

Nanostructured Composite Adsorber Membranes for the Reduction of Trace Substances in Water: The Example of Bisphenol A

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ABSTRACT: The increasing contamination of water with biopersistent substances is considered to become one of the key environmental problems in the next decades. These so-called micropollutants show considerable toxic or otherwise negative effects even at concentrations in the ppt level or ppb level. For the experimental proof-of-concept study we chose 2,2-bis(4-hydroxyphenyl)-propane known under the name bisphenol A (BPA). The extensive use of BPA-based polymers has led to widespread environmental distribution of BPA. BPA is an endocrine disrupting compound which has an impact on the hormonal system (endocrine system) of humans and animals even at low concentrations. To tackle the problem of the micropollutants in the aquatic environment, efforts are being made to develop new adsorber materials with specific properties for extracting these various substances in one step with one membrane. For this reason cross-linked polymer nanoparticles were synthesized by miniemulsion polymerization and their adsorption properties were characterized. The properties of the polymer particles were adjusted for BPA by variation of the monomer, cross-linker and the stoichiometric ratio. Comparative adsorption tests were carried out with silica gel, commercial adsorber material (RP-C18), activated carbon, and the adjusted adsorber material P(4-VP-*co*-EGDMA). The advantage of the nanoscale, nonporous polymer particles compared with commercial adsorber material is the relatively large and rapidly accessible external surface. The adjusted adsorber material P(4-VP-*co*-EGDMA) and the activated carbon absorbed almost the complete quantity of BPA supplied. The advantage of the polymer adsorber material compared with activated carbon is the greater ease of regenerability. The BPA can be extracted from the polymer by means of ethanol or can be desorbed by means of a pH value shift. The adsorptive polymer particles were incorporated into a porous polymer matrix by an immersion phase separation process to build an affinity membrane. The production process for the membrane is controlled in such a way as to create an inner sponge-like structure in which the polymer nanoparticles are firmly embedded and nevertheless are easily accessible to the adsorbate. The sponge-like-structured membrane has the higher flux compared with a commercial UF membrane. The polymer particles were deposited in the pores of the sponge-like membrane structure during the membrane formation process and so are freely accessible to BPA. Tests were carried out in which the retained quantity of BPA of a commercially available UF membrane was compared with the retained quantity of BPA of a particle loaded membrane. This allows the construction of membranes for specific requirements in order to extract micropollutants ideally in one step with a functional membrane.

1. TRACE SUBSTANCES IN WATER

Today, possibly due to the increased population on earth and modern life, an increasing amount of possibly irritating substances are released into the aquatic environment.^{1–3} In numerous measurement campaigns, scientific studies, and in research work in recent years a variety of trace substances such as active pharmaceutical ingredients, industrial chemicals, and pesticides have been identified in European waters.^{4–8} Because of their levels of concentration, which are typically in the range ng L^{-1} to $\mu\text{g L}^{-1}$, these substances are called trace substances or also micropollutants. Various scientific studies have shown that these trace substances also have effects on organisms in the lower $\mu\text{g L}^{-1}$ and in some cases even in the ng L^{-1} range.^{6,9–12} For many years little attention was paid to these persistent substances, which are also to be found in treatment plant discharges.^{8,13–15} Nevertheless, the treatment plant discharges were identified at a very early stage as one of the main entry paths of trace substances into the environment.^{16,17} However, suitable analytical methods were not yet available to detect and identify the substances at these levels of concentration. With the progressive improvement in recent decades of analytical

methods for detecting such substances and their use for the analysis of wastewater, surface waters, and groundwater it became possible to detect a large number of compounds in the aquatic environment. These also include such problematical substances as for example precursor compounds of endocrine disrupting substances and also other substances with endocrine potential.¹⁸

Endocrine active substances, also called endocrine disruptors, have at the molecular level, as nonautogenic substances, an influence on the hormone-controlled processes in the living organism that are responsible for the reproduction and development of the organism as well as for maintaining the metabolism. In 1996 the European Commission formulated a definition of endocrine disruptors. This is: “An endocrine

Special Issue: Recent Advances in Nanotechnology-based Water Purification Methods

Received: December 12, 2012

Revised: May 16, 2013

Accepted: May 16, 2013

Published: May 16, 2013

disruptor is an exogenous substance, which in an intact organism or its offspring causes impairments to health as a result of a change of endocrine functions".¹⁹ The endocrine disruptors also include the substance class of bisphenols. The best known and worldwide most frequently used bisphenol is 2,2-bis(4-hydroxyphenyl)-propane known under the name bisphenol A.

In 2006 the annual world production of bisphenol A (BPA) amounted to approximately 3.2 million tons.^{20,21} Of the endocrine disruptors identified in the environment BPA captures the attention of numerous scientists and regulatory authorities because of its high global production and its widespread use in polycarbonates, epoxy resins, and many plastic products. Today BPA is to be found in many products of everyday use. For example in CDs and DVDs, in sales checks and tickets made of thermal paper, in epoxy resins that are used as coatings for metal food and drink cans and in polycarbonates, which are used as housings for computers, kettles, etc. How dangerous BPA really is for human health and the environment is at present still a controversial issue. According to a report of the Food and Drug Administration (FDA) from the year 2010,²² the National Toxicology Program expressed concerns regarding the effects of BPA on the brain, behavior, and prostate gland of fetuses, infants, and children. In 2008 BPA was banned in Canada for the manufacture of plastic baby bottles.²³ In July 2011 sales of baby bottles containing BPA were banned throughout the European Union.²⁴ According to Fu and Kawamura²⁵ the discovery of BPA in aerosol samples of urban, ocean, and polar regions indicates that this substance is a ubiquitous component of the atmosphere. BPA is released into the environment via wastewater, which largely comes from plants producing or processing BPA. Since the 1970s BPA has been detected in waters and alluvial sediments. For example, BPA was detected in U.S. American river water in concentrations of $0.14 \mu\text{g L}^{-1}$ to $12.0 \mu\text{g L}^{-1}$.²⁶ Together with the wastewater stream BPA reaches either the treatment plants of the industrial companies or the municipal sewage treatment plants. An investigation of various treatment plants in Germany revealed degradation rates of 61% to 98%.²⁷ If too little oxygen is in the treatment plants (anaerobic), either the BPA content is not reduced at all or only extremely slowly.^{6,28}

For the reasons described above we selected BPA as a model substance and target molecule for the development of nanostructured composite adsorber membranes.

2. NANOSTRUCTURED COMPOSITE ADSORBER MEMBRANES

By embedding polymer nanoparticles in a membrane selectivity can be generated and thus the adsorption capacity of the membranes can be increased. The production process for the membrane is controlled in such a way as to create an inner sponge-like structure in which the polymer nanoparticles are firmly embedded and nevertheless are easily accessible to the adsorbate. The structure of the membrane should be designed so that even at low transmembrane pressures (<2 bar) flux rates above those of ultrafiltration membranes are achieved. Thus the aim of the work at the IGVT and IGB is to develop membranes that achieve higher flux rates and have a better retention capacity for small molecules at pressures below the operating pressures of nano- and ultrafiltration membranes. Figure 1 shows a schematic representation of the inner structure of such a membrane.

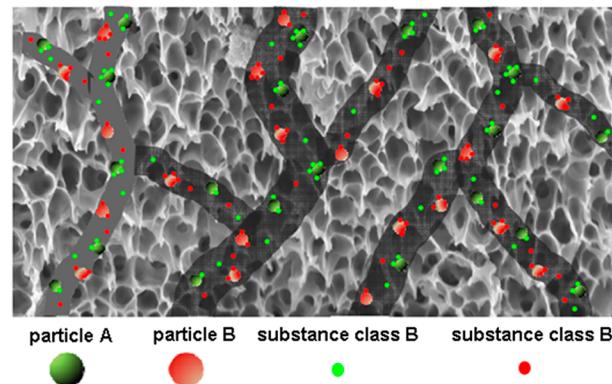


Figure 1. Schematic representation of the inner structure of composite adsorber membranes based on high affinity nanoparticles as the selecting material.

2.1. Production of the Polymer Adsorbers. Our particulate polymer adsorbers are produced by means of miniemulsion polymerization (MiniEP). Compared with conventional bulk syntheses the MiniEP offers for the production of polymer nanoparticles, the advantage being that in a single-stage synthesis polymer particles can be synthesized with a defined, spherical morphology. For the preparation of a miniemulsion, the system consisting of the monomers and hydrophobic agent (oil phase) as well as water with a surfactant (water phase), are subjected to a high shear. The shearing forces can be created by means of ultrasound or high-pressure homogenization in order to emulsify the oil phase in the water phase. Further advantages of the MiniEP are that, after the thermal or UV-initiated polymerization, a polymer dispersion with a very low surfactant content is obtained;²⁹ also, a wide range of comparatively inexpensive monomers are available on the market for polymer nanoparticle synthesis. Since the monomer droplets are converted almost one to one into polymer particles, the monomer droplets with a size of 50 to 500 nm result in polymer particles in the same size range. Figure 2 shows a schematic diagram of a MiniEP.

The monomers (mono-, bi- and trifunctional) used for the particle synthesis are selected on the basis of physical-chemical

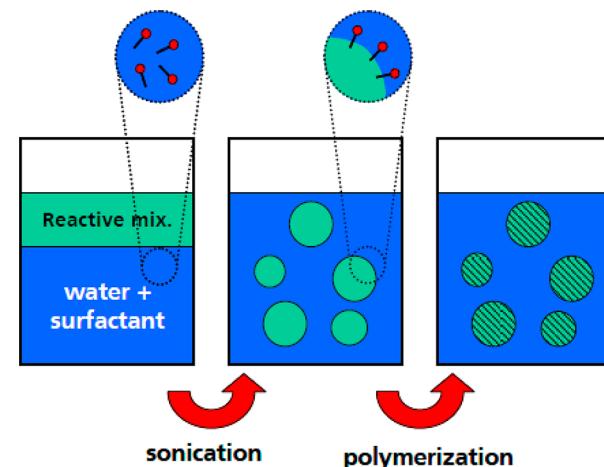


Figure 2. Schematic diagram of the miniemulsion polymerization: A reactive mix of polymerizable components is dispersed in water with the help of surfactants and by using high shear applied by, in this case, sonication and is polymerized to render polymer particles.

properties such as solubility, miscibility, and log P value as well as on the basis of possible noncovalent interactions with the target molecules. Ionic, hydrophobic, and $\pi-\pi$ -interactions with the target molecules are possible, resulting from the choice of monomers for the synthesis of the polymer particles in aqueous solutions.

The advantage of the nanoscale, nonporous polymer particles compared with commercial adsorber material or chromatography material is the relatively large and rapidly accessible external surface (between $35 \text{ m}^2 \text{ g}^{-1}$ and $100 \text{ m}^2 \text{ g}^{-1}$). Commercially available, porous adsorber or chromatography material in the particle size range between 3 and $300 \mu\text{m}$ does have a very large specific total surface area (between $150 \text{ m}^2 \text{ g}^{-1}$ and $1500 \text{ m}^2 \text{ g}^{-1}$); however, only about 1% to 5% of the surface of the material is directly accessible. This means that access to the inner surface is diffusion-limited and hence contact times of several minutes are necessary for the adsorbent substances to diffuse into the inner of the adsorber and thus to be adsorbed. Since the contact time with membrane filtration is only a matter of seconds, such materials are not suitable for embedding in the membranes as adsorber material. Also, the relatively large adsorber particles—compared with the membrane thickness (approximately $100 \mu\text{m}$)—would substantially decrease the mechanical stability of the membranes. Figure 3 shows a schematic representation of the various steps of an adsorption process for porous polymer particles and also for a composite adsorber membrane.

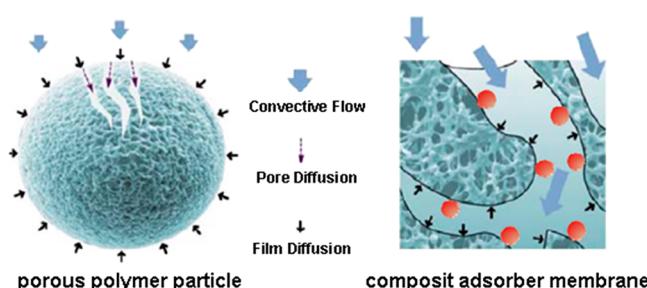


Figure 3. Schematic representation of adsorption to porous adsorbents (left) and nonporous adsorbents (right) that are embedded in a membrane matrix [modified according to ref 30].

Particle Syntheses. The particles were prepared by mixing of 3.099 g of ethylene glycol dimethacrylate (EGDMA) as cross-linker, 1.641 g of 4-vinylpyridine (4-VP), 0.225 g of hexadecane as hydrophobic agent (HD), and 90 mg of initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) as oil phase in a 50 mL glass reactor. An amount of 45 mL of water, containing 64.8 mg dissolved sodium dodecyl sulfate (SDS) was added to the oil phase. The two phases were dispersed by stirring for 30 min at room temperature followed by sonicating for 2 min (Branson Digital Sonifier, model 450-D, 60% power) to form the nanodroplets. The nanodroplets were transformed to solid spherical monoliths by photoinitiation in 2 h. The reaction was carried out in a UV reactor system (UV-RS-2, Heraeus Noblelight GmbH, Kleinostheim, Germany) that contained a medium pressure mercury-vapor lamp with a broad emission spectrum in the UV range above 190 nm. The polymer was purified of unreacted monomer and surfactant by different successive washing steps with water and acetonitrile.

2.2. Membrane Production. The membranes loaded with polymer adsorber particles are produced by means of (wet) phase inversion technology. The process of (wet) phase

inversion is also used for the industrial production of microfiltration, ultrafiltration, and dialysis membranes.³¹ In (wet) phase inversion a polymer solution is spread to form a thin layer on a glass slide and immersed in a water bath or precipitation bath (water serves as a nonsolvent). To embed the polymer particles in the membranes, the particles in the polymer solution are dispersed before spreading them on the glass slide.

The (wet) phase inversion technology is based on the phase separation of an originally homogeneous polymer solution by contact with a nonsolvent in liquid form; replacing solvents with nonsolvents results in phase separation. The polymer-lean phase forms the pores, while the polymer-rich phase creates the porous matrix. The pore structure resulting from phase separation is in most cases a liquid/solid separation. The originally thermodynamically stable system after immersion in the nonsolvent bath by the solvent/nonsolvent replacement is restored to a state in which the separation can be achieved in two phases by minimum changes of the Gibbs free energy.^{31,32} The appropriate kinetics of the separation depends on a very large number of parameters and has a very great influence on the final morphology of the membrane. The mathematical description of the complete process is therefore extremely difficult. The currently available models can only in exceptional cases approximately predict the resulting membrane structures. Thus optimum membrane structures are in practice primarily determined empirically by variation of the key influencing parameters.

The structure of membranes can be described as sponge-like or finger-like (cavities). Finger-like cavities are generally formed when the nonsolvent rapidly penetrates the polymer solution. In some cases the very large cavities can result in a lower mechanical stability of the membrane, consequently use at high pressure is limited.^{31,32} This is one of the reasons why we pursue the aim of producing membranes that have a sponge-like structure in order to guarantee the highest possible mechanical stability of the membrane. Also, the polymer particles in the sponge-like structure are more firmly embedded, easily accessible to the adsorbate and high flow rates can be achieved.

Polyether sulfone (PES) was chosen as the membrane matrix material (Figure 4). PES is a material that is very often used in

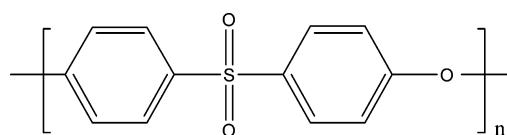


Figure 4. Chemical structure of the membrane matrix polymer: polyether sulfone.

the making of membranes. It is used primarily to produce micro- and ultrafiltration membranes.³¹ PES is characterized by its very good pH stability (pH 2 to pH 13) and chemical stability compared with chlorous solutions, alcohols, lyes and acids. This is especially important with regard to the cleaning of the membranes with the aim of removing fouling and scaling layers, which adds to the length of their useful life. Also, the membranes should be regenerable to ensure a multiple reuse of the membranes. Thus the substances adsorbed on the membrane matrix and the polymer particles have to be desorbable by means of solvent or pH shift. PES exhibits

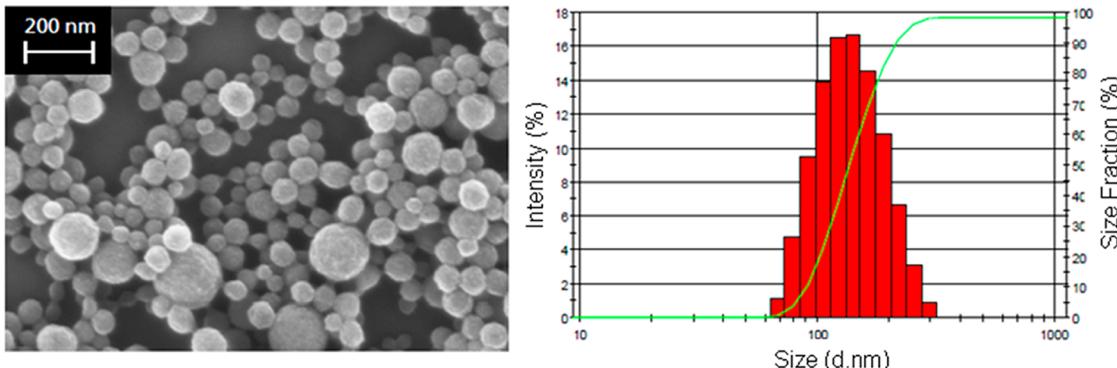


Figure 5. SEM image of poly-(4-vinylpyridine-co-ethylene glycol dimethacrylate) polymer adsorber particles (left) and their particle size distribution (right).

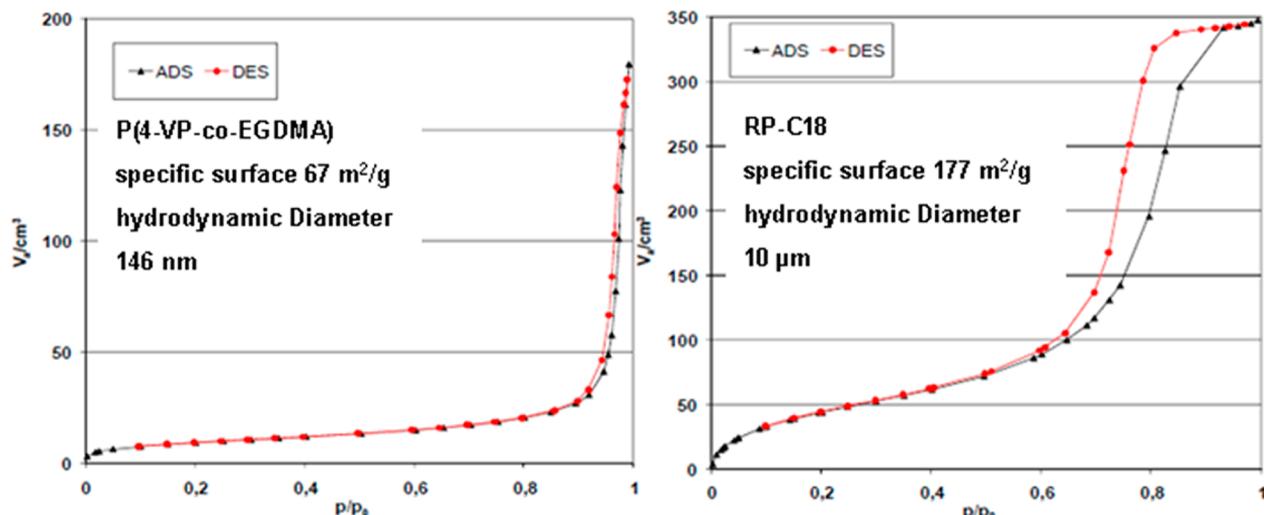


Figure 6. Adsorption and desorption isotherms of P(4-VP-co-EGDMA) polymer adsorber particles synthesized at the IGVT (left) and chromatography column material RP-C18 (right).

both good mechanical and good thermal stability ($T_g = 220^\circ\text{C}$).

Preparation of Particle-Loaded Membranes. All membranes were prepared by the wet phase inversion process. All membranes were prepared with a PES content of 16 wt % of the total mass of the casting solution without the adsorber particles. To prepare an anti-BPA membrane, 0.480 g of the P(4-VP-co-EGDMA) particles was added to 5.8 g of *N*-ethyl-2-pyrrolidone and dispersed by ultrasonication with a sonication bar for 10 min until a homogeneous dispersion is obtained. Then 3.2 g of polyethersulfone (Solvay—Veradel 3000P) and 11.0 g of polyethylene glycol (PEG 600) as pore forming agent were added to the dispersion. PES and PEG were dissolved in the dope solution by continuous stirring for 24 h at least. The resultant homogeneous polymer solution with the dispersed P(4-VP-co-EGDMA) particles was sonicated 15 min to remove air bubbles. The dope solution was poured onto a clean glass plate and it was cast on the glass plate using a casting knife with a height of 0.2 mm. Immediately after casting, the glass plate with the cast film was put into climate chamber at 25°C and 80% relative humidity for 5 min. Then the glass plate was transferred into a water bath containing distilled water. After a few minutes a thin polymeric film was peeled off the glass plate. The membrane was intensely washed with distilled water and stored in water until use. To prepare a reference membrane a

nonparticle loaded membrane was prepared with the same procedure as mentioned above without addition of particles.

3. PROOF OF CONCEPT—THE NANOSTRUCTURED COMPOSITE ADSORBER MEMBRANE

The following section describes some selected results of the tests in particle production and characterization, and also membrane production and membrane characterization.

3.1. Particle Characterization. After the synthesis of the particles these are purified in various washing steps and subsequently characterized. Here the particle size and the particle size distribution are determined by means of dynamic light scattering, the morphology of the particles by means of scanning electron microscopic (SEM) images, the specific surface by means of N_2 -gas adsorption measurements (Brunauer–Emmett–Teller BET method) and the adsorption behavior by balance adsorption tests. Some results of the particle characterization are summarized below. Figure 5 shows on the left-hand side an SEM image of poly-(4-vinylpyridine-co-ethylene glycol dimethacrylate) [P(4-VP-co-EGDMA)] particles; the particle size distribution of this polymer particle is on the right.

Figure 6 shows the adsorption and desorption isotherms of the N_2 gas adsorption measurements (BET method) of two different materials. On the left-hand side Figure 6 shows the

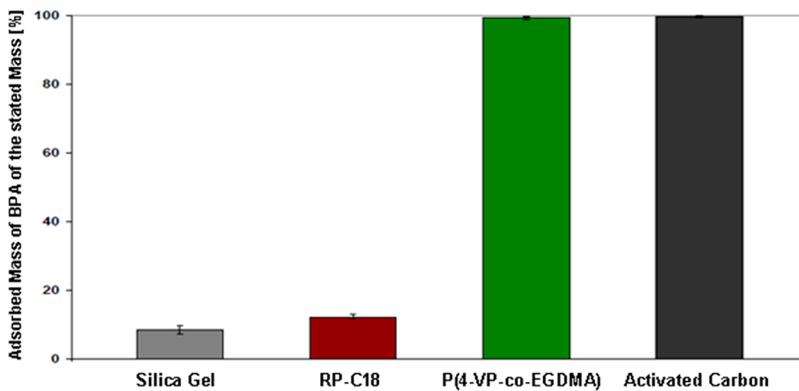


Figure 7. Results of the balance adsorption tests using four different materials with aqueous BPA solutions at a concentration of 150 ppm.

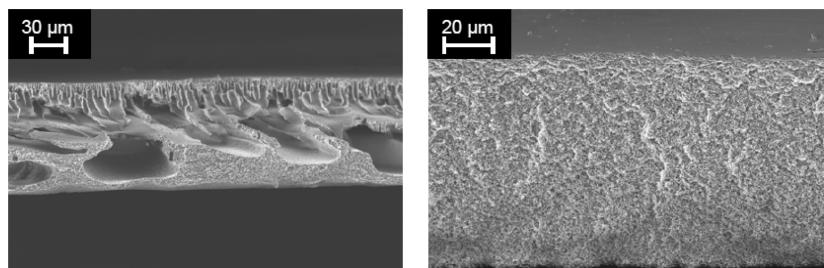


Figure 8. SEM images of the cross-section of two PES membranes. Additives were added to the polymer solution of the membrane shown on the right in order to obtain the sponge-like structure.

isotherms of one of our typical adsorber materials. It can be seen clearly that the adsorption and desorption isotherms of the polymer adsorber material produced by us, compared with the purchased chromatography column material RP-C18, does not exhibit any hysteresis. This indicates that the sample of our own production is a rather nonporous material.

After classification of the adsorption isotherms according to IUPAC the isotherm measured is assigned to type II (most frequent form of isotherm for nonporous materials). In contrast to this, the isotherm of the chromatography column material RP-C18 is an isotherm of type IV porous material, which is characterized by pronounced adsorption hystereses. This adsorption hysteresis comes about as a result of multilayer adsorption with subsequent capillary condensation in the mesopores or through the desorption of the adsorbate from the pores at a lower pressure than with capillary condensation.³³

Figure 7 represents the results of balance adsorption tests with four different adsorber or chromatography materials. The adsorption tests were carried out with silica gel, RP-C18, activated carbon, and adsorber material P(4-VP-co-EGDMA) produced by us. For these adsorption tests 10 mg of the adsorber materials was incubated for 2 h in a tempered thermomixer (10 °C). These tests were carried out with 1 mL of concentrated aqueous BPA solutions (150 ppm) in order to determine whether larger quantities of BPA can also be completely adsorbed by the various adsorber materials. It can be seen clearly that the polymer (green) and the activated carbon (dark gray) produced at the IGVT/IGB absorbed almost the complete quantity (>99%) of BPA supplied. The advantage of the polymer adsorber material compared with activated carbon is the greater ease of regenerability. The BPA can be extracted from the polymer by means of ethanol or can be desorbed by means of a pH value shift,^{34–36} what is currently being studied in our laboratories.

3.2. Membrane Characterization. After production the membranes are purified in various washing steps and subsequently characterized. Here the flux values are determined, the structure of the membrane is represented by means of SEM images and the adsorption behavior is determined on the basis of filtration tests. Additionally, rheological measurements are carried out with the polymer solutions in order to identify the connections between the composition of the polymer solution and the viscosity, as well as of the membrane structure and the viscosity. Subsequently, some results of the membrane characterization are described.

Figure 8 shows two SEM images representing the cross-section of two PES membranes. It can be seen clearly that the membrane shown on the left-hand side has a large number of big, finger-like pores. In contrast to this, the membrane on the right has a sponge structure throughout. The different structures come about because additives were added to the polymer solution of the membrane on the right. On the one hand these increase the viscosity of the polymer solution (see Table 1), which has a very considerable influence on the membrane formation process and thus on the structure of the membrane; and second the additives included a so-called pore-

Table 1. Viscosity of Polymer Solutions and Flux of Selected Membranes

	membrane with sponge-like structure	membrane with finger-pore structure	commercial UF membrane 10 KDa
viscosity polymer solution [Pa s]	5.25	0.279	
water flux at 1 bar [L h ⁻¹ m ⁻²]	484 ± 43	261 ± 26	194 ± 35

former that supports the creation of the sponge-like structure throughout.

Table 1 shows the flux values and viscosities of the polymer solutions of three different membranes. The sponge-like-structured membrane with $484 \text{ L h}^{-1} \text{ m}^{-2}$ clearly has the highest flux, followed by the membrane with the finger-like pore structure with $261 \text{ L h}^{-1} \text{ m}^{-2}$ and the commercial UF membrane (molecular weight cut off MWCO = 10 KDa), which has a water flux of $194 \text{ L h}^{-1} \text{ m}^{-2}$.

The higher water flux value of the membrane with the sponge-like structure probably comes about because this membrane has a somewhat more open-pored structure on the surface than the membrane with the finger-like pores and the UF membrane. This will be further verified by measurements of the size of the pores.

Figure 9 is an SEM image of the inner structure of a PES membrane in which polymer particles were embedded. This is

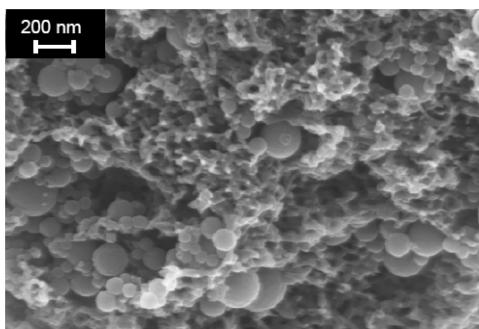


Figure 9. SEM image of the inner structure of a PES membrane with embedded polymer adsorber particles.

an SEM image of the inner structure of the membrane magnified 50 000 times. It can be seen clearly that the polymer particles were deposited in the pores of the sponge-like membrane structure during the membrane formation process and so are freely accessible to BPA.

For the filtration tests with the membranes, a filtration cell was used with a maximum volume of 50 mL and an inside diameter of 44 mm. Individual pieces of membrane with a diameter of 44 mm were punched out from the approximately DIN A4 sized membranes. The filtration tests were all conducted as dead-end filtration and with one bar transmembrane pressure. The results of the filtration tests were all achieved with membranes that had the finger-like membrane structure. No filtration tests have been carried out yet with the new membranes that have an exclusively sponge-like structure.

Figure 10 shows the results of a filtration test with a PES membrane (gray diamond shapes) without polymer particles and that of a PES membrane with embedded polymer adsorber particles (green triangles). In this test 40 mL of a BPA solution with a concentration of 200 ppb were pressed through the membrane with 1 bar. During the tests a sample of the permeate was taken every 2.5 mL and the BPA concentration of the permeate was measured by means of HPLC. It can be seen clearly that the PES membrane (gray diamond shapes) can hold back the BPA completely up to a permeate volume of 5 mL. Subsequently the concentration of BPA in the permeate increases sharply. In contrast to this, the membrane in which polymer particles (green triangles) are embedded was able to hold back the BPA completely up to a permeate volume of 35 mL.

If the total mass of BPA contained in the solution and the mass of BPA that was held back by the various membranes are calculated, in the case of the PES membrane without polymer particles (gray diamond shapes) 77.1% retention of the total BPA mass is achieved and with the membrane in which polymer adsorber particles (green triangles) were embedded the result is 99.6% retention. In addition, tests were carried out in which the retained quantity of BPA of a commercially available UF membrane (MWCO = 10KDa) was compared with the retained quantity of BPA of a membrane made at the IGBT (Figure 11). For this purpose 50 mL of a BPA solution with a concentration of 1 ppm was filtered through the membrane and the residual concentration of BPA in the permeate was measured. The UF membrane was able to hold

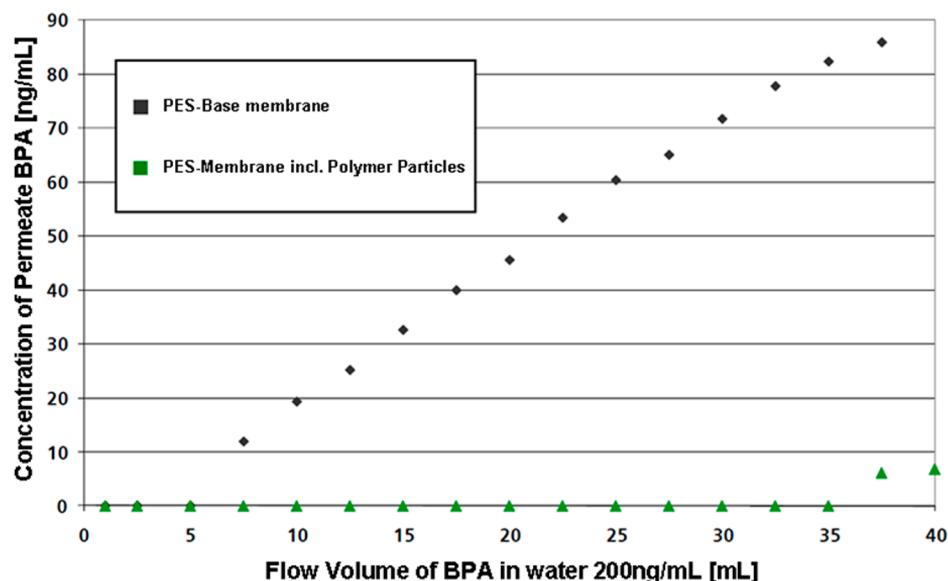


Figure 10. Concentration profile of the permeate of a BPA solution with a concentration of 200 ppb filtered with a PES membrane without polymer particles (gray diamond shapes) and a PES membrane with polymer particles (green triangles).

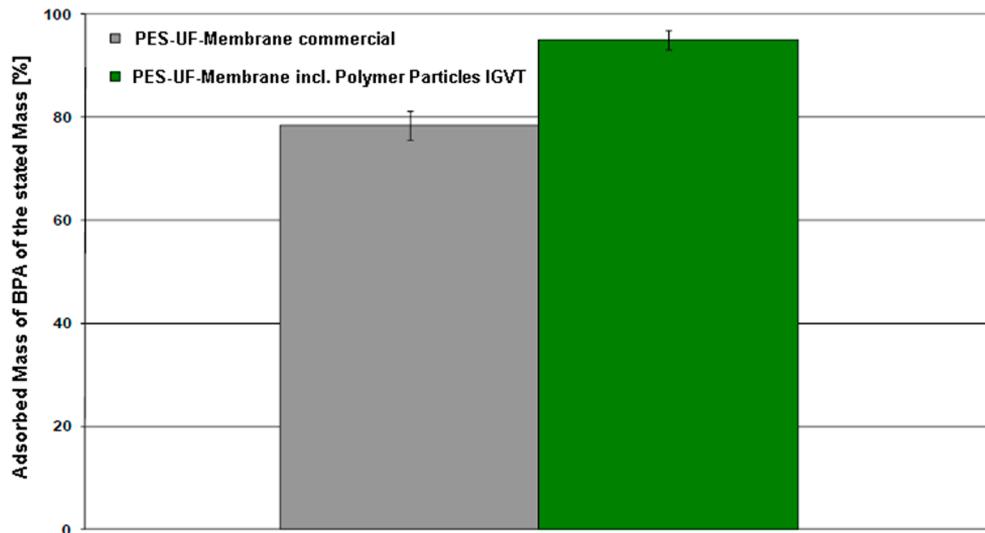


Figure 11. Comparison of the retained mass of BPA of a commercially available UF membrane (MWCO = 10KDa) and of a PES membrane made at the IGBT with embedded polymer adsorber particles.

back a maximum of 78.5% BPA of the total mass supplied (50 µg BPA). This nanostructured composite adsorber membrane retained 95.1% of the BPA contained in the solution; thus we conclude that the concept works.

4. OUTLOOK

The structure of the composite adsorber membrane may still be optimized; as well, further functional polymer adsorbents may be synthesized, for example, for other drug classes. The concept to embed functional particles in solid membranes is open for further innovation by combining different polymer particles in the same membrane and thus engineer individual membranes for specific tasks.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported under the Seventh Framework Programme of the European Community (2007–2013) (WaterMIM; project number 226524) with the project title “Water Treatment by Molecularly Imprinted Materials”.

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