Oil/Water Separation

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Rapid and Efficient Separation of Oil from Oil-in-Water Emulsions Using a Janus Cotton Fabric

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Abstract: *A novel bi-functional Janus cotton fabric is used to separate oil from oil-in-water emulsions. This fabric is superhydrophobic on one surface and polyamine-bearing on the other. When used as a filter, the polyamine-bearing side causes the micrometer-sized oil droplets to coalesce. The coalesced oil then fills fabric pores on the superhydrophobic side and selectively permeates it. Oil separation using this method is rapid and the separated oil is pure. Furthermore, the content of the model oil hexadecane (HD) in water after a separation can be reduced to less than 0.03 ± 0.03 vol%. These features demonstrate the practical potential of this technology.*

The separation of oil from emulsions is industrially important.[1–3] For example, the mixture extracted with hot steam from oil sands during oil production in Alberta of Canada is an emulsion.[4,5] To separate oil, some current methods involve adding chemicals to destabilize an emulsion and then separating the coalesced oil by sedimentation or centrifugation.[4] However, these methods are costly and tedious. We report herein oil separation from oil-in-water emulsions by filtration using a Janus cotton fabric that is coated on one side by a polyamine and on the other side by a hydrophobic polymer. Oil separation using this method does not require chemical additives and is rapid and efficient.

The separation was rapid because we used fabrics that have pores with side lengths reaching 200 μm. Pores that were larger than the emulsified droplets could be used because the polyamine-bearing side of the fabric destabilized emulsions and caused the micrometer-sized oil droplets to coalesce. The coalesced oil then readily filled the fabric pores on the superhydrophobic side. We further propose that the impregnating oil not only blocks water permeation but also serves as sites for additional oil deposition and also as the reservoirs fueling selective oil transport through the superhydrophobic side. The separation was clean because water has a low solubility in oil and bulk water could not enter the oil-filled fabric pores on the superhydrophobic side.

Although there have been no reports on oil and water separation by filtration using Janus fabrics, superhydrophobic/oleophilic or superoleophobic/hydrophilic filters consisting of surface-treated fabrics and metal meshes have been used for this purpose.[1–3] These filters are particularly effective in separating simple emulsions that are created by shearing oil/water mixtures without a surfactant. In such a simple emulsion, droplets of the minority phase readily coalesce and do so particularly facilely on fabrics and meshes that act as nucleation sites for coalescing.[6] Because of droplet aggregation, the coalesced oil phase of an oil-in-water emulsion, for example, readily fills the pores of the superhydrophobic filters and the oil plugs produced then reject water entrance but allow selective oil permeation.[7–10] In the case of a superoleophobic/hydrophilic filter, water fills the pores of the filter and the water plugs produced block oil entrance but allow selective water permeation.[11–13]

However, traditional large-pore filters cannot be used to separate oil or water from an emulsion stabilized by a surfactant. Surfactant-stabilized droplets normally have diameters less than ten micrometers[14] and do not readily coalesce. Imagine the filtration of an oil-in-water emulsion by a superhydrophobic fabric that has pores sized at hundreds of micrometers. Since the emulsified oil droplets do not coalesce, they cannot plug the fabric pores. Rather, they would be rejected together with their surrounding water by the filter.

To separate components of an emulsion, the pore sizes of the filters need to be comparable with or smaller than those of the emulsified droplets. Under these conditions, the filling of the pores would not require droplet fusion but only slight droplet deformation. Thus, polymer membranes with pore diameters smaller than several micrometers have been used for this task.[14–18] To use metal meshes, their pore sizes of tens of micrometers had to be first reduced. This was achieved via the deposition of a surface-active polymer onto the mesh wires[19] or via the growth of inorganic nanostructures from them.[11] However, the separation rate of a filter is proportional to the cross-sectional area of the pores and decreasing the pore sizes decreases the separation rate of the filter.[1–3,18]

We hypothesized that we could separate emulsified oil at large filter pore sizes with a novel Janus fabric that coalesced emulsified oil droplets on one side and provided selective oil permeation on the other side. To test our hypothesis, we grafted poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA) and poly(dimethylsiloxane) (PDMS) onto the opposite faces of a cotton fabric. PDMAEMA was selected because it could ionize in water and coalesce emulsion droplets by screening the electrostatic repulsion.[20] PDMS was used because of its low surface tension[21] ($20\,\mathrm{mN\,m^{-1}}$) and its ability to render cotton fabrics superhydrophobic.[22,23]

To prepare Janus cotton fabrics, past methods have invoked coating fabrics on one side by the deposition of a highly viscous non-permeating polymer solution[24] or by the

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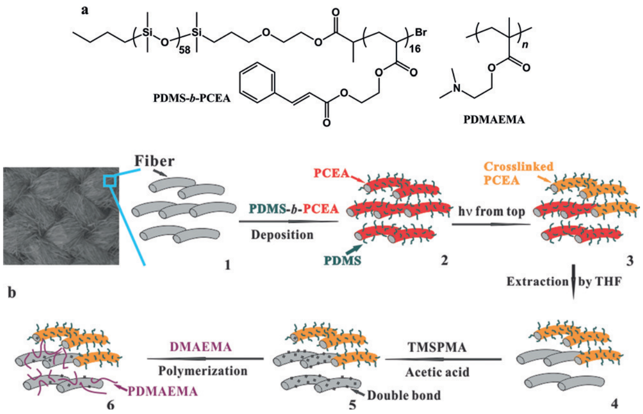
polymerization of monomer droplets that were selectively aero-sprayed onto one side of a fabric.[25] In another method,[26,27] fabric fibers were initially coated by TiO_2 and other reagents to render the whole fabric superhydrophobic. Photolyzing only one face of the coated fabric turned the TiO_2 coating on that side hydrophilic.

To prepare our bifunctional Janus fabric, all fibers of the fabric were first coated with a brush layer of a diblock copolymer PDMS-*b*-PCEA (Structure 1, Scheme 1a), where PCEA denotes poly(2-cinnamoyloxyethyl acrylate).[22] In this brush layer, PCEA preferentially coated the individual cotton fibers and PDMS chains were exposed to air (1→2, Scheme 1b). To crosslink the PCEA layer on only one side of the fabric,[28,29] we irradiated one side of a coated fabric and optimized the exposure time (2→3, Scheme 1b). In the third step, the irradiated fabric was extracted in hot THF to remove the PDMS-*b*-PCEA that was not sufficiently crosslinked (3→4). This treatment yielded fabric with a hydrophobic gradient that decreased from being superhydrophobic on the irradiated side to water absorbing on the non-irradiated side. Subsequently, we grafted propyl methacrylate groups onto the fibers on the hydrophilic side using the sol–gel chemistry of trimethoxysilyl propyl methacrylate (TMSPMA) catalyzed by acetic acid (4→5, Scheme 1b).[30] To graft the PDMAEMA chains, the modified fabric was then immersed into a DMAEMA solution in THF containing the initiator azobisisobutyronitrile. The free radical copolymerization of the propyl methacrylate double bonds on the fiber surfaces with DMAEMA yielded grafted PDMAEMA chains (5→6, Scheme 1b).

In practice, a plain-weave fabric with side lengths reaching 200 μm for the inter-thread pores (Figure 1a) was used. To graft PDMS, we used a PDMS-*b*-PCEA sample that consisted of 58 DMS units and 16 CEA units (Supporting Information).[22] To produce a Janus fabric, we irradiated a PDMS-*b*-PCEA-coated fabric on one side for 5 min and then extracted uncrosslinked polymer with hot THF. The amount of polymer retained at this stage was determined in two ways, first by monitoring the weight gain with a microbalance (4.8 ± 1.3 wt%), and second, by thermogravimetric analysis (TGA) (5.1 ± 4.7 wt%). While the two numbers agreed with each other within experimental error, the TGA result had a large error because a small error in the determined residual mass of a sample at 600 °C propagated to a large error in the final calculated grafted polymer amount (see the Supporting Information). To confirm the Janus property of the fabric, we dispensed dyed water on the irradiated and non-irradiated sides. Whereas water beaded up on the irradiated side of the fabric (Figure 1b), it readily wetted the non-irradiated side (Figure 1c).



Scheme 1. a) Chemical structures for PDMS-*b*-PCEA and PDMAEMA. b) Representation of events occurring on the surfaces of a short section of seven fibers in a fabric thread during Janus fabric preparation. We note the PCEA crosslinking density on the fibers should decrease gradually from the top to the bottom of a thread, and the abrupt decrease shown in (b) is an exaggeration.

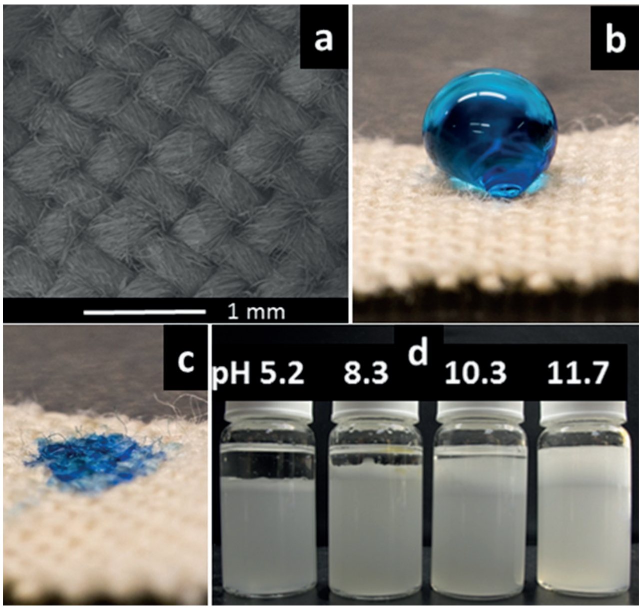


Figure 1. a) SEM image of the cotton fabric used. b) Photograph of a dyed water droplet placed on the PDMS-coated side of a Janus fabric after PDMS-*b*-PCEA coating, photolysis, and extraction with hot THF (stage 4 in Scheme 1b). c) Photograph of the former Janus fabric after the dispensing of a dyed water droplet onto the other side bearing cellulose fibers. d) Photograph of vials containing HD emulsion at $v/v = 2/8$ 1.0 h after the addition of a piece of PDMAEMA-bearing fabric (1.5×1.5 cm^2) to each vial. The fabrics were equilibrated with water at pH 5.2, 8.3, 10.3, or 11.7 before they were rinsed, dried, and added into the vials.

Going through steps 4→6 of Scheme 1b allowed us to graft PDMAEMA onto the fabric. The success of the grafting step was confirmed by an IR spectroscopic analysis (Supporting Information). We discovered that the amount of grafted PDMAEMA increased as the monomer concentration in the solution of polymerizing DMAEMA increased (Supporting Information). However, our optimization experiments demonstrated that high grafted PDMAEMA amounts adversely affected oil/water separation (Supporting Information, Figure S7). Thus, all results other than those reported in Figure S7 were obtained using fabrics that were treated under the optimized conditions and had the grafted PDMAEMA mass fraction of 0.9 ± 0.3 wt% and 0.8 ± 0.1 wt% as determined by TGA and a microbalance, respectively.

Further visual evidence supporting PDMAEMA grafting was the pH dependence of the de-emulsification capability of PDMAEMA-bearing fabrics. In such an experiment, pristine cotton fabric swatches, at 1.5×1.5 cm^2 each, were grafted with PDMAEMA by going through steps 4→6 of Scheme 1b under the standard conditions. The fabrics were then equilibrated with dilute HCl or NaOH solutions that had final solution pH values of 5.2, 8.3, 10.3, and 11.7, respectively. These swatches were subsequently rinsed in THF/water at $v/v=5/5$, dried under vacuum, and inserted into vials that each contained 20.0 mL of a HD-in-water emulsion at a hexadecane (HD) volume fraction f_H of 20% (the preparation is described in the Supporting Information). Figure 1d shows a photograph taken of the vials 60 min after the addition of a fabric into each vial. The extent of the phase separation or de-emulsification decreased as the fabric equilibration pH increased. We infer that this behavior must be due to the grafted PDMAEMA chains whose degree of protonation decreased as the fabric treatment pH increased.

The Janus fabric samples thus prepared under the optimized conditions remained superhydrophobic on the PDMS-coated side with a high water contact angle (153 ± 2)°. Thus, the fabric could be used to separate various simple oil/water mixtures by filtration regardless if the PDMS- or PDMAEMA-coated side faced the feed mixture. The fabric orientation was inconsequential in this case because the PDMAEMA-coated side had no selectivity. When it faced a simple mixture, both HD and water permeated it and only HD then permeated the PDMS-coated side. When the PDMS-coated side faced the feed, only HD entered the fabric pores and permeated the fabric.

Interestingly, the Janus fabric separated oil from oil-in-water emulsions only if the PDMAEMA-coated side faced the feed emulsions. The fabric orientation was important in these cases because no liquid permeated the fabric when the PDMS-coated side faced a feed emulsion. The PDMS-coated side rejected emulsion including the HD droplets because the HD droplets were small at 3.7 ± 0.6 μm (Supporting Information) and were too stable to coalesce. Our assumption is that only aggregates that had sizes larger than or comparable with the pore sizes would readily fill up the pores surrounded by the PDMS-coated fibers.

To separate an HD-in-water emulsion at $f_H=20\%$, two H-shaped devices were used. Figure 2a shows a photograph of the larger H-shaped device used and a photograph of the smaller device is featured in the Supporting Information, Figure S1. The two half cells of each device were connected via two perforated rubber disks and were held in place with a clamp. Sandwiched between the perforated disks was a bifunctional fabric. To start an experiment, either 10.0 or 40.0 mL of the emulsion was poured into the left cell of the smaller or larger device that was magnetically stirred. While the emulsion shown in Figure 2a was cloudy as expected, it exhibited a reddish tint because the HD phase was doped with a hydrophobic red dye, Oil Red O. Figure 2b shows the system status 300 s after the emulsion was added to the left cell. A clear red liquid permeated the fabric that was pretreated at pH 11.7 and was collected in the right cell. Moreover, the residual mixture in the left cell had lost most of its reddish tint. These observations suggest the selective permeation of HD. Our ^{1}H NMR analysis confirmed that the permeated liquid was HD that was free of detectable water.

Figure 2c plots data collected using the smaller H-shaped device. The volume of HD collected in the right cell increased with time after 10.0 mL of the emulsion was added to the left half cell. The three sets of data were obtained using fabric swatches that had been previously equilibrated in water at the pH values of 5.2, 10.3, and 11.7, respectively. The oil separation rate was constant within experimental error or increased slightly as the fabric treatment pH increased. These trends differed from that shown in Figure 1d, where the de-emulsification ability of the fabric samples decreased as the fabric treatment pH increased. This discrepancy could be rationalized by the fact that HD separation involved more than just de-emulsification but at least three steps, which included the diffusion of the HD droplets to the vicinity of the PDMAEMA chains, the coalescence of the HD droplets, and the transportation of the coalesced HD phase through the fabric with a hydrophobicity gradient. Thus, increasing the de-emulsification rate alone did not necessarily increase HD permeation rate. Rather, the increased number of charged DMAEMA units at lower fabric treatment pH values could have inhibited HD transportation through the asymmetric fabric.[31]

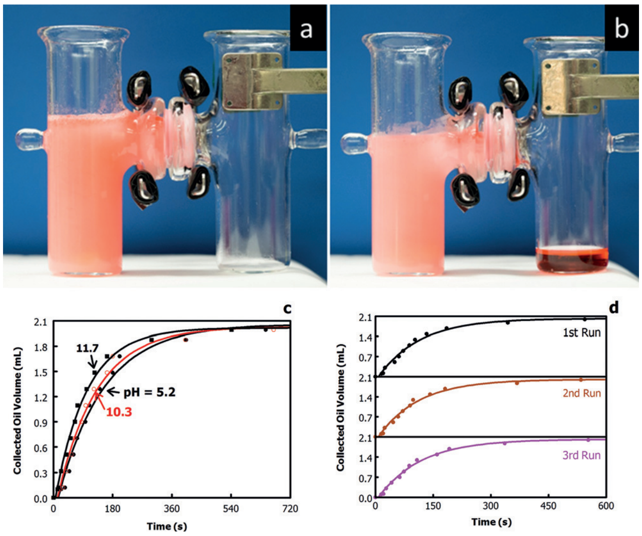


Figure 2. Photographs showing the status of a separation experiment at a) time $t=0$ and b) $t=300$ s after 40.0 mL of a HD emulsion at $f_H=20\%$ was added into the left cell of the larger H-shaped device. c) Increases in the volume of HD collected in the right cell after 10.0 mL of a HD emulsion at $f_H=20\%$ was added into the left cell of the smaller H-shaped device. The pH values denote those of aqueous solutions in which the fabric samples were equilibrated before they were cleaned, dried, and used. d) Data for three consecutive experiments showing increases with time in the volume of HD collected in the right cell of the smaller device.

Using the slope of a straight line constructed from the initial three points of the permeation data of Figure 2c we obtained a permeation rate of 0.021 mL s^{-1} for the pH 11.7 fabric. This rate together with the permeation area of 0.50 cm^2 yielded a high flux of 1.5×10^3 L m^{-2} h^{-1}. Another important feature of the data of Figure 2c was that the final collected HD volume approached the theoretical value of 2.0 mL in each trial. Thus, the separation was efficient.

Figure 2d shows data for three consecutive separations that were performed using the same fabric. In each case, reagents from a previous trial were removed before another 10.0 mL of emulsion was added to the feed side of the cell.

The consecutive use of the fabric did not change the oil permeation kinetics or the final collected oil volume, which was 2.0 mL. This conclusion was further confirmed by comparing the fitting parameters generated from treating the different sets of experimental data (Supporting Information).

For the separation of HD at $f_H = 1.0\,\%$, a 500 mL three-neck round-bottomed flask with one mouth covered by an asymmetric fabric was used (Supporting Information). Starting with 300 mL of an emulsion, the separated HD amount reached 2.1 g by 1.5 h and 2.2 g by 15 h. The latter mass translated into a HD volume of 2.9 mL, which was very close to or the same as 3.0 mL that was in the original emulsion. Thus, by the end of the separation, no more than 0.1 ± 0.1 mL of HD was present in 297 mL of water. Thus, the separation limit of this technique should be below 0.03 ± 0.03 vol % of HD, and the separation was thus highly efficient.

We have also separated HD from HD-in-water emulsions at $f_H = 10\,\%$ and $30\,\%$. Furthermore, we separated oil from oil-in-water emulsions with the oil being toluene and chlorobenzene, and the data are presented in the Supporting Information, Figures S8 and S9. To investigate the effect of varying applied pressure on the rate of chlorobenzene separation from a chlorobenzene-in-water emulsion at 20 vol % chlorobenzene, a vertically-placed burette with its bottom end covered by a Janus fabric was used. We then poured 5.0, 8.0, and 10.0 mL of the emulsion into the burette to yield the initial liquid column heights of 5.4, 8.7, and 10.9 cm, respectively. These heights corresponded to the hydrostatic pressures of $0.54\times$, $0.88\times$, and 1.10×10^3 Pa on the filter. Under these pressures, we obtained the initial chlorobenzene permeation rates of $3.5\times$, $5.3\times$, and 10.5×10^3 L m^{-2} h^{-1}, respectively, for the fabric (Supporting Information). While the first permeation rate was already impressively high, the rate increased rapidly as the applied pressure increased.

In conclusion, we have developed a novel method to prepare a Janus cotton fabric. The prepared PDMS- and PDMAEMA-bearing Janus fabrics functioned as filters to separate oil from various simple oil/water mixtures as well as oil from various oil-in-water emulsions. The oil separation flux was high and the separation was efficient. If their fabrication can be simplified, future generation of these bi-functional fabrics may find practical applications.

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