SIMULTANEOUS APPLICATION OF MEMBRANE ULTRAFILTRATION, ACTIVATED CARBON ADSORPTION, AND ULTRASOUND IRRADIATION FOR FOULING CONTROL IN SECONDARY WASTEWATER TREATMENT

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ABSTRACT

Water scarcity is a growing global concern and the meager fraction of the remaining renewable water is further reduced by environmental pollution. At present, meeting the world's water demand entails efforts to protect the remaining fresh water sources from contamination or conserve water by reuse processes. Both actions necessitate advanced treatment techniques to remove hazardous substances and improve quality of wastewater effluent.

Membrane filtration is one promising technology in the treatment of wastewater. However, the increasing use of membranes necessitates techniques to improve performance especially to control fouling - the main burden to membrane operation. This paper investigates the integration of ultrasound irradiation and activated carbon adsorption to cross-flow membrane ultrafiltration of secondary wastewater treatment plant effluent in a novel hybrid USAMe process. Experiments employing membrane alone, membrane with ultrasound, and membrane with adsorption were also performed. Fouling is analyzed through the continuous monitoring of trans-membrane pressure in a constant flux operation and through the measurement of specific resistances obtained during a systematic cleaning process. The influence of ultrasonic frequency to performance and the eco-toxicity of the effluent to *Daphnia magna* were also studied.

All amendment techniques have improved membrane performance and have contributed to the enhancement in the main hybrid process. Superior results were achieved in the USAMe process operated at lower ultrasonic frequency. USAMe permeates produced "no effect" in eco-toxicity tests, denoting the generation of safe effluents.

Keywords: adsorbent, anti-fouling, emerging contaminants, flux enhancement, hybrid membrane processes, sonless

1. Introduction

Membrane filtration as an advanced treatment method is superior over others in terms of compactness, ease of automation, no chemical requirement, full-barrier to bacteria, and non-generation of harmful disinfection by-products (American Water Works Association, 1995; Crittenden *et al*., 2012). However, the problem of fouling limits its application. Natural organic matter (NOM) present in wastewater fouls the membrane by several mechanisms such as concentration polarization, formation of a gel layer or cake layer, by pore blocking, or by adsorption to the membrane and pore walls (Kim *et al*., 2009; Lee and Cho, 2004). The low pressure membranes more commonly employed in wastewater treatment are more susceptible to severe fouling since small fractions of NOM also enter and adsorb inside the pores, leading to constriction and blocking (Lee and Cho, 2004). Several areas of improvement were investigated to deal with fouling, of which, backwashing and chemical cleaning are the most common techniques in application (Kyllönen *et al*., 2006). However, besides increasing operational costs by pumping requirements and chemical addition, these likewise decrease productivity by introducing cleaning downtimes, shortens membrane lifespan due to chemical degradation, and introduces a load of chemical waste.

To lessen the frequency of membrane cleaning, ways of preventing or minimizing fouling before it happens are explored. Ultrasound is one of the technologies utilized for this purpose. Cavitation, the continuous growth and collapse of microbubbles caused by ultrasound, produces physical and mechanical effects (Mason and Peters, 2002) that continuously cleans the membrane, hence minimizing process disruptions. Ultrasound is also capable of NOM degradation (Naddeo *et al*., 2007), further boosting treatment efficiency. Adsorption is another important method employed for fouling prevention (Thiruvenkatachari *et al*., 2006; Ying and Ping, 2006, Kim *et al*., 2007). Penetration of NOM particles into the pores are prevented through adsorption of these contaminants before reaching the membrane surface.

This is the first study to integrate both ultrasound irradiation and activated carbon adsorption to cross-flow membrane ultrafiltration in a hybrid process called USAMe (patented by the University of Salerno) for the treatment of real wastewater. This combination aims to enhance fouling control through the combined effects of the two auxiliary methods to the membrane operation. The experiment employs a hollow fiber membrane ultrafilter operated in cross-flow mode, which is more commonly employed in industries, to simulate industrial operations.

2. Materials and methods

2.1. Materials

The feed to all tests is secondary wastewater spiked with emerging contaminants (ECs). The wastewater was taken downstream of secondary sedimentation tanks from a wastewater treatment plant serving 400,000 inhabitants in Salerno, Italy. Wastewater characteristics are 7.6 - 8.3 pH, a 25 - 60 mg/L COD as tested through Open Reflux Method, and a 1-4 mg/L BOD tested by OxiTop BOD Measurement Instrumentation. The adsorbent used is powdered activated carbon model #434454 purchased from Carlo Erba Reagenti (Italy). This underwent several washings, boiling, drying, and constant weighing processes before used. The membrane is a Polysulfone Hollow Fiber (A/F Technology Corporation, USA) having a nominal molecular weight cut-off of 100 kDa.

2.2. Experimental set-up

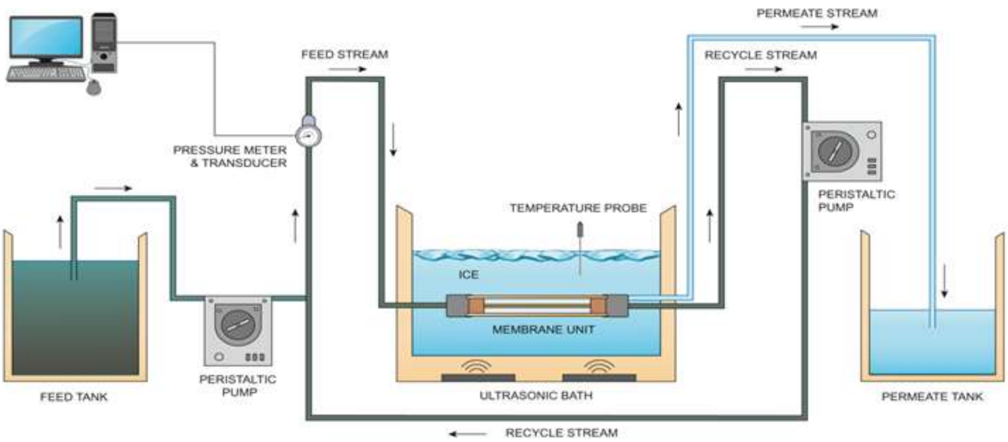

Figure 1: USAMe Experimental Set-up

The membrane unit is a hollow fiber membrane enclosed in a glass tube to enable collection of permeate by an inside-outside flow pattern with an effective transfer area of 6.6 cm^{2}. This is held in a fixed horizontal position at 5 cm from the base of a TI-H-10 Ultrasonic Bath (Elma®, Germany) filled with 5L of DI water. The cross-flow configuration set-up is illustrated in Figure 1. Two peristaltic pumps (323 S/D Watson-Marlow, UK) deliver the

feed and recycle streams. A permeate flux value of 150 L/m^2h, typical for industrial ultrafilters (Crittendan *et al*., 2012), was maintained. The adsorbent inside the fiber circulates through the system. The trans-membrane pressure (TMP) throughout the process was monitored and recorded by a PCE-932 full line pressure meter and PS100 transducer (PCE Instruments, Italy) connected to a personal computer which gives a continuous display of the TMP profile.

2.3. Procedure

Clean water tests were performed before each experiment to determine the TMP of deionized (DI) water through a clean membrane. This is done by adjusting DI water temperature to 25°C and running this through the membrane at the desired flux until a stable TMP is achieved. The whole batch of adsorbent computed based on a dose of 4.5 g/m^2 of membrane area, the dose which gave stable results for ECs removal in preliminary tests with synthetic wastewater (Secondes *et al*., 2014), was pre-deposited into the system before the start of the experiment. The ultrasonic bath was set to the maximum electrical power of 800 W for the two tested frequencies – 35kHz and 130 kHz – which corresponds to 35 W/L and 29 W/L specific ultrasound densities, respectively, as measured through calorimetric method (Mason and Peters, 2000). Feed wastewater was run through the system, adsorbent circulates through the mixed and recycle streams, and ultrasound was applied continuously while maintaining the bath temperature at 25±2 °C. TMP was recorded as soon as the first drop of permeate emerges from the collection line. Permeate was collected at the end of each twenty-minute interval for a duration of 4 hours. At the end of each run, systematic cleaning was performed to determine specific resistance values (Li *et al*., 2011; Ying and Ping, 2006). Membrane was first flushed with DI water at 200 RPM for 10 minutes to completely remove external fouling, which could consist of concentration polarization, gel and cake layers. TMP through the washed membrane was then determined. Cleaning was continued by backwashing with DI water and using US intermittently until the clean water TMP is recovered and the absorbance of wash water register negligible values.

In addition to the experiments with USAMe, experiments involving membrane ultrafiltration alone (Me), combined adsorption and membrane ultrafiltration (AMe), and combined ultrasound and membrane ultrafiltration (USMe) were also performed to investigate the effect of each auxiliary method on membrane performance.

2.4. Toxicological test

The toxicity of wastewater, feed wastewater, and generated permeates were tested to *Daphnia magna* according to the standard methods (ISO, 1996). Ten mL volumes of undiluted samples in triplicate were used in each test. New-born daphnids were exposed to these samples and grown at 20±1°C. They were fed with *P. subcapitata* and baker's yeast. In each treatment schedule, a certain number of daphnids were scored according to their immobilization frequency in 10 mL sample volumes.

3. Calculations performed

The flow through membranes is governed by Darcy's Law (Eq. 1) which relates *TMP* to resistance in a constant flux process. In the equation, J is the volumetric permeate flux, μ is the viscosity of the feed, and R_T is the total resistance.

$$J = \frac{TMP}{\mu RT} \quad (1)$$

Fouling analysis performed through systematic cleaning applies Darcy's Law in a resistance-in-series model (Crittenden *et al*., 2012; Li *et al*., 2011) to determine the values of the different types of resistances. In the following equations, R_M, R_I, and R_E are the membrane, internal, and external resistances, respectively. External resistance is caused by particulates present outside the membrane surface which are easily removed by simple washing. Internal resistance, on the other hand, refers to that caused by particulates trapped inside the pores. The subscripts $_C$ and $_W$ refer to the flow of DI water through the clean and externally washed membrane, respectively.

$$R_M = \frac{TMP_C}{\mu J_C} \quad (2)$$

$$R_M = \frac{TMP_W}{\mu J_W} - R_M \quad (3)$$

$$R_M = \frac{TMP}{\mu J} - \left(R_M + R_I\right) \quad (4)$$

$$R_{TOTAL} = R_M + R_I + R_E \quad (5)$$

4. Results and discussions

4.1. Fouling in the Membrane Ultrafilter

Graphs of TMP versus time are shown in Fig 2. The number, 35 and 130, following the acronym for the process, refer to the kHz frequency of ultrasound used in the experiment. The TMP profile for the ultrafiltration experiment is shown as the uppermost curve. Two apparent regions occur; the first region of continuously increasing TMP represents the development of fouling resistance as a result of accumulation of NOM particles adjacent to the membrane surface. As filtration progresses and fouling grows, greater TMPs are necessary to maintain the imposed permeate flux. The second region, which is nearly horizontal, represents the maximum TMP achieved and indicates severe fouling in the membrane. The point of deflection between the two curves indicates a critical point, denoted as $t_{critical,}$ where continued filtration beyond this point does not result to any significant change in TMP anymore. This phenomenon is comparable to reaching the critical flux in a constant operating pressure process (Peinemann & Nunes, 2010). This point is indicative of severe fouling and the attainment of a steady-state condition where the rate of attachment of particles into the membrane balances the rate of back-transport of particles into the bulk solution. Table 1 presents a summary of the ultrafiltration data.

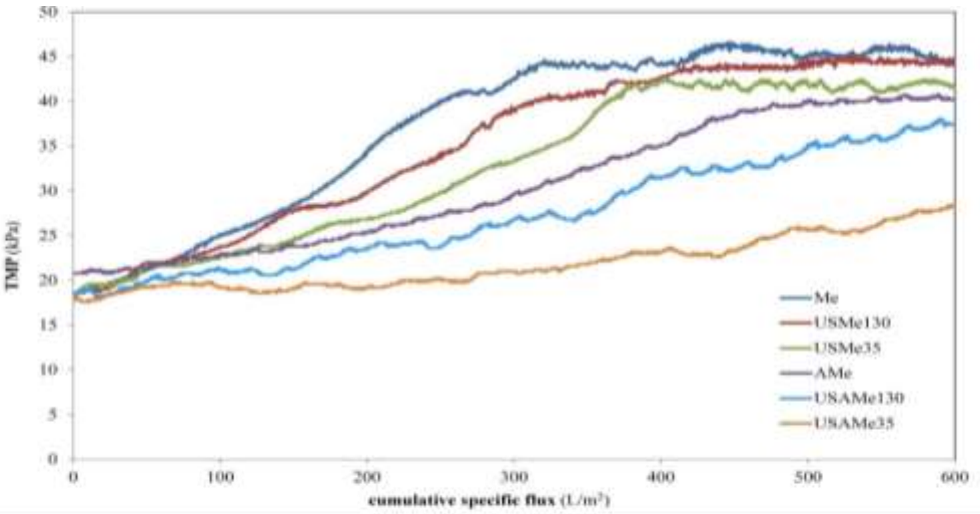

Figure 2: TMP profile of the different membrane process

Table 1: Membrane ultrafiltration data

Parameter	Value	Parameter	Value [kPa]	Parameter	Value ($10^{12}m^{-1}$)
Flux	150 L/m^2h	TMP_C	18.4	R_M	0.491
Temperature	25^oC	TMP_W	28.05	R_I	0.257
Viscosity	0.0009 kg/ms	TMP	46.2	R_E	0.484
$t_{critical}$	126 min			R_T	1.232

4.2. Fouling control in the hybrid USAMe process

The TMP profile of USAMe processes, illustrated as the two lowermost curves in Fig. 2, are significantly below that of the membrane alone. The slope dTMP/dT represents the fouling rate (Diez, *et al*., 2014), therefore the maintenance of TMPs at lower values and its deferred TMP build-up indicates that the hybrid USAMe process is effective in controlling fouling in the membrane.

Experiments employing dual-method processes were also performed to understand the enhancement mechanisms. Results of the AMe and USMe combinations are also illustrated in Fig. 2. Both ultrasound and adsorption have shown capacity to enhance membrane performance. Ultrasonic control of fouling, as observed in similar studies, are attributable to continuous membrane cleaning brought about by the mechanical effects of cavitation and acoustic streaming that dislodge and drive away particles from the membrane as soon as they get there (Cai *et al*., 2010; Muthukumaran *et al*., 2005). In the case of adsorption, higher TMP values at the initial stage were observed due to the deterrent effect of PAC particles on permeability. But as the process continues, PAC's hindrance to permeation was outdone by its capacity to absorb fouling substances, eventually developing lesser TMPs in the membrane.

Comparison of AMe and USMe TMP profiles in Fig.2 shows better enhancements achieved from adsorption than ultrasound. This indicates the adsorbent's major role in improving membrane performance. In the USAMe process, both auxiliary methods work hand in hand to boost the performance. US decrease the amount of NOM reaching the membrane by enhancing adsorption of foulants onto PAC while NOM particles adsorb onto suspended adsorbents circulating through the system, acoustic streaming provide the stirring action that enhance this mass transfer (Hamdaoui and Naffrechoux, 2009). Powerful microjets could break up the adsorbent surface of destroy particles thereby permitting penetration of adsorbate into the inner structure or increasing its surface area plus the microstreaming and microstreamers that could push molecules into the micropores, hence increasing pore diffusion coefficient (Saravia and Frimmel, 2008). The above mechanisms all results to improved NOM adsorption and the subsequent fouling control. Also, in the hybrid process, ultrasound could facilitate agglomeration (Muthukumaran *et al*., 2005) of PAC-NOM aggregates, forming a loose layer on the surface of the membrane and serving as a secondary filter that retains foulants but offers lesser resistance to flow. These loose clusters can easily be detached from the membrane by cavitation forces and the heavier aggregates consequently develop greater back-transport velocity, enabling them to be easily moved by acoustic streaming and cross-flow velocity. Thus, the cleaning action of US is also made simpler in the presence of PAC. The presented mechanisms are supported by the computed resistance values shown in Table 2.

Table 2: Resistances developed in the different membrane processes

PROCESS	R_I	R_E	R_T
Me	0.257	0.484	1.232
AMe	0.176	0.403	1.075
USMe130	0.164	0.527	1.187
USMe35	0.114	0.506	1.115
USAMe130	0.299	0.224	1.019
USAMe35	0.208	0.050	0.749

4.3. Influence of ultrasonic frequency

Since the feed and the PAC particles are inside the membrane and is further enclosed in a glass tube, acoustic power reaching the inner zone of the membrane is reduced due to attenuation. The stronger acoustic intensity delivered by the 35 kHz US (Mason and Peters, 2002) allow greater cavitational effects and mechanical forces to reach the inner zone. This made USAMe35 superior in cleaning the membrane and enhancing the adsorption of foulants, hence resulting to greater fouling abatement.

4.4.Toxicity

Raw wastewater, feed samples, and USAMe effluents produced “No Effect” to *D. Magna*. Slight immobilization of daphnids resulted from ultrasonication at 130 kHz, which is attributable to the more effective EC degradation at higher ultrasonic frequency (Mason and Peters, 2002) that could generate transformation products of unknown effects. Nevertheless, toxicity results still qualify within the “No Effect” toxicity level, indicating production of safe effluents.

5. Conclusions

Auxiliary methods were found effective in enhancing membrane performance through fouling control, showing enhancements in the increasing order: USMe>AMe>USAMe, with fouling control under 35 kHz superior that that of 130 kHz for processes employing ultrasound. The contribution of adsorption to control fouling is higher than that of ultrasound, but both methods work together in the hybrid process as the employment of one method enhances the performance of the other method.

This study demonstrated the capacity of the USAMe process to effectively enhance performance and control fouling in a hollow fiber membrane of cross-flow configuration, thus showing great potential for an industrial application. In addition, toxicological tests reveal production of safe effluents. This hybrid process could also offer several advantages, which include compact design and simple operation, system stability, increased productivity, longer membrane lifespan, enhanced permeate quality, and easy integration to the existing wastewater treatment facilities.

The efficiency of the USAMe process is influenced by important process variables, such as ultrasonic frequency and adsorption dose, or may also be affected by the permeate flux, recycle ratio, membrane material, and ultrasound source and configuration. Thus, optimization of these variables are worthy of investigation.

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