seems to have a more hydrophobic surface than the Reference membrane. It is expected that this higher hydrophobicity is mainly caused by the hydrophobic Polysiloxane groups. Due to the alternation of hydrophobic and hydrophilic groups in the PSU-PEO-PSilox membrane, it is furthermore assumed that this amphiphilic property makes it harder for a wider variety of molecules to adhere to the membranes' surface compared to purely a hydrophilic or hydrophobic membrane surface.

4. Conclusions

The three full scale pilot studies show that the novel membrane, made of PESU with polysulfone-polyethylene oxide-polysiloxane additives, has improved longterm performances compared to a Reference module. In each case, the PSU-PEO-PSilox membrane was able to run with significantly lower TMP levels than the reference membrane for prolonged periods of time. This clearly demonstrates that the anti-adhesion characteristics of the membrane are able to reduce the energy costs for running a membrane plant. This effect is enhanced by the lower TMP levels in BW mode, which also show that the fouling build-up on the membranes is removed significantly easier from the low-adhesion surface.

It has also been shown that the novel membrane can operate at higher flux levels compared to the reference membrane without the risk that the membrane suffers from more irreversible types of fouling. Another benefit which can be obtained by adding the Siloxane additive is the reduced frequency of CEB's, thus saving in chemical usage as well as increasing the total recovery (lower downtime and less water consumption for CEB).

The level of improvements that can be obtained with the novel membrane depends on many parameters, like the general water quality, temperature, type of foulants etc. The pilot studies clearly demonstrate that these improvements can be quite significant.

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