

Accepted Manuscript

Title: Fouling control of a membrane coupled photo catalytic process treating greywater

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PII: S0043-1354(09)00347-9

DOI: [10.1016/j.watres.2009.05.030](https://doi.org/10.1016/j.watres.2009.05.030)

Reference: WR 7449

To appear in: *Water Research*

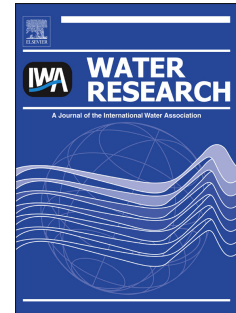
Received Date: 27 February 2009

Revised Date: 18 May 2009

Accepted Date: 21 May 2009

Please cite this article as: Pidou, M., Parsons, S.A., Raymond, G., Jeffrey, P., Stephenson, T., Jefferson, B. Fouling control of a membrane coupled photo catalytic process treating greywater, *Water Research* (2009), doi: [10.1016/j.watres.2009.05.030](https://doi.org/10.1016/j.watres.2009.05.030)

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1 Fouling control of a membrane coupled photo catalytic process treating greywater

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10

11 Abstract

12 Fouling in membrane coupled photocatalytic reactors was investigated in the case of grey water treatment by
13 establishing the link between product type, dose, irradiation time and fouling rates in a cross flow membrane cell
14 fitted with a 0.4 micron pore sized polyethylene membrane. Rapid fouling occurred only with shower gels and
15 conditioners and was linked to changes in the organo-TiO₂ aggregate size postulated to be caused by polymers
16 within the products. Fouling was reduced to a negligible level when sufficient irradiation was applied
17 demonstrating that the membrane component of the process is not the issue and that scale up and implementation
18 of the process relates to effective design of the UV reactor.

19

20 *Keywords:* greywater, photo catalysis, titanium dioxide, fouling

21

22 INTRODUCTION

23 A wide range of new engineered nanoparticles are becoming available for use in water and
24 wastewater treatment (Jefferson, 2008). Recent examples include nano silver coatings on
25 socks to inhibit microbial growth and hence odour (Ross, 2004) and zero valent iron nano
26 particles for groundwater remediation (Huang *et al.*, 2008; Ahmadimoghaddam *et al.*, 2008).
27 Whilst research is continuing into developing new nanoparticles actual uptake of the existing
28 ones is rather limited in water treatment (Jefferson, 2008). The problem is a classical chemical

29 engineering one: how to implement (scale up) a nano scale process at the meso or macro scale
30 (Wintermantel, 1999). For context, water treatment facilities vary greatly but typically treat
31 flows in the order of 10s to 100s of ML.d⁻¹. Converted to nano particles, which are typically
32 in the size range 1-100 nm this equates to 7.2×10^{26} particles and thus there is a challenge. The
33 nano particles provide very large specific surface areas with which to provide high mass
34 transfer and reaction kinetic coefficients yet fixing such a large number of very small particles
35 so that they remain in the treatment process and do not exit with the product water is
36 extremely challenging. Typical energy and operating costs for water treatment are in the order
37 of 0.5 kWh.m^{-3} and $\text{€}0.2\text{-}0.5.\text{m}^{-3}$ which means solutions can not be overly complicated or
38 complex. Reported solutions to the problem involve either immobilisation to solid substrate
39 (Rachel et al, 2002) or retention by filtration with membranes (Rivero *et al.*, 2006; Chin et al,
40 2007).

41 One embodiment of this concept is the membrane chemical reactor (MCR) (Parsons et al,
42 2000; Jefferson et al, 2001) which utilises nano sized titanium dioxide (TiO₂) particles in
43 combination with a UV light source to generate highly reactive hydroxyl radicals which have
44 a redox potential of 2.33 V, only surpassed by F₂ (Huang *et al.*, 1993). The TiO₂ particles are
45 retained in the system by means of a membrane filtration unit that is configured externally to
46 the membrane but operated in an air lift, low pressure manner equivalent to that of a
47 submerged membrane system (LeClech *et al.*, 2003). Long term trials for the treatment of grey
48 water have shown it to be an effective system comparable to that of a membrane bioreactor
49 (Pidou *et al.*, 2008). For instance, average effluent residuals of below 10 mg.L^{-1} for bio-
50 chemical oxygen demand (BOD), below 1 NTU for turbidity, below 2 mg.L^{-1} for suspended
51 solids (SS) and no pathogens were observed throughout the trial at a hydraulic residence time
52 of 2 hours (Pidou *et al.*, 2008). The observed residual levels mean that the technology is
53 viable for treating greywater to the most stringent water quality standards available for urban

54 reuse (Pidou *et al.*, 2007). Consequently, it provides an alternative to biological systems such
55 as membrane bioreactors (MBRs) where the small scale of operation, proximity to the end
56 users and the potential for toxic shocks provides a relatively high process failure risk
57 (Jefferson *et al.*, 1999; Knops *et al.*, 2007). Similar high performance of photocatalytic
58 systems have been reported for the treatment of dyes (Molinari *et al.*, 2002; Mozia *et al.*,
59 2007), humic acid (Lee *et al.*, 2001; Fu *et al.*, 2006; Erdei *et al.*, 2008), bisphenol A
60 (Thiruvengkatachari *et al.*, 2005; Chin *et al.*, 2007) or pesticides (Oller *et al.*, 2006; Lhomme *et*
61 *al.*, 2008) hence the appropriateness of the technology as a treatment solution is well
62 established.

63 However, during the greywater investigation significant membrane fouling was observed.
64 Consequently, the system could only be run for about 10 days at a flux of $5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (LMH)
65 before a chemical cleaning of the membrane was necessary (Pidou *et al.*, 2008). This was
66 found to be contradictory to results of a previous study in which the MCR pilot plant was
67 operated in batch mode (Rivero *et al.*, 2006). Very little or no fouling was observed during
68 the batch experiments for fluxes up to $120 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. Such differences in operation are
69 surprising but the results obtained during the batch operation tests can be explained by the
70 fact that the greywater was rapidly treated and consequently for the higher fluxes the TiO_2
71 was dispersed in fairly clean water and very little or no fouling was observed. This suggests
72 that the fouling propensity of TiO_2 changes significantly in the presence of a waste, in this
73 case greywater.

74 A paucity of literature on operation of such photocatalytic hybrid membrane systems,
75 especially for medium to high strength organic wastes, potentially limits the uptake of the
76 technology to full scale operation. Specifically two key questions remain unanswered: (1)
77 how to develop systems that can treat sensible flows whilst ensuring all the TiO_2 in the system

78 is active and hence degrades the organics and (2) how to ensure the membranes does not foul
79 in systems that answer question 1.

80 The current paper addresses question 2 by examining the impact of different grey water
81 products on the fouling behaviour of the system elucidating the major changes in the system
82 when fouling occurs.

83

84 **MATERIALS AND METHODS**

85 *Filtration system*

86 A bench-scale filtration system was used to replicate the fouling experienced when operating
87 the membrane chemical reactor (MC-RTM) (Water Innovate Limited, UK). Trials were
88 conducted to study the influence of different parameters on titanium dioxide (TiO₂) and its
89 properties to foul membranes. This system was composed of a 9-litre PVC tank in which the
90 TiO₂ and greywater slurry was placed. The slurry was pumped across the membrane module
91 (Perspex, 28 cm × 20 cm × 8 cm) and back to the reactor at a crossflow velocity of 0.16 m.s⁻¹.
92 The treated water was permeated through the membrane by a peristaltic pump (505Du,
93 Watson-Marlow, UK) and a pressure transducer (RS components, UK) was fitted in the
94 permeate line to record the trans-membrane pressure (TMP). Because it was a batch system,
95 the permeate was sent back into the tank to avoid any volume loss. The membranes used in
96 the module were polyethylene sheets with a pore size of 0.4 μm and a surface area of 0.019
97 m².

98

99 *Methods*

100 A range of products (all bought in a supermarket) including shower gel, shampoo, bathroom
101 cleaner, conditioner, hand soap and bubble bath were diluted in tap water at a concentration of
102 2 or 3 g.L⁻¹ and placed in the reactor with 5 g.L⁻¹ of TiO₂. These concentrations were chosen

103 because they represent the upper range for organic concentrations reported in the literature in
104 terms of COD in feed grey waters from sampled sites around the world (Pidou *et al.*, 2007).
105 The COD concentration of the products were measured prior to use at 360, 280, 280, 250, 190
106 mg.L⁻¹ for the shower gel, conditioner, bubble bath, shampoo and hand soap respectively.
107 Indeed, concentrations of products of 3 g.L⁻¹ corresponded to solutions with COD
108 concentrations between 570 and 890 mg.L⁻¹. The TiO₂ dose was selected from previous trials
109 which demonstrated it be the optimum concentration for grey water treatment (Rivero *et al.*,
110 2006). Ingredients of each of the products as listed in provided in Table 1. Tests using the flux
111 step method generally used to characterise membrane fouling in MBRs (Le Clech *et al.*, 2003)
112 were then carried out and the fouling rates determined for the different slurries. Fouling
113 experiments were conducted under dark light conditions to best replicate practical system
114 where the membrane is configured such that it is not in direct contact with the UV light to
115 prevent damage to the membrane structure (Rivero *et al.*, 2006). All tests were duplicated. For
116 the photo-catalysis tests, the slurry was placed in a stirred tank under a 100W UVA lamp
117 (Black-Ray, CA, USA) for a range of time ranging between 0.5 and 2 hours.

118

119 *Analytical procedures*

120 Particle sizes were measured with a Malvern Mastersizer 2000 particle analyser (Malvern
121 Instruments Ltd, Worcestershire, UK). It was not possible to measure the particle size with
122 the TiO₂ concentration of 5 g.L⁻¹ as the detection cell saturated because of too many particles.
123 Consequently, the TiO₂ concentration had to be decreased to 1 g.L⁻¹. Product concentrations
124 were reduced commensurately to maintain a dose ratio between 400-600 mg.gTiO₂⁻¹ to match
125 experiments in the fouling trials. Five measurements of each sample were performed and the
126 average value of the median particle size d₅₀ (µm) was taken.

127 **RESULTS**

128 Cross flow filtration of organo-TiO₂ slurries containing bathroom cleaner, shampoo, hand
129 soap or bubble bath dosed at a level of 600 mg.gTiO₂⁻¹ resulted in insignificant fouling across
130 the range of fluxes studied with a maximum fouling rate of 0.6 mbar.min⁻¹ (Figure 1) and was
131 not significantly different from the TiO₂ system in tap water only. Consequently, the flux
132 required to generate rapid fouling of such systems exceeded the maximum value tested in the
133 laboratory set up and supports the previous finding that TiO₂ systems can be operated at
134 fluxes around 100 LMH without fouling problems (Rivero *et al.*, 2006). In contrast, cross flow
135 filtration of shower gel, conditioner or real greywater samples results in significant fouling
136 (Figure 1). To illustrate maximum fouling rates of 6.6 mbar.min⁻¹ at a flux of 35 LMH and 8.9
137 mbar.min⁻¹ at a flux of 28 LMH were observed for the conditioner and shower gel
138 respectively. In comparison, a real greywater collected from the bathrooms of a student hall of
139 residence revealed a fouling propensity in between those observed for the individual products.
140 This is consistent with the fact that the greywater would be made up of a mix of these
141 products. Consequently, the fouling behaviour of organo-TiO₂ mixtures appears to be related
142 to the character of the organics bound to the TiO₂ surfaces. Comparison between the current
143 system and more traditional hybrid membrane reactor processes such as MBRs suggests that
144 the MCR setup is potentially not bound to the same limitations as MBRs as it potentially can
145 operate at significantly higher fluxes (Pollice *et al.*, 2005; Le Clech *et al.*, 2003 and 2005). To
146 illustrate, an example set of data is included in Figure 1 with the fouling profile for an MBR
147 treating greywater. At fluxes below 25 LMH the fouling rate remains low at 0.6 mbar.min⁻¹
148 whereas beyond this limit the fouling rate increase dramatically reaching a maximum
149 measured value of 8.1 mbar.min⁻¹ at a flux of 35 LMH (Figure 1). Based on an operational
150 description, the critical flux is defined as the crossover between these phases (Brookes *et al.*,
151 2006) and in the current case is defined as 22 LMH which indicates an upper limit for
152 operational practice. Comparison with literature values reveals a similar range for both critical

153 flux (6-32 LMH) and fouling rate (0.1-10 mbar.min⁻¹) for operational MBR systems (Pollice
154 *et al.*, 2005; Le Clech *et al.*, 2003 and 2005) confirming the potential differences between
155 MCR and MBRs.

156 More detailed analysis of the link between the character of organo-TiO₂ mixtures and fouling
157 revealed the dose ratio to be significant (Figure 2) with reduced fouling as the organic content
158 within the TiO₂ matrix decreased. To illustrate, in the case of shower gel as the organic
159 source, fouling rates of 8.9, 3.8, 1.6 and 0.2 mbar.min⁻¹ were observed at a flux of 28 LMH
160 for dose ratios of 600, 400, 200 and 100 mg.gTiO₂ (Figure 2a). A similar situation was
161 observed in the case of systems based on conditioner mixtures where the fouling rate
162 observed at a flux of 30 LMH was 1.8, 0.9, 0.1 for dose ratios of 600, 400 and 200 mg.gTiO₂
163 indicating that fouling can be controlled in the system by limiting the concentration of certain
164 types of organics in the system (Figure 2b). Examples of previously reported investigations of
165 membrane couple photocatalytic processes have focussed on dilute systems with slurry
166 concentrations of <1 g.L⁻¹ and low organic feeds resulting in dose ratios of 10mg_{dye}.g⁻¹ for
167 methylene blue dye (Sopajaree *et al.*, 1999), 48mg_{TOC}.g⁻¹ for fulvic acid (Fu *et al.*, 2006)
168 compared to 114-178 mg_{COD}.g⁻¹ investigated here at TiO₂ doses of 5 g.L⁻¹. In dilute
169 conditions, reaction rates have been seen to increase as slurry concentration increases (and
170 dose ratio decreases) as an impact of enhanced mass transfer of the catalyst to the lamp
171 although fouling is also seen to increase as slurry dose increases (Sopajaree *et al.*, 1999).

172 Comparison between different commercially available shower gels revealed only the original
173 choice of product resulted in the extreme fouling pattern (Figure 3). For instance, fouling rates
174 remained low and stable at a rate between 0.1 and 0.4 mbar.min⁻¹ up to fluxes of 70 LMH for
175 four alternative brands of shower gels. All five products are commonly available and range
176 from leading brands to unbranded and environmentally labelled versions. Identification of
177 specific chemicals associated to the observed results is difficult as exact product contents are

178 not available. However comparison of the ingredient lists suggests that the major differences
179 observed are associated with the inclusion of a polymer (Palmeth 25 Acrylate copolymer) in
180 the shower gel.

181 Analysis of the size of the TiO₂ in the system revealed that in the absence of organics the
182 TiO₂ aggregates had a median floc size of 15,000 nm and a maximum size of 120,000 nm
183 (Figure 4) which equate to 300-2400 NP diameters demonstrating the significant role
184 aggregation plays in the system. Analysis of the organo-TiO₂ complexes revealed a
185 significant difference with the median size altered to 290,000 nm for a non fouling component
186 and to 1,102,000 nm (22,040 NP diameters) in the case of the shower gel that caused rapid
187 fouling. The mixed greywater from the student flats produced a median floc size between the
188 extremes of 130,000 nm which are much larger than previous reported sizing of organo-TiO₂
189 aggregates at around a median size of 1-3000 nm (Ollis, 2003; Choo et al, 2008).
190 Consequently, addition of organics did not significantly alter the size of the aggregating
191 system apart from specific products which could generate over a 7000% increase in the
192 aggregate size. This observation is compatible with the inclusion of polymers in general as
193 they principally act as aggregating chemicals (Henderson et al, 2009). Comparison with
194 fouling rate data revealed a power law relationship of the form $dP/dt = \alpha d_{50}^{\beta}$ with exponents
195 of $\alpha = 0.019$ and $\beta = 0.83$ at a flux of 30 LMH and $\alpha = 0.061$ and $\beta = 0.27$ at a flux of 15
196 LMH indicating the importance of aggregate size on fouling in the system.

197 Fouling rates of the high fouling systems were reduced to a level similar to those observed for
198 the other systems after irradiation under UV light for 16 hours, a time period previously
199 observed to ensure complete irradiation. Similar results were observed for all three organo-
200 TiO₂ complexes that caused fouling (Figure 5). For instances, fouling rates at 30 LMH
201 decreased from previous levels of 0.3, 1.9 and 1.3 for the shampoo, conditioner and mixed
202 greywater systems to between 0.02-0.13 mbar.min⁻¹ after irradiation. Further, fouling rates did

203 not increase up to the maximum flux tested in the set up of 70 LMH (Figure 5a) confirming
204 the previous findings of Rivero *et al* (2006) indicating the importance of effective treatment in
205 the UV stage of the process if stable operation is to be achieved. More detailed analysis in the
206 case of the shower gel system revealed a reduction in fouling rate as irradiation time was
207 increased from 30 minutes to 120 minutes suggesting that a minimum amount of irradiation is
208 required to treat the audit of TiO₂ surface within the system. To illustrate, fouling rates of
209 10.9, 4.7, 0.9 and 0.7 mbar.min⁻¹ were observed at a flux rate of 50 LMH after irradiation for
210 30, 45, 90 and 120 minutes respectively (Figure 5b). Significant fouling reduction has also
211 been observed in a photocatalytic hybrid membrane reactor treating humic acids where a 120
212 minute reaction time resulted in flux recover to more than 80% of the clean water flux (Fang
213 et al, 2005). The results suggest that in the set up investigated in the current study a minimum
214 UV residence time of 120 minutes in the CSTR tank is required to reduce fouling to
215 acceptable levels. A key question for the future relates to understanding how much organic
216 material must be removed from the TiO₂ surface to reduce fouling. Circumstantially it would
217 appear that almost complete removal of the organics is necessary due to the relationship
218 between irradiation time and fouling. Ultimately, successful reactor design will need to be based
219 on an understanding of this issue to deliver the most economic technology possible.

220 **DISCUSSION**

221 The work presented in the current study demonstrates one of the barriers to implementation of
222 hybrid membrane processes utilising photo catalysis, namely, the potential for rapid fouling
223 due to undesirable changes to the aggregates of nano TiO₂ when combined with specific
224 chemicals. In the current case this appears to be related to the presence of polymers within
225 some greywater products which greatly enhance the aggregation process forming very large
226 organo-TiO₂ aggregates that reduce the operating flux achievable within the system.

227 The exact reason for the impact of aggregate size on fouling are not currently clear but are
228 likely to reflect one or a combination of possible effects. Larger aggregates are more likely to
229 break when exposed to an elevated energy dissipation field (Jarvis et al, 2005) such as in the
230 reactor or the membrane tank and hence the much larger aggregates formed with the shower
231 gel are likely to generate significant quantities of fines which can clog the membrane pores
232 (Jefferson *et al*, 2004). The larger aggregates are also less likely to receive uniform UV
233 exposure over the whole organo-TiO₂ surface increasing the risk that only a proportion of the
234 TiO₂ is photo catalysed and hence not effectively treated. At the slurry concentrations under
235 investigation here (5g.L⁻¹) modelled light intensity patterns suggest that illumination occurs
236 only very close to the lamp (Pareek et al, 2003) such that only TiO₂ surfaces that effectively
237 contact the lamp will be treated. In fact illuminations effectively drops off once the catalyst
238 loadings reaches 0.1 g.L⁻¹.

239 In the case of horizontal configured membranes, such as the cross flow test membrane
240 systems used here, another factor needs to be considered in terms of the inertial lift generated
241 by the cross flow velocity that prevents cake build up and hence critical flux. In the current
242 case inertial lift theory suggests that all but the shower gel aggregates would lift at velocities
243 considerably below the one used. However, in the case of the shower gel tests the inertial lift
244 velocity is 0.154 m.s⁻¹ which is around the actual velocity the test cell was operated at. Visual
245 inspection during the experiments confirmed this although it is an outcome of supra critical
246 flux operation rather than a direct cause. As stated earlier the original fouling problem was
247 observed during long term trials with a continuously operating unit with the membrane
248 vertically orientated which suggests that cake layer build up through insufficient inertial lift is
249 unlikely to be the sole reason but could definitely be responsible for some of the observed
250 fouling in the current case.

251 CONCLUSIONS

252 Ultimately, whatever the mechanism of fouling, management of the organo-TiO₂ aggregates
253 is crucial for effective operation of such technologies. Given that sufficient irradiation of the
254 organo-TiO₂ complex resolved the fouling problems in the current study suggests that the key
255 to uptake of the technology is in effective design of the UV reactor systems rather than
256 improvements in the membrane. The challenge becomes how to ensure enough of the TiO₂
257 surface reacts with the UV light. Transmittance in such systems is generally very low and
258 hence TiO₂ particles must contact the lamp to ensure treatment. This becomes difficult when
259 considering large aggregates of sizes in the ranges observed here as they will contain
260 thousands of individual TiO₂ particles. However, if nanotechnology solutions like the
261 membrane photocatalytic systems are implemented for large scale water treatment in the
262 future solutions will need to be generated. Current systems are more suitable to small scale
263 applications such as urban reuse of industrial water treatment where flow requirements are
264 more manageable.

265

266 **ACKNOWLEDGEMENTS**

267 This work forms part of the ‘Water Cycle Management for New Developments’ (WaND)
268 project funded under the Engineering & Physical Science Research Council’s ‘Sustainable
269 Urban Environment’ Programme by EPSRC, UK government and industrial collaborators
270 [www.wand.uk.net]. Permission from Water Innovate Ltd, UK, to use the MC-R™
271 technology is acknowledged.

272

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Product	Ingredients as listed
Shampoo	Cocamidopropyl Betaine, DMDM hydantoin, Citric Acid, Tetrasodium EDTA, Polysorbate 20, Panthenol, Parfum, Isopropyl Palmitate, Hexylene Glycol, Ammonium Laureth Sulfate, Ammonium Lauryl Sulfate, Ammonium Chloride, Hydroxypropyltrimonium, Hydrolysed wheat Protein, Tocophenyl Acetate, Triamine HCl, Ascorbic Acid, Sodium Cocoyl Isethionate, Sodium Laurophoacetate, Sodium Methyl Cocoyl Taurate, Dimethicone Bisamo, Hydroxypropyl Copolyol, Quaternium 80, Polyquaternium 7, PEG 18 glyceryloleate/cocoate, Sodium xylene Sulfonate, Magnesium Chloride, Magnesium Nitrate, Propylene glycol, Triethanolamine, PEG 60 hydrogenated castor oil, Methylchloroisothiazolinone, Methylisothiazolinone
Bubble bath	Cocamidopropyl Betaine, Sodium Chloride, Sodium Sulfate, Citric Acid, Tetrasodium EDTA, Parfum, Glycerin, Benzophenone 4, Iodopropynyl Butylcarbonate, CI 74160, Cocamide DEA, Methylidibromo Glutaronitrile, Phenoxyethanol, Hexylene Glycol, CI 16035, CI 19140
Hand soap	Sodium C12-C13 pareth sulfate, Cocamidopropyl Betaine, Sodium Chloride, Lauryl Polyglucose, Sodium Sulfate, DMDM hydantoin, Citric Acid, Tetrasodium EDTA, CI 17200, CI 42090, Parfum
Conditioner	DMDM hydantoin, Citric Acid, Tetrasodium EDTA, Cyclopentaxyloxane, Stearamidopropyl diethylamine, Cethyl Alcohol, Quaternium 18 Stearyl alcohol, PEG-2M, Cethearyl Alcohol, Polysorbate 60, Benzyl Alcohol, Panthenyl Ethyl Ether, Panthenol, Dimethicone, Hydroxyethylcellulose, Glyceryl Stereate, Oleyl Alcohol, Parfum
Shower gel 1	Sodium C12-C13 pareth sulfate, Cocamidopropyl Betaine, Sodium Sulfate, DMDM hydantoin, Tetrasodium EDTA, Parfum, Acrylates, Palmeth 25 Acrylate copolymere, Glycerin, Isopropyl Palmitate, Benzophenone 4, Iodopropynyl Butylcarbonate, CI 74160, Methylchloroisothiazolinone, Methylisothiazolinone, Decyl glucoside, Formic acid, Lactic acid, Sodium hydroxide, Limonene, Benzyl Salicylate
Shower gel 2	Cocamidopropyl Betaine, Sodium Chloride, Sodium Sulfate, Citric Acid, Tetrasodium EDTA, CI 42090, Polysorbate 20, Parfum, Polyquaternium 7, Propylene glycol, Sodium hydroxide, Formaldehyde, Sodium benzoate, Ethoxydiglycol, Sorbic acid, Chamomilla Recutita, Hamamelis Virginiana, Humulus Lupulus, Methylparaben, Rosmarinus Officinalis, Thymus Vulgaris, Propylparaben, CI 47005
Shower gel 3	Sodium Chloride, Sodium Sulfate, Citric Acid, Tetrasodium EDTA, CI 42090, Parfum, Glycerin, Methylidibromo Glutaronitrile, Phenoxyethanol, Hexylene Glycol, Sodium benzoate, Lauramidopropyl Betaine, PEG-7 Glyceril Cocoate, Disodium Lauramido MEA-Sulfosuccinate, Guar Hydroxypropyltrimonium Chloride, Sodium citrate, Disodium phosphate, CI 19140

Figure 1: Fouling rates for different products (3 g.L⁻¹).

Figure 2: Influence of the concentration of (a) shower gel and (b) conditioner on fouling rates.

Figure 3: Fouling rates for different shower gels (2 g.L⁻¹).

Figure 4: Particle size distribution of the TiO₂ flocs in different solutions

Figure 5: Influence of UV illumination on fouling rates.

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