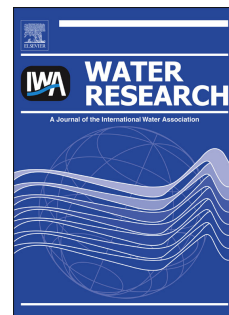


Accepted Manuscript

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

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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-TiO₂ 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

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 7.2×10^{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 (TiO₂) 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 F₂ (Huang *et al*, 1993). The TiO₂ 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 biochemical 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

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 (Thiruvengkatachari *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 $5 \text{ L.m}^{-2}.\text{h}^{-1}$ (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 $120 \text{ L.m}^{-2}.\text{h}^{-1}$. 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

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-RTM) (Water Innovate Limited, UK). Trials were conducted to study the influence of different parameters on titanium dioxide (TiO₂) and its properties to foul membranes. This system was composed of a 9-litre PVC tank in which the TiO₂ 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 m².

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 TiO₂. These concentrations were chosen

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 TiO₂ 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 TiO₂ concentration of 5 g.L⁻¹ as the detection cell saturated because of too many particles. Consequently, the TiO₂ concentration had to be decreased to 1 g.L⁻¹. Product concentrations were reduced commensurately to maintain a dose ratio between 400-600 mg.gTiO₂⁻¹ to match experiments in the fouling trials. Five measurements of each sample were performed and the average value of the median particle size d₅₀ (µm) was taken.

RESULTS

Cross flow filtration of organo-TiO₂ slurries containing bathroom cleaner, shampoo, hand soap or bubble bath dosed at a level of 600 mg.gTiO₂⁻¹ 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 TiO₂ 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 TiO₂ 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 organo-TiO₂ mixtures appears to be related to the character of the organics bound to the TiO₂ 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

flux (6-32 LMH) and fouling rate ($0.1-10 \text{ mbar}\cdot\text{min}^{-1}$) for operational MBR systems (Pollice *et al.*, 2005; Le Clech *et al.*, 2003 and 2005) confirming the potential differences between MCR and MBRs.

More detailed analysis of the link between the character of organo-TiO₂ mixtures and fouling revealed the dose ratio to be significant (Figure 2) with reduced fouling as the organic content within the TiO₂ matrix decreased. To illustrate, in the case of shower gel as the organic source, fouling rates of 8.9, 3.8, 1.6 and $0.2 \text{ mbar}\cdot\text{min}^{-1}$ were observed at a flux of 28 LMH for dose ratios of 600, 400, 200 and $100 \text{ mg}\cdot\text{gTiO}_2$ (Figure 2a). A similar situation was observed in the case of systems based on conditioner mixtures where the fouling rate observed at a flux of 30 LMH was 1.8, 0.9, 0.1 for dose ratios of 600, 400 and $200 \text{ mg}\cdot\text{gTiO}_2$ indicating that fouling can be controlled in the system by limiting the concentration of certain types of organics in the system (Figure 2b). Examples of previously reported investigations of membrane couple photocatalytic processes have focussed on dilute systems with slurry concentrations of $<1 \text{ g}\cdot\text{L}^{-1}$ and low organic feeds resulting in dose ratios of $10 \text{ mg}_{\text{dye}}\cdot\text{g}^{-1}$ for methylene blue dye (Sopajaree *et al.*, 1999), $48 \text{ mg}_{\text{TOC}}\cdot\text{g}^{-1}$ for fulvic acid (Fu *et al.*, 2006) compared to $114-178 \text{ mg}_{\text{COD}}\cdot\text{g}^{-1}$ investigated here at TiO₂ doses of $5 \text{ g}\cdot\text{L}^{-1}$. In dilute conditions, reaction rates have been seen to increase as slurry concentration increases (and dose ratio decreases) as an impact of enhanced mass transfer of the catalyst to the lamp although fouling is also seen to increase as slurry dose increases (Sopajaree *et al.*, 1999).

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

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 copolymer) 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

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 TiO₂ 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 TiO₂ 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 be 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 TiO₂ 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-TiO₂ aggregates that reduce the operating flux achievable within the system.

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-TiO₂ surface increasing the risk that only a proportion of the TiO₂ 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 TiO₂ 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

Ultimately, whatever the mechanism of fouling, management of the organo-TiO₂ aggregates is crucial for effective operation of such technologies. Given that sufficient irradiation of the organo-TiO₂ 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 TiO₂ surface reacts with the UV light. Transmittance in such systems is generally very low and hence TiO₂ 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 TiO₂ particles. However, if nanotechnology solutions like the membrane photocatalytic systems are 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.

ACKNOWLEDGEMENTS

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

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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 Laurophosphate, Sodium Methyl Cocoyl Taurate, Dimethicone Bisammonium, Hydroxypropyl Copolyol, Quaternium 80, Polyquaternium 7, PEG 18 glyceryloleate/cocoyate, 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, Methylchloroisothiazolinone, 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, Cyclopentasyloxane, Stearamidopropyl diethylamine, Cetyl 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 copolymers, 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, Methylchloroisothiazolinone, Phenoxyethanol, Hexylene Glycol, Sodium benzoate, Lauramidopropyl Betaine, PEG-7 Glyceril Cocoyate, Disodium Lauramido MEA-Sulfosuccinate, Guar Hydroxypropyltrimonium Chloride, Sodium citrate, Disodium phosphate, CI 19140

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

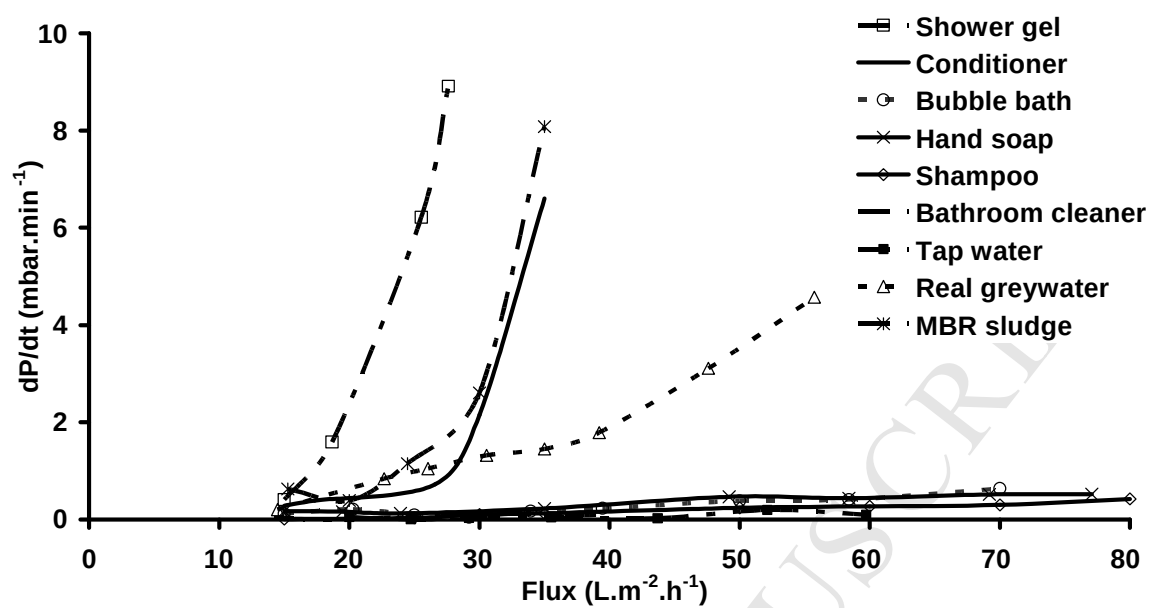
Figure 2: Influence of the concentration of (a) shower gel and (b) conditioner on fouling rates.

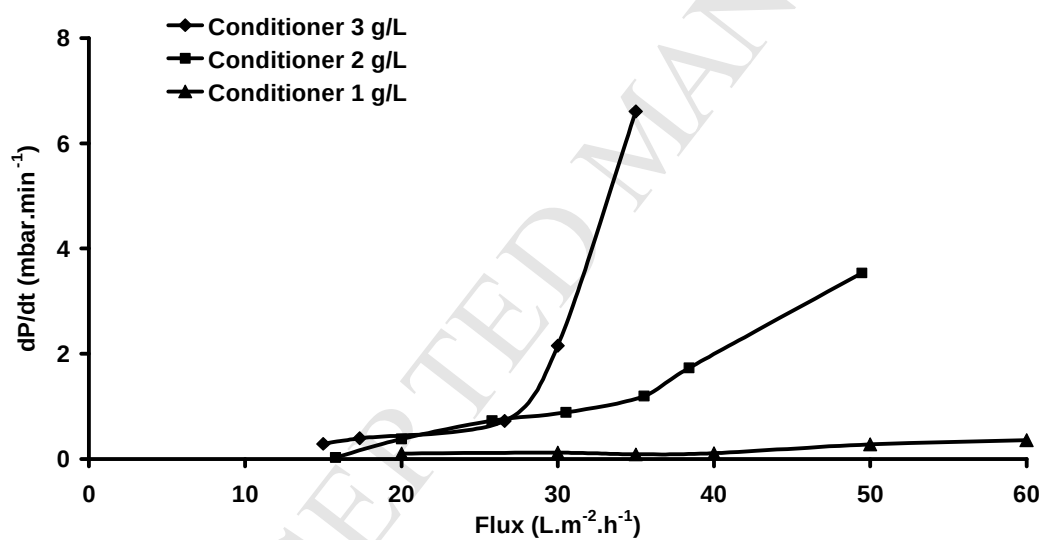
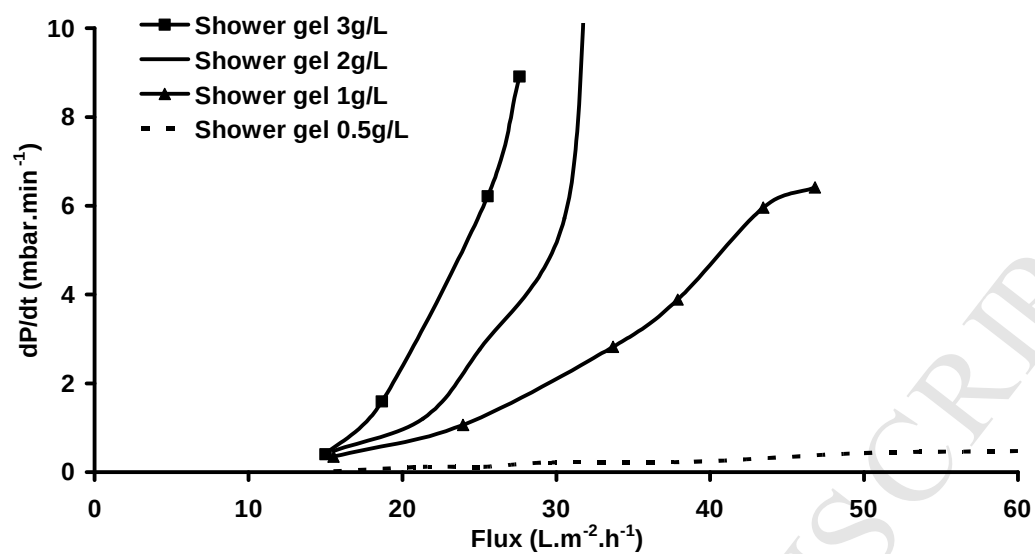
Figure 3: Fouling rates for different shower gels (2 g.L⁻¹).

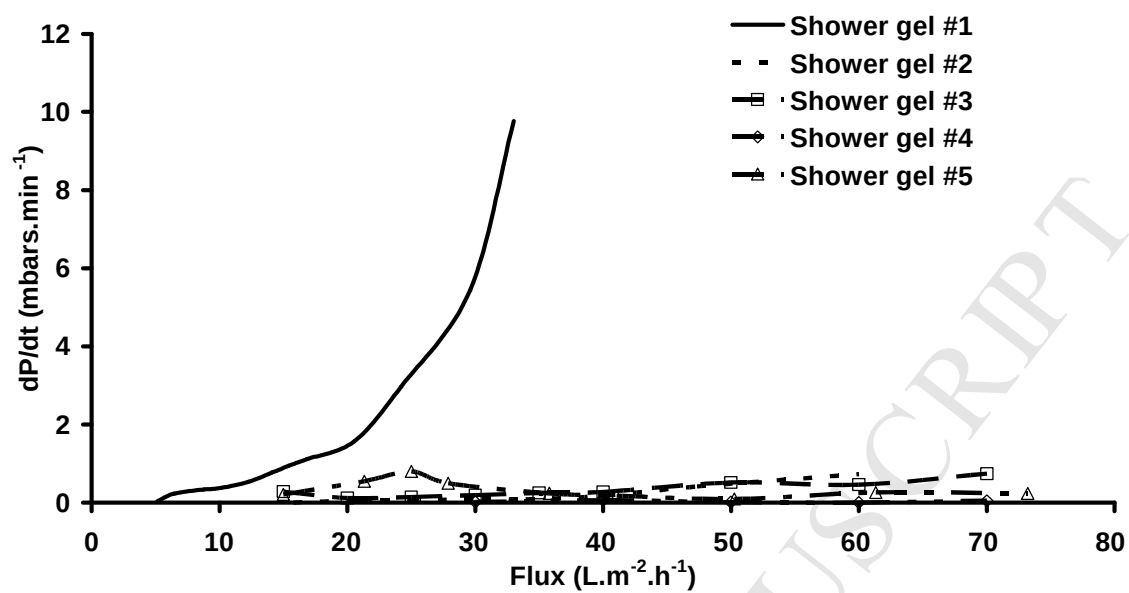
Figure 4: Particle size distribution of the TiO₂ flocs in different solutions

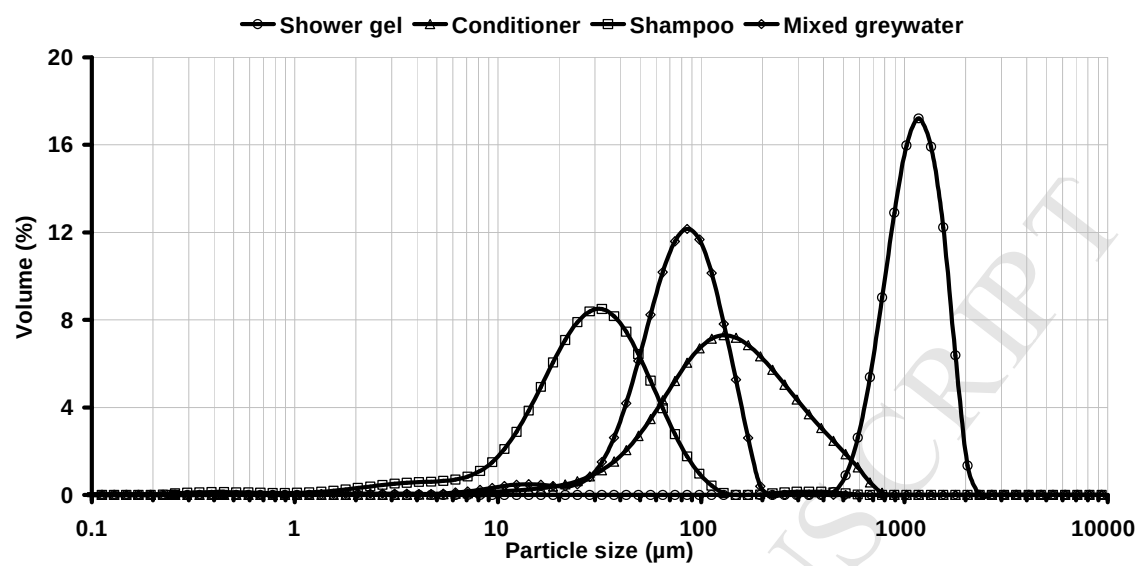
Figure 5: Influence of UV illumination on fouling rates.

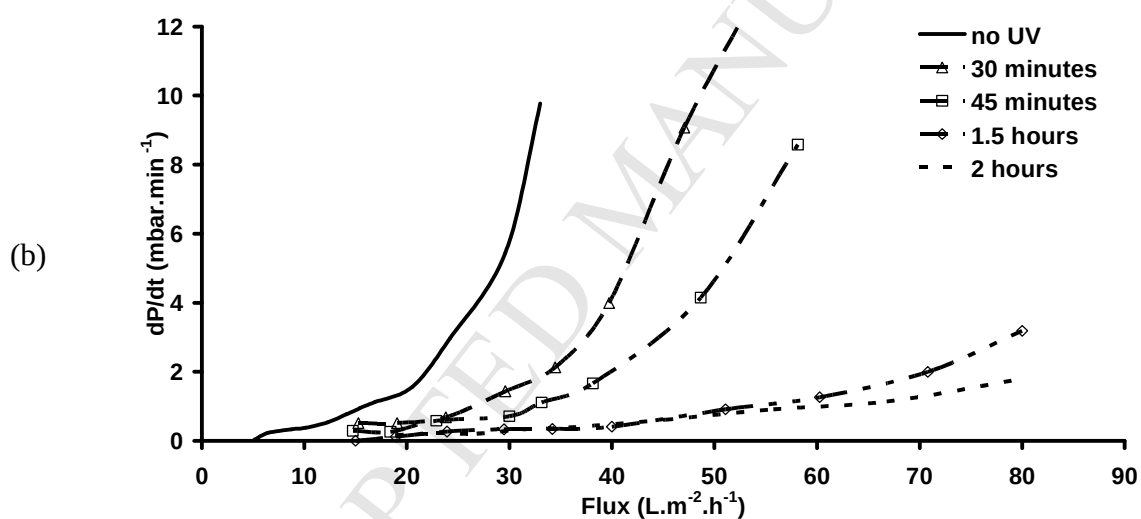
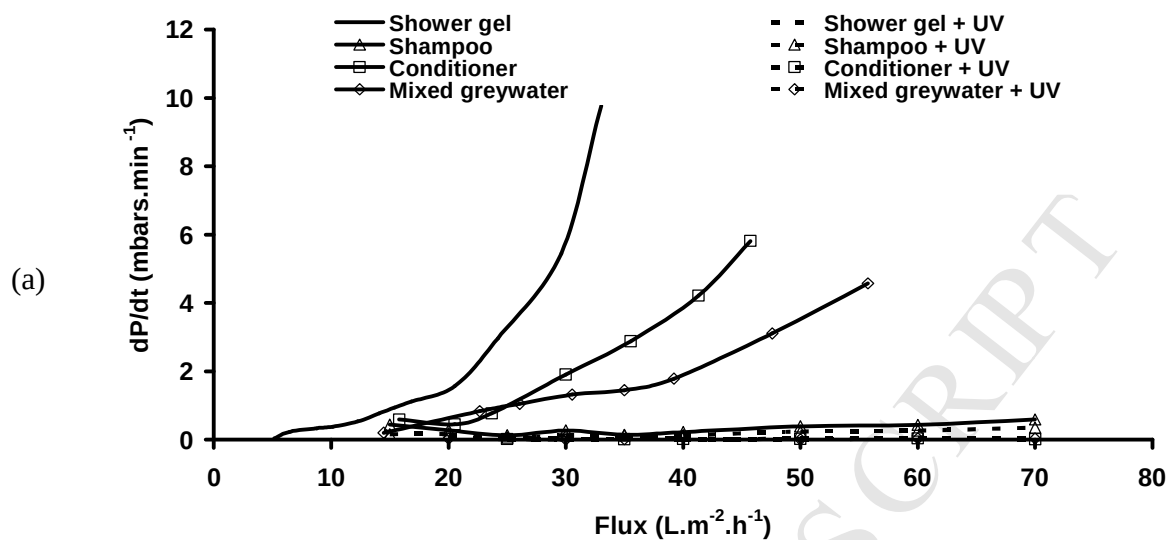
ACCEPTED MANUSCRIPT













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Fouling control of a membrane coupled photocatalytic process treating greywater

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2009-09-01T00:00:00Z

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