Membrane chemical reactor (MCR) combining photocatalysis and microfiltration for grey water treatment

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Abstract Urban water recycling is now becoming an important issue where water resources are becoming scarce. This paper looks at reusing grey water; the preference is treatment processes based on biological systems to remove the dissolved organic content. Here, an alternative process, photocatalysis is discussed as it is an attractive technology that could be well-suited for treating the recalcitrant organic compounds found in grey water. The photocatalytic process oxidises organic reactants at a catalyst surface in the presence of ultraviolet light. Given enough exposure time, organic compounds will be oxidized into CO_2 and water. The best contact is achieved in a slurry reactor but a second step to separate and recover the catalyst is need. This paper discusses a new membrane chemical reactor (MCR) combining photocatalysis and microfiltration for grey water treatment.

Keywords Grey water; photocatalysis; membrane chemical reactor (MCR)

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Introduction

Grey water arises from domestic washing operations and includes the waste from hand basins, kitchen sinks and washing machines. Grey water quality varies widely by geographical location, demographics and level of household occupancy. The concentration of organics found in grey water is similar to domestic wastewater but the chemical nature is quite different. The relatively low value for biodegradable organic matter and the nutrient imbalance limit the effectiveness of biological treatment. The use of cleaning agents has also been reported as having a major impact on treatment. Many treatment schemes proposed use physical and biological processes and have problems adjusting to the shock loading of organic matter and domestic cleaning chemicals. No grey water treatment standards exist in the UK but some countries in Europe have adopted a set of water quality criteria based on WHO guidelines (WHO, 1989).

Photocatalytic oxidation (PCO) is an emerging technology that could be suited to treating the recalcitrant organic compounds found in grey water. As a chemical process it can deal with rapid changes in influent quality and could operate over short hydraulic retention times obviating the need for large storage reservoirs. Heterogeneous photocatalysis using a solid material such as titanium dioxide (TiO_2) has received widespread attention for water treatment. The electronically excited photocatalyst, TiO_2 forms e^-/h^+ pairs and has been shown to oxidise and reduce many organic molecules. The efficiency of PCO is severely hampered by two main factors: mass transfer limitations and fouling of the solid catalyst. If PCO is used under conditions of high stirring, the turbulence helps in cleaning of the catalyst and will increase the efficiency of the process (Gogate and Pandit, 2004).

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Research into reactor design for photocatalysis is very active. The best contact can be achieved in a slurry tank reactor, but the problem of separating the solid particles in order to allow continuous operation arises. A hybrid process which combines photocatalysis and microfiltration (MF), can significantly improve the process. Despite the potential advantages of using this membrane chemical reactor (MCR), research of a combined use of both technologies is not sufficiently developed yet (Parsons *et al.*, 2001; Molinari *et al.*, 2002).

Microfiltration (MF) is a pressure-driven membrane process for the separation of fine particles, and the successful use of this technology has been limited by membrane fouling, which deteriorates the membrane performance as flux declines vs. time. The performance of liquid phase pressure-driven membrane processes is significantly influenced due to a compact layer formation. With cross-flow MF the fluid to be filtered flows parallel to the membrane surface. This reduces the formation of a filter cake and keeps it at a low level. However, there are several techniques to reduce membrane fouling problems. The introduction of gas/liquid two-phase flow has been shown significantly to enhance the performance of some membrane process applications, especially in microfiltration (Cui *et al.*, 2003). In some hybrid membrane processes, such as membrane bioreactors (MBRs), gas bubbles are required for oxygen supply so can serve a double purpose. In photocatalysis with TiO_2 a good supply of oxygen can help the oxidation process and as the solid needs to be well mixed it is possible to use air bubbles to achieve better mixing in the tank.

An air flux is required to introduce air into the MF membranes to reduce fouling and a perfect mixture in the reactor using air bubbles can also be achieved. As a device to introduce air in the system is already needed, liquid from the tank to the separation module can be pulsed by air-lift. If a system with an optimum performance is desired, its energy requirements should be taken into account and they can be considerably reduced if the system does not need any additional pump to move the liquid phase. The concept of critical flux introduced by Field *et al.* (1995) suggests that there is a flux below which species have negligible interaction with the membrane. For particles this can be visualised as the flux below which there is no deposition on the membrane. Operation below critical flux is usually assumed when the transmembrane pressure is steady and does not rise.

This paper will discuss the application of a MCR to treat grey water, which couple an advanced oxidation process to an air lift membrane unit. It will be split into two sections, one relating to hydraulic control and the other to reactor performance. Here, we report the results of experiments carried out to study the sustainable flux conditions of a combined PCO:MF process to find the best operating conditions for the membrane. Then experiments focusing on the AOP performance will be reported in terms of overall organics removal and compliance with reuse standards.

Methods

Experiments were conducted using a stainless steel tank of 8 L capacity and a membrane module with hollow fibres microfiltration membranes (Milleniumpore). Table 1 shows

Table 1 Main membrane characteristics

Membrane working length (m)	1
Lumen internal diameter (mm)	5
Pore size (μm)	0.05
Number of lumens	10
Total membrane area (m^2)	0.157
Cross-section area (mm^2)	200

the main membrane characteristics. Four 25 W UVC lamps (Philips) were placed in the reactor and air was used to keep the solution in suspension. The experimental set-up is shown in Figure 1. To achieve constant flow of permeate from the microfiltration module a peristaltic pump (Watson Marlow) was needed. A pressure transducer (RS, Corby) and a Pico data logging system (Pico Technology Ltd, Cambridge) were included to record the pressure on the permeate side of the membranes. The raw grey water was collected from the shower of one of the researchers. Table 2 presents average values for some parameters.

The first stage of the PCO process is the adsorption of organic compounds on to the TiO_2 catalyst. Hombikat UV-100 titanium dioxide photocatalyst was used for all the experiments (Sachtlebaen Chemie GmbH). Grey water and TiO_2 were added into the reactor and well mixed prior to irradiation and then samples were withdrawn at regular intervals for analysis.

Two series of experiments were carried out. First, experiments with TiO_2 only in clean water were carried out to see the influence of the solid particles in membrane fouling. To pulse the mixture of water and TiO_2 air-lift was used. Air velocity varies from 0.5 to 1.25 m/s. Then, experiments with TiO_2 and grey water were carried out with the same range of air velocity. TiO_2 concentrations of 5 and 10 g/L were used.

Results and discussion

The most commonly used short-term experiment to determine the critical flux value (J_c) is incrementally to increase the flux for a fixed duration for each increment, giving a stable transmembrane pressure (TMP) at low flux but an ever-increasing rate of TMP increase at higher fluxes. This flux-step method defines the highest flux for which TMP remains stable as J_c. However, no single protocol of this method exists. In this work, a constant permeate flux was maintained during regular intervals of 15 min thanks to a peristaltic pump and the TMP was continuously recorded. After each time interval the flux was increased (Figures 2 and 3).

Both figures correspond to experiments carried out with water. Figure 2 shows the results for an experiment without TiO_2 while Figure 3 corresponds to water with TiO_2. It can be observed that for water, fluxes of 250 L/m^{2}h and TMP up to 0.8 bar could be

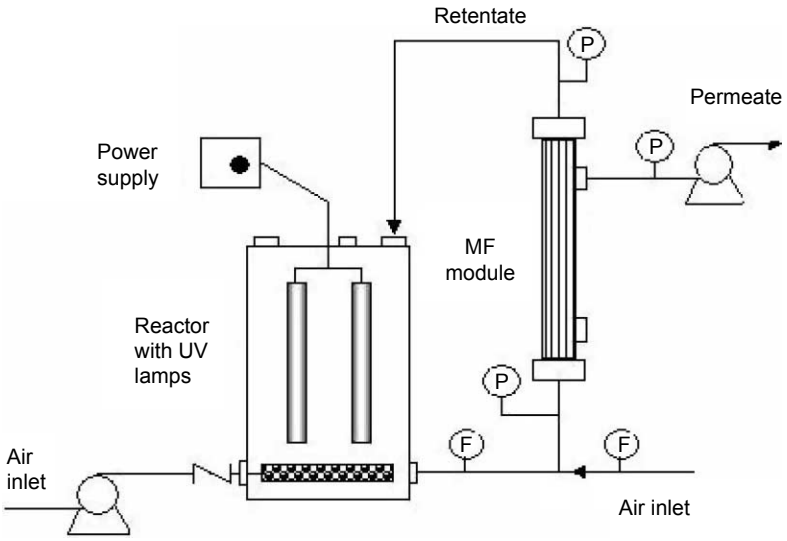

Figure 1 Diagram for the reactor system

Table 2 Raw grey water analysis

Parameter	Value
COD (mg/L)	273.8 ± 51.0
Turbidity (NTU)	20.9 ± 6.3
BOD (mg/L)	102.2 ± 28.4

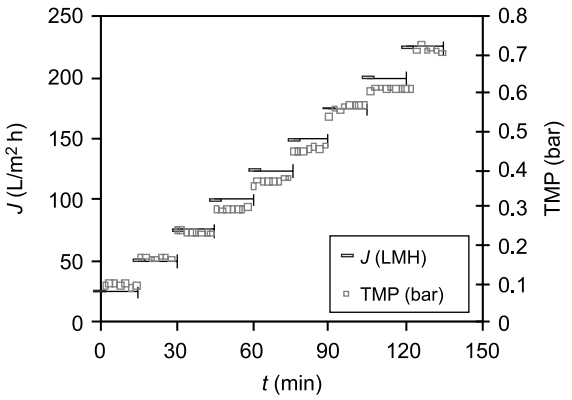

Figure 2 Permeate flux (J) and TMP range (u_{liq} = 0.5 m/s, TiO_2 = 0 g/L)

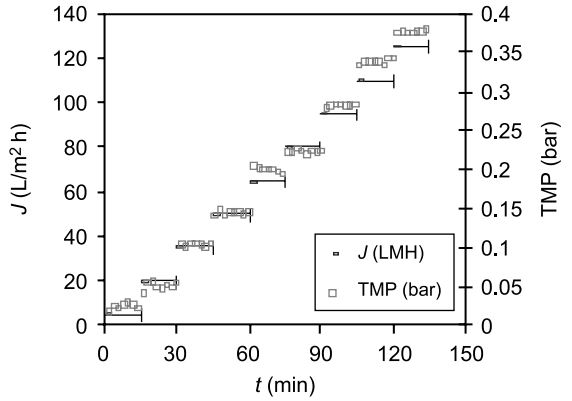

Figure 3 Permeate flux (J) and TMP range (u_{air} = 0.5 m/s, TiO_2 = 10 g/L)

achieved but when 10 g/L of catalyst was added to water this was reduced to 140 L/m^{2}h and 0.4 bar. The critical flux is generally determined visually as the last flux step at which the TMP remains constant. Therefore, in both cases no critical flux value was obtained in this range of permeate flux.

Plots of *J* vs. TMP are often used to determine membrane permeability for a specific application. Figures 4 and 5 show the membrane permeability when adding 5 and 10 g/L of TiO_2 to water, respectively at air velocities of 0.5 to 1.25 m/s. As could be expected, in both cases the permeability is slightly higher when the air velocity increases. Permeability was tested periodically with tap water. An average value of 341.4 L/m^{2}h bar was obtained.

After studying the performance of the process with water and the TiO_2, grey water was tested. Several experiments were carried out using air-flow rates of 0.5 and 1.25 m/s

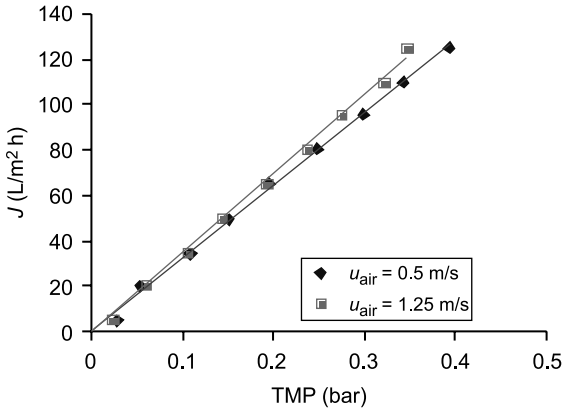

Figure 4 Permeability graph for tests carried out with $[TiO_2] = 5$ g/L

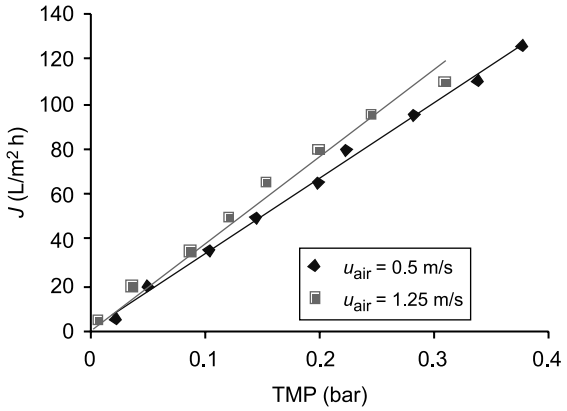

Figure 5 Permeability graph for tests carried out with $[TiO_2] = 10$ g/L

and varying the concentration of catalyst up to 10 g/L. Figure 6 shows permeate flux vs. TMP for grey water experiments with an air-flow rate of 0.5 m/s. It shows that it is possible to work in a range of permeate fluxes between 5 and 55 L/m^{2}h with a sustainable flux with no clear signs of membrane fouling working up to 0.6 bar of TMP. These results will help to set the conditions for long-term running of the process. It can also be

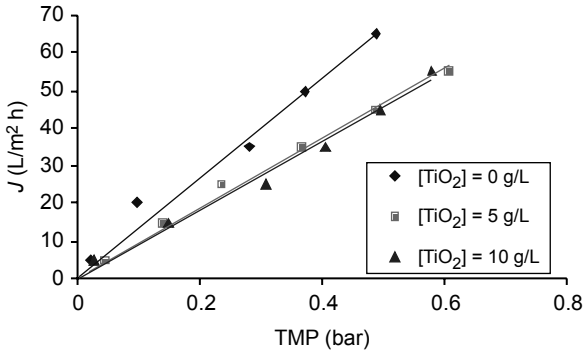

Figure 6 Permeability graphs for grey water experiments carried out with different catalyst concentration ($u_{air} = 0.5$ m/s)

observed that in terms of the MF performance there is little difference between using 5 or 10 g/L of catalyst.

The surface of TiO_2 exhibits high hydrophilicity under ultraviolet radiation so it is also interesting to evaluate whether the microfiltration operation could change significantly while the photocatalytic process is running (Irie *et al.*, 2004). Several experiments have been carried out with the same flow rate and concentration of catalyst but with or without UV light. Some of the results are shown in Figure 7. In all the cases there was no negative impact on the performance of the MF when the UV lights were on, and if anything, the permeability was slightly higher.

To assess the removal of organic matter in the reactor the bulk parameters of COD and BOD were analysed. Experiments with permeate fluxes of 15 and 55 L/m^2h were carried out varying the amount of catalyst in the reactor and the air velocity in the MF module (Tables 3 and 4).

Although there is no UK standard for water quality suitable for grey water recycling, the more restrictive value has been set to 10 mg/L for BOD_5 value (Jefferson *et al.*, 1999). It can be seen that the MCR can meet these values. It can also be observed that as the higher is the catalyst concentration the better is the BOD reduction achieved, although BOD values below 10 mg/L could be found when using 5 g/L of TiO_2. Related to COD value, reductions up to 74% were achievable. Alongside BOD, turbidity is another key quality parameter for grey water re-use. Table 5 shows the turbidity reduction

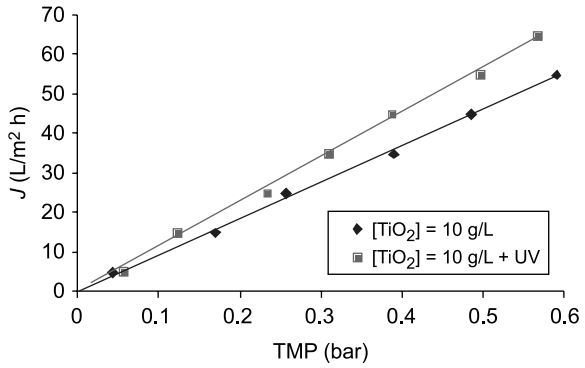

Figure 7 Comparison of the microfiltration performance simultaneously with photocatalysis

Table 3 Organic parameters for tests carried out with a permeate flux of 15 L/m^2h

u_{air} (m/s)	TiO_2 (g/L)	COD_i (mg/L)	COD_f (mg/L)	COD reduction (%)	BOD_i (mg/L)	BOD_f (mg/L)	COD reduction (%)
0.5	5	324	72	78	135	17	87
1.25	5	324	56	83	135	5	96
0.5	10	290	68	77	114	2	98
1.25	10	252	68	73	128	5	96

Table 4 Organic parameters for tests carried out with a permeate flux of 55 L/m^2h

u_{air} (m/s)	TiO_2 (g/L)	COD_i (mg/L)	COD_f (mg/L)	COD reduction (%)	BOD_i (mg/L)	BOD_f (mg/L)	BOD reduction (%)
0.5	5	324	98	70	135	14	90
1.25	5	324	86	73	135	9	93
0.5	10	290	76	74	114	2	98
1.25	10	252	84	67	128	10	92

Table 5 Grey water turbidity reduction (turbidity units: NTU)

u_{air} (m/s)	TiO_2 (g/L)	Raw water	Permeate flux = 15 L/m²h		Permeate flux = 55 L/m²h	
			Permeate	Turbidity reduction (%)	Permeate	Turbidity reduction (%)
0.5	5	18.7	0.64	97	0.63	97
1.25	5	18.7	1.10	94	0.35	98
0.5	10	15.6	1.35	91	3.57	77
1.25	10	16.9	1.67	90	1.77	91

achieved after the MCR treatment for two different permeate fluxes. In this case, the more restrictive value has been set to 1–2 NTU (Jefferson *et al.*, 1999). It can be observed that smaller values of turbidity were obtained when using 5 g/L of catalyst. Nevertheless, working with 10 g/L of catalyst, turbidity values less than 2 NTU were achieved.

Conclusions

The results showed that it was possible to operate a combined photocatalysis and microfiltration process continuously to treat grey water to WHO standards for reuse.

The key factor related to any microfiltration system is the fouling of the membranes because it increases the hydraulic resistance of the membrane. This problem can be reduced by operating at lower permeate fluxes, although in this case, membrane area requirements increase. In this study, permeate fluxes up to 60 L/m²h were achieved with TMP values less than 0.6 bar.

After examining the results it could be observed that using 5 g/L of TiO_2 as the catalyst for the photocatalytic process BOD was reduced below 10 mg/L, which meets the most restrictive quality standards and criteria suitable for domestic water recycling. A COD reduction of an average value of 70% was achieved in all the experiments. Finally, turbidity values were reduced below 1 NTU, even after having added TiO_2 particles. The catalyst was fully recovered and the process could run on a continuous mode, which was a significant improvement for the operation.

Future studies will try to achieve working with higher permeate fluxes as it has not been possible yet to reach a critical flux. Organic matter removal and grey water turbidity will be monitored to ensure that the desired reduction is still achieved.

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