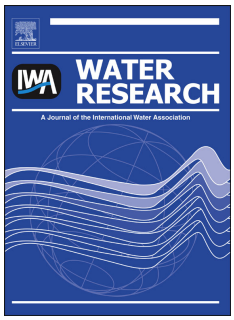
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# Fouling control of a membrane coupled photo catalytic process treating greywater

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**Abstract**

Fouling in membrane coupled photocatalytic reactors was investigated in the case of grey water treatment by establishing the link between product type, dose, irradiation time and fouling rates in a cross flow membrane cell fitted with a 0.4 micron pore sized polyethylene membrane. Rapid fouling occurred only with shower gels and conditioners and was linked to changes in the organo-$TiO_2$ aggregate size postulated to be caused by polymers within the products. Fouling was reduced to a negligible level when sufficient irradiation was applied demonstrating that the membrane component of the process is not the issue and that scale up and implementation of the process relates to effective design of the UV reactor.

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

## INTRODUCTION

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

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engineering one: how to implement (scale up) a nano scale process at the meso or macro scale (Wintermantel, 1999). For context, water treatment facilities vary greatly but typically treat flows in the order of 10s to 100s of $ML.d^{-1}$. Converted to nano particles, which are typically in the size range 1-100 nm this equates to $7.2x10^{26}$ particles and thus there is a challenge. The nano particles provide very large specific surface areas with which to provide high mass transfer and reaction kinetic coefficients yet fixing such a large number of very small particles so that they remain in the treatment process and do not exit with the product water is extremely challenging. Typical energy and operating costs for water treatment are in the order of 0.5 $kWh.m^{-3}$ and €0.2-0.5.$m^{-3}$ which means solutions can not be overly complicated or complex. Reported solutions to the problem involve either immobilisation to solid substrate (Rachel et al, 2002) or retention by filtration with membranes (Rivero *et al.*, 2006; Chin et al, 2007).

One embodiment of this concept is the membrane chemical reactor (MCR) (Parsons et al, 2000; Jefferson et al, 2001) which utilises nano sized titanium dioxide ($TiO_2$) particles in combination with a UV light source to generate highly reactive hydroxyl radicals which have a redox potential of 2.33 V, only surpassed by $F_2$ (Huang *et al*, 1993). The $TiO_2$ particles are retained in the system by means of a membrane filtration unit that is configured externally to the membrane but operated in an air lift, low pressure manner equivalent to that of a submerged membrane system (LeClech *et al*, 2003). Long term trials for the treatment of grey water have shown it to be an effective system comparable to that of a membrane bioreactor (Pidou *et al.*, 2008). For instance, average effluent residuals of below 10 $mg.L^{-1}$ for bio-chemical oxygen demand (BOD), below 1 NTU for turbidity, below 2 $mg.L^{-1}$ for suspended solids (SS) and no pathogens were observed throughout the trial at a hydraulic residence time of 2 hours (Pidou *et al.*, 2008). The observed residual levels mean that the technology is viable for treating greywater to the most stringent water quality standards available for urban

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

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

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

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

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

## MATERIALS AND METHODS

### *Filtration system*

A bench-scale filtration system was used to replicate the fouling experienced when operating the membrane chemical reactor (MC-R$^{TM}$) (Water Innovate Limited, UK). Trials were conducted to study the influence of different parameters on titanium dioxide ($TiO_2$) and its properties to foul membranes. This system was composed of a 9-litre PVC tank in which the $TiO_2$ and greywater slurry was placed. The slurry was pumped across the membrane module (Perspex, 28 cm × 20 cm × 8 cm) and back to the reactor at a crossflow velocity of 0.16 $m.s^{-1}$. The treated water was permeated through the membrane by a peristaltic pump (505Du, Watson-Marlow, UK) and a pressure transducer (RS components, UK) was fitted in the permeate line to record the trans-membrane pressure (TMP). Because it was a batch system, the permeate was sent back into the tank to avoid any volume loss. The membranes used in the module were polyethylene sheets with a pore size of 0.4 µm and a surface area of 0.019 $m^2$.

### *Methods*

A range of products (all bought in a supermarket) including shower gel, shampoo, bathroom cleaner, conditioner, hand soap and bubble bath were diluted in tap water at a concentration of 2 or 3 $g.L^{-1}$ and placed in the reactor with 5 $g.L^{-1}$ of $TiO_2$. These concentrations were chosen

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because they represent the upper range for organic concentrations reported in the literature in terms of COD in feed grey waters from sampled sites around the world (Pidou *et al.*, 2007). The COD concentration of the products were measured prior to use at 360, 280, 280, 250, 190 $mg.L^{-1}$ for the shower gel, conditioner, bubble bath, shampoo and hand soap respectively. Indeed, concentrations of products of 3 $g.L^{-1}$ corresponded to solutions with COD concentrations between 570 and 890 $mg.L^{-1}$. The $TiO_2$ dose was selected from previous trials which demonstrated it be the optimum concentration for grey water treatment (Rivero *et al.*, 2006). Ingredients of each of the products as listed in provided in Table 1. Tests using the flux step method generally used to characterise membrane fouling in MBRs (Le Clech *et al.*, 2003) were then carried out and the fouling rates determined for the different slurries. Fouling experiments were conducted under dark light conditions to best replicate practical system where the membrane is configured such that it is not in direct contact with the UV light to prevent damage to the membrane structure (Rivero *et al.*, 2006). All tests were duplicated. For the photo-catalysis tests, the slurry was placed in a stirred tank under a 100W UVA lamp (Black-Ray, CA, USA) for a range of time ranging between 0.5 and 2 hours.

***Analytical procedures***

Particle sizes were measured with a Malvern Mastersizer 2000 particle analyser (Malvern Instruments Ltd, Worcestershire, UK). It was not possible to measure the particle size with the $TiO_2$ concentration of 5 $g.L^{-1}$ as the detection cell saturated because of too many particles. Consequently, the $TiO_2$ concentration had to be decreased to 1 $g.L^{-1}$. Product concentrations were reduced commensurately to maintain a dose ratio between 400-600 $mg.gTiO_2^{-1}$ to match experiments in the fouling trials. Five measurements of each sample were performed and the average value of the median particle size $d_{50}$ (µm) was taken.

**RESULTS**

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Cross flow filtration of organo-$TiO_2$ slurries containing bathroom cleaner, shampoo, hand soap or bubble bath dosed at a level of 600 mg.g$TiO_2^{-1}$ resulted in insignificant fouling across the range of fluxes studied with a maximum fouling rate of 0.6 mbar.min$^{-1}$ (Figure 1) and was not significantly different from the $TiO_2$ system in tap water only. Consequently, the flux required to generate rapid fouling of such systems exceeded the maximum value tested in the laboratory set up and supports the previous finding that $TiO_2$ systems can be operated at fluxes around 100 LMH without fouling problems (Rivero *et al*, 2006). In contrast, cross flow filtration of shower gel, conditioner or real greywater samples results in significant fouling (Figure 1). To illustrate maximum fouling rates of 6.6 mbar.min$^{-1}$ at a flux of 35 LMH and 8.9 mbar.min$^{-1}$ at a flux of 28 LMH were observed for the conditioner and shower gel respectively. In comparison, a real greywater collected from the bathrooms of a student hall of residence revealed a fouling propensity in between those observed for the individual products. This is consistent with the fact that the greywater would be made up of a mix of these products. Consequently, the fouling behaviour of oragno-$TiO_2$ mixtures appears to be related to the character of the organics bound to the $TiO_2$ surfaces. Comparison between the current system and more traditional hybrid membrane reactor processes such as MBRs suggests that the MCR setup is potentially not bound to the same limitations as MBRs as it potentially can operate at significantly higher fluxes (Pollice *et al.*, 2005; Le Clech *et al.*, 2003 and 2005). To illustrate, an example set of data is included in Figure 1 with the fouling profile for an MBR treating greywater. At fluxes below 25 LMH the fouling rate remains low at 0.6 mbar.min$^{-1}$ whereas beyond this limit the fouling rate increase dramatically reaching a maximum measured value of 8.1 mbar.min$^{-1}$ at a flux of 35 LMH (Figure 1). Based on an operational description, the critical flux is defined as the crossover between these phases (Brookes et al, 2006) and in the current case is defined as 22 LMH which indicates an upper limit for operational practice. Comparison with literature values reveals a similar range for both critical

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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-$TiO_2$ mixtures and fouling
157 revealed the dose ratio to be significant (Figure 2) with reduced fouling as the organic content
158 within the $TiO_2$ 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.g$TiO_2$ (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.g$TiO_2$
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 $TiO_2$ 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

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

Analysis of the size of the $TiO_2$ in the system revealed that in the absence of organics the $TiO_2$ aggregates had a median floc size of 15,000 nm and a maximum size of 120,000 nm (Figure 4) which equate to 300-2400 NP diameters demonstrating the significant role aggregation plays in the system. Analysis of the organo-$TiO_2$ complexes revealed a significant difference with the median size altered to 290,000 nm for a non fouling component and to 1,102,000 nm (22,040 NP diameters) in the case of the shower gel that caused rapid fouling. The mixed greywater from the student flats produced a median floc size between the extremes of 130,000 nm which are much larger than previous reported sizing of organo-$TiO_2$ aggregates at around a median size of 1-3000 nm (Ollis, 2003; Choo et al, 2008). Consequently, addition of organics did not significantly alter the size of the aggregating system apart from specific products which could generate over a 7000% increase in the aggregate size. This observation is compatible with the inclusion of polymers in general as they principally act as aggregating chemicals (Henderson et al, 2009). Comparison with fouling rate data revealed a power law relationship of the form $dP/dt = \alpha d_{50}^{\beta}$ with exponents 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 LMH indicating the importance of aggregate size on fouling in the system.

Fouling rates of the high fouling systems were reduced to a level similar to those observed for the other systems after irradiation under UV light for 16 hours, a time period previously observed to ensure complete irradiation. Similar results were observed for all three organo-$TiO_2$ complexes that caused fouling (Figure 5). For instances, fouling rates at 30 LMH decreased from previous levels of 0.3, 1.9 and 1.3 for the shampoo, conditioner and mixed greywater systems to between 0.02-0.13 $mbar.min^{-1}$ after irradiation. Further, fouling rates did

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not increase up to the maximum flux tested in the set up of 70 LMH (Figure 5a) confirming the previous findings of Rivero *et al* (2006) indicating the importance of effective treatment in the UV stage of the process if stable operation is to be achieved. More detailed analysis in the case of the shower gel system revealed a reduction in fouling rate as irradiation time was increased from 30 minutes to 120 minutes suggesting that a minimum amount of irradiation is required to treat the audit of $TiO_2$ surface within the system. To illustrate, fouling rates of 10.9, 4.7, 0.9 and 0.7 $mbar.min^{-1}$ were observed at a flux rate of 50 LMH after irradiation for 30, 45, 90 and 120 minutes respectively (Figure 5b). Significant fouling reduction has also been observed in a photocatalytic hybrid membrane reactor treating humic acids where a 120 minute reaction time resulted in flux recover to more than 80% of the clean water flux (Fang et al, 2005). The results suggest that in the set up investigated in the current study a minimum UV residence time of 120 minutes in the CSTR tank is required to reduce fouling to acceptable levels. A key question for the future relates to understanding how much organic material must be removed from the $TiO_2$ surface to reduce fouling. Circumstantially it would appear that almost complete removal of the organics is necessary due to the relationship between irradiation time and fouling. Ultimately, successful reactor design will need to based on an understanding of this issue to deliver the most economic technology possible.

## DISCUSSION

The work presented in the current study demonstrates one of the barriers to implementation of hybrid membrane processes utilising photo catalysis, namely, the potential for rapid fouling due to undesirable changes to the aggregates of nano $TiO_2$ when combined with specific chemicals. In the current case this appears to be related to the presence of polymers within some greywater products which greatly enhance the aggregation process forming very large organo-$TiO_2$ aggregates that reduce the operating flux achievable within the system.

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The exact reason for the impact of aggregate size on fouling are not currently clear but are likely to reflect one or a combination of possible effects. Larger aggregates are more likely to break when exposed to an elevated energy dissipation field (Jarvis et al, 2005) such as in the reactor or the membrane tank and hence the much larger aggregates formed with the shower gel are likely to generate significant quantities of fines which can clog the membrane pores (Jefferson *et al*, 2004). The larger aggregates are also less likely to receive uniform UV exposure over the whole organo-$TiO_2$ surface increasing the risk that only a proportion of the $TiO_2$ is photo catalysed and hence not effectively treated. At the slurry concentrations under investigation here ($5g.L^{-1}$) modelled light intensity patterns suggest that illumination occurs only very close to the lamp (Pareek et al, 2003) such that only $TiO_2$ surfaces that effectively contact the lamp will be treated. In fact illuminations effectively drops off once the catalyst loadings reaches $0.1\ g.L^{-1}$.

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

## CONCLUSIONS

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Ultimately, whatever the mechanism of fouling, management of the organo-$TiO_2$ aggregates is crucial for effective operation of such technologies. Given that sufficient irradiation of the organo-$TiO_2$ complex resolved the fouling problems in the current study suggests that the key to uptake of the technology is in effective design of the UV reactor systems rather than improvements in the membrane. The challenge becomes how to ensure enough of the $TIO_2$ surface reacts with the UV light. Transmittance in such systems is generally very low and hence $TiO_2$ particles must contact the lamp to ensure treatment. This becomes difficult when considering large aggregates of sizes in the ranges observed here as they will contain thousands of individual $TiO_2$ particles. However, if nanotechnology solutions like the membrane photocatalytic systems are be implemented for large scale water treatment in the future solutions will need to be generated. Current systems are more suitable to small scale applications such as urban reuse of industrial water treatment where flow requirements are more manageable.

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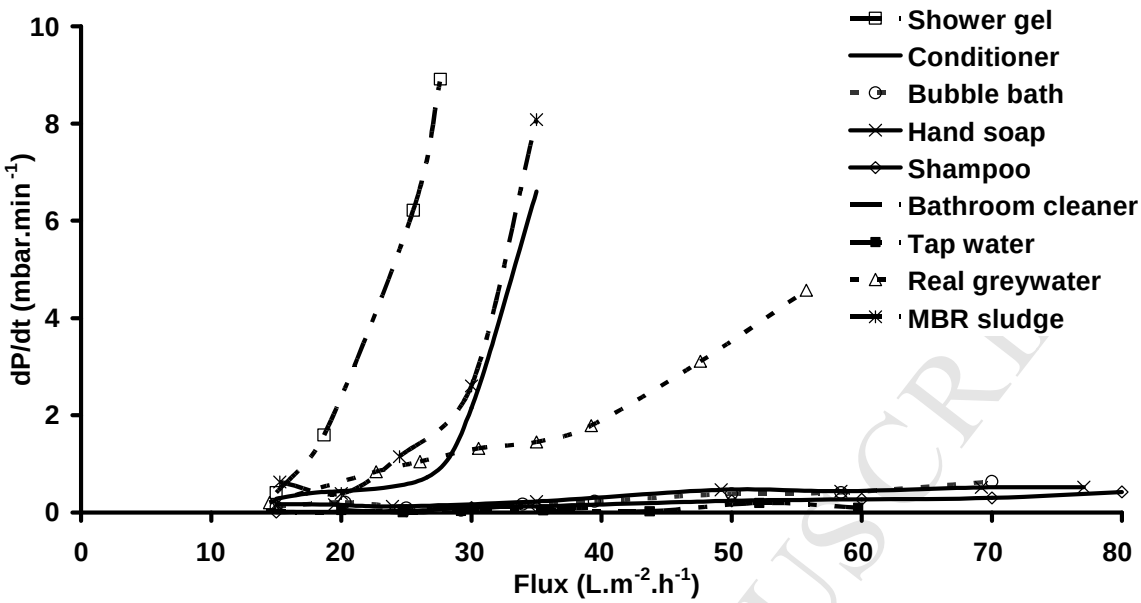
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| Product | Ingredients as listed |
|---|---|
| Shampoo | Cocamidopropyl Betaine, DMDM hydantoin, Citric Acid, Tetrasodium EDTA, Polysorbate 20, Panthenol , Parfum, Isopropyl Palmitate, Hexylene Glycol, Ammonium Laureth Sulfate, Ammonium Lauryl Sulfate, Ammonium Chloride, Hydroxypropyltrimonium, Hydrolysed wheat Protein, Tocophenyl Acetate, Triamine HCl, Ascorbic Acid, Sodium Cocoyl Isethionate, Sodium Lauroaphoacetate, 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, Methyldibromo 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, Cl 47005 |
| Shower gel 3 | Sodium Chloride, Sodium Sulfate, Citric Acid, Tetrasodium EDTA, CI 42090, Parfum, Glycerin, Methyldibromo Glutaronitrile, Phenoxyethanol, Hexylene Glycol, Sodium benzoate, Lauramidopropyl Betaine, PEG-7 Glyceril Cocoate, Disodium Lauramido MEA-Sulfosuccinate, Guar Hydroxypropyltrimonium Chloride, Sodium citrate, Disodium phosphate, Cl 19140 |

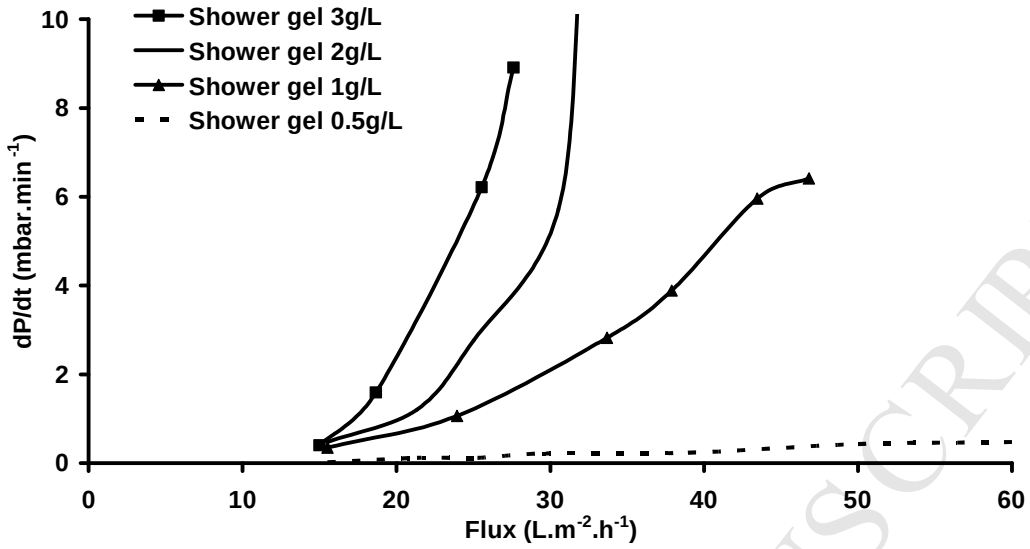
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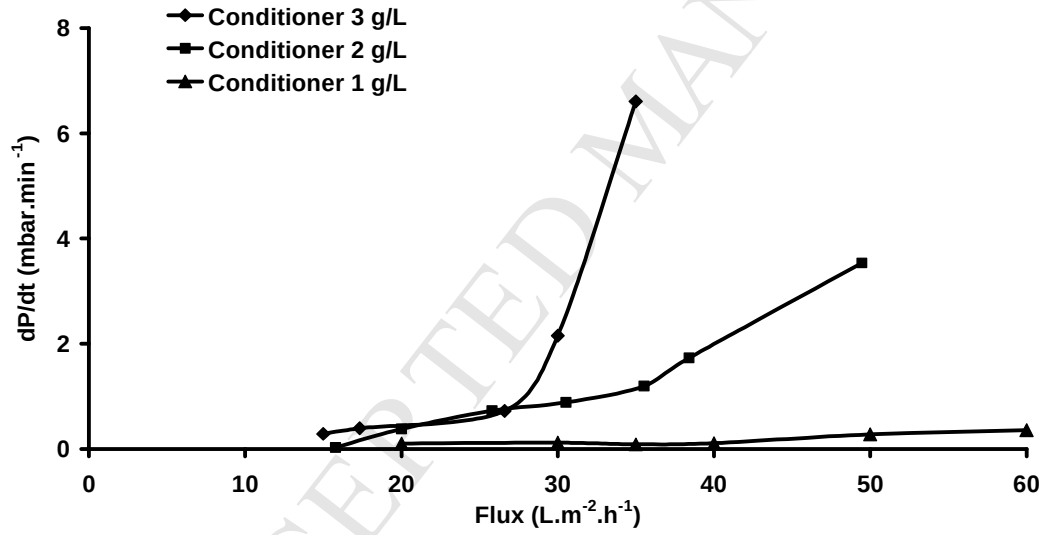
**Figure 1:** Fouling rates for different products (3 $g.L^{-1}$).
**Figure 2:** Influence of the concentration of (a) shower gel and (b) conditioner on fouling rates.
**Figure 3:** Fouling rates for different shower gels (2 $g.L^{-1}$).
**Figure 4:** Particle size distribution of the $TiO_2$ flocs in different solutions
**Figure 5:** Influence of UV illumination on fouling rates.

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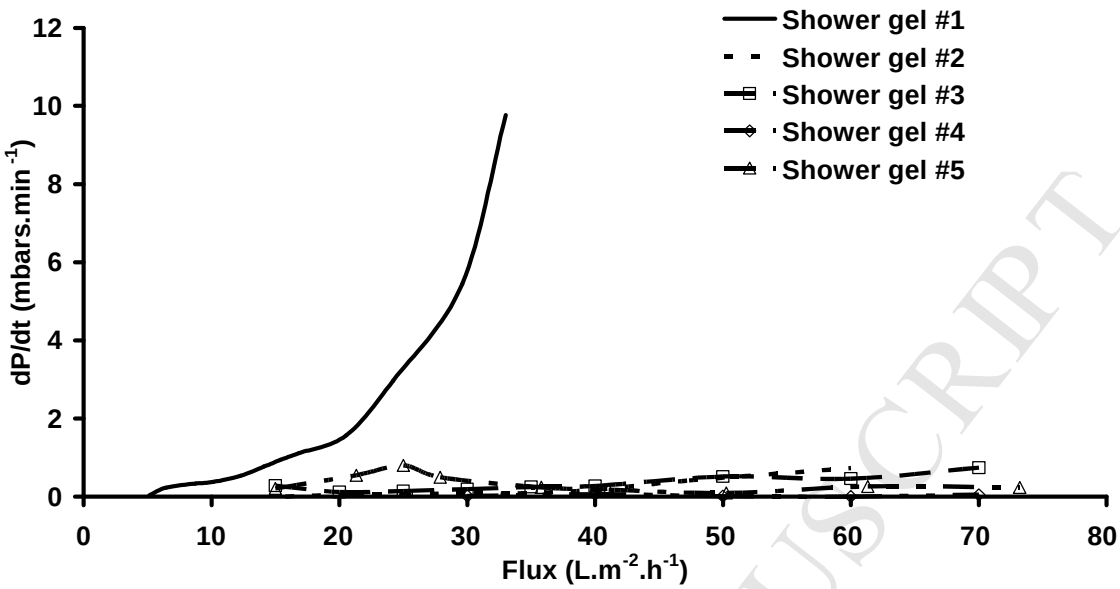



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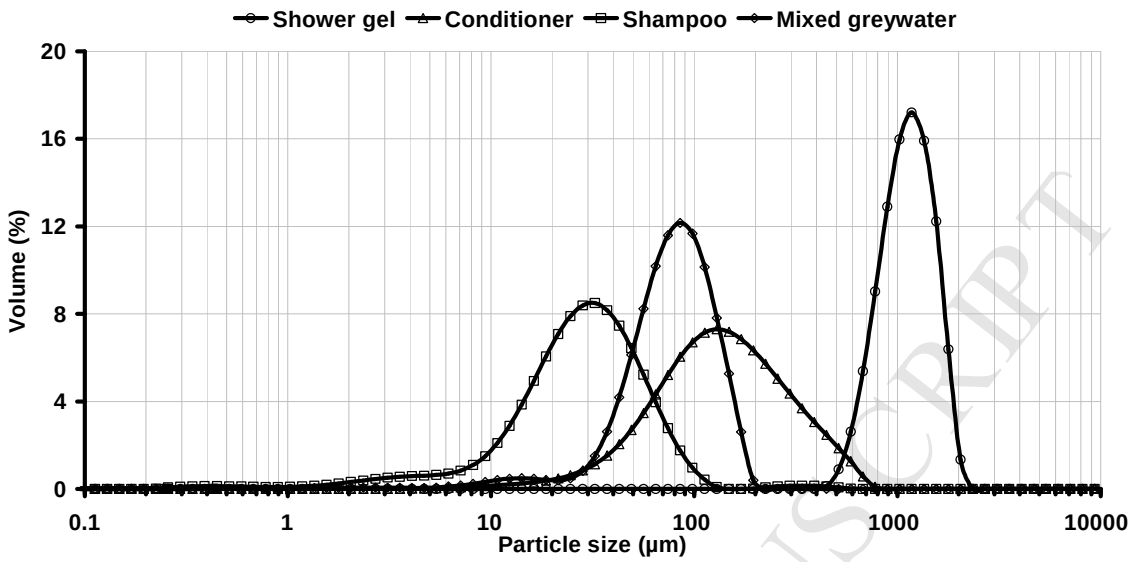



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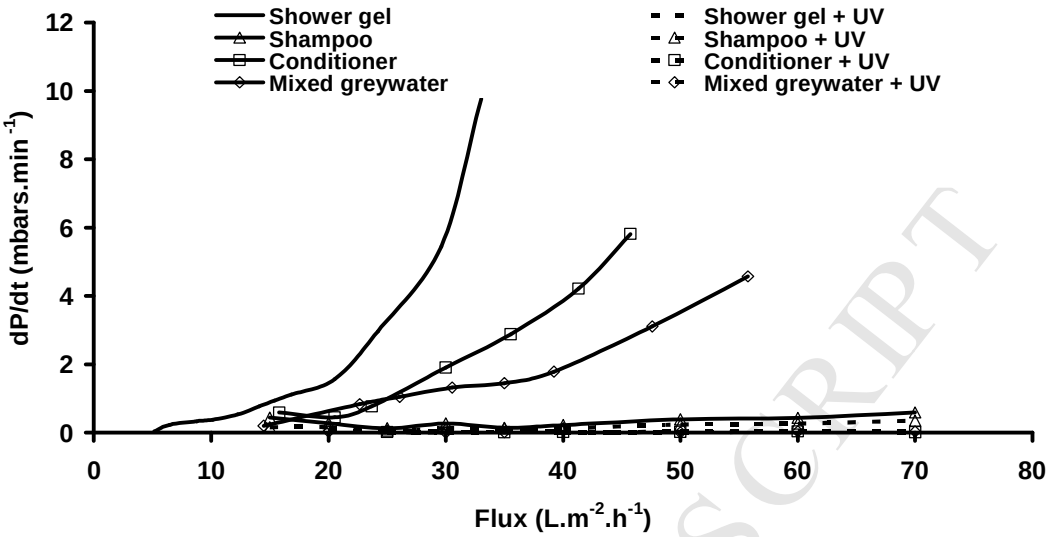



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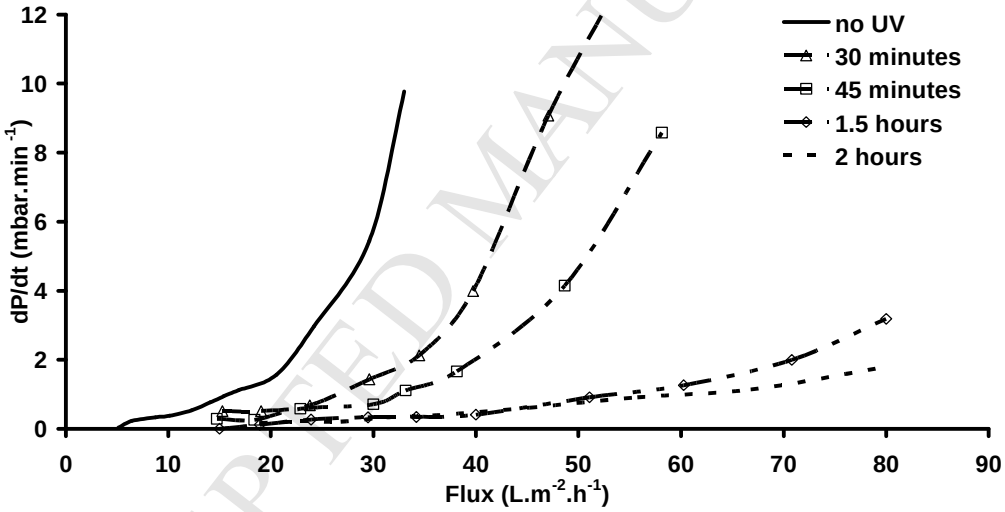



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(a)




(b)




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# Fouling control of a membrane coupled photocatalytic process treating greywater

**Pidou, Marc; Parsons, Simon A.; Raymond, Gaelle; Jeffrey, Paul; Stephenson, Tom ...**

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Elsevier Science B.V., Amsterdam.
http://dx.doi.org/10.1016/j.watres.2009.05.030
Marc Pidou, Simon A. Parsons, Gaelle Raymond, Paul Jeffrey, Tom Stephenson, Bruce Jefferson, Fouling control of a membrane coupled photocatalytic process treating greywater, Water Research, Volume 43, Issue 16, AOPs for Effluent Treatment, September 2009, Pages 3932-3939

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