

Effect of periodic backwash in the submerged membrane adsorption hybrid system (SMAHS) for wastewater treatment

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Abstract

The submerged membrane adsorption hybrid system (SMAHS) is an attractive solution in treating wastewater; however it faces membrane fouling although to a less extent. In this study, different adsorbents and resins were investigated in order to find a substitute to the powdered activated carbon (PAC); The effect of new backflush was also studied in further reducing the membrane fouling. The SMAHS led to 72–86% dissolved organic carbon (DOC) removal. A detailed study on the transmembrane pressure development led to a conclusion that there is a critical flux and this value is around 16 l/h.m² for the wastewater studied.

Keywords: Submerged membrane; Hybrid system; Adsorption; Ion exchange; NOM; BTSE; Modified Freundlich; Periodic backwash

1. Introduction

Natural water as well as the biologically treated sewage effluents (BTSE) contains organics that are one of the main targets in water treatment. In fact, humic substances which are the major fraction of aquatic organics are the precursors of

the disinfection by products which are harmful for human beings [1].

The origin of the organic matter is variable, however Drewes and Croué [2] found that the effluent of a wastewater treatment plant with high sludge residence time had the same structural characteristics as the natural organic matter (NOM) found in rivers.

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Besides, F. Li et al. [3] analysed the dissolved organic matter for different water sources (rivers, groundwater, wastewater after biological treatment and synthetic water of humic acids) by high performance size exclusion chromatography and found similar chromatogram peaks for ground and river water, whereas the same peaks are found in wastewater and many others.

Ultrafiltration can retain DOM only partially leading to an important fouling. NF is more efficient but has inherent drawbacks: lower permeate flux and higher transmembrane pressure, thus higher cost of investment and operation.

Membrane filtration has to be enhanced by physicochemical process to achieve superior organics removal. This is why studies of coupled processes (adsorption and or flocculation + UF or MF) have been proposed recently [4–6].

Hybrid systems (or chemically assisted membrane separation) are emerging as highly promising technologies for water and wastewater treatment.

In this study, the combination of a submerged hollow fibre membrane with powdered activated carbon (PAC) adsorption (adsorption–membrane hybrid system) was used to remove organics from a synthetic wastewater representing biologically treated sewage effluent (BTSE).

This study incorporates also a study of alternative adsorbents and resins that could compete with PAC.

This study considers only the physicochemical behaviour of the process without taking into account the biological activity in the removal of organics.

2. Equipments and methods

2.1. Synthetic waters

Two kinds of synthetic waters were prepared to study the behaviour of natural and effluent organic matter. The synthetic natural organic matter was prepared by using the Biohumic product from Bioiberica S.A. It is a product with agricultural vocation composed of 85% humic and fulvic acids.

A calibration curve between the TOC and UV254 nm (Fig. 1) was obtained which allows an easy follow-up of the concentration by UV absorption.

The second secondary synthetic wastewater effluent (BTSE) was prepared from persistent organic compounds that are slowly biodegradable. The composition recommended by Seo [7] is presented in Table 1.

A calibration curve between TOC and UV254nm (Fig. 2) was also obtained.

2.2. Adsorbents and resins

Several adsorbents and resins were tested in order to find out a substitute of PAC which could

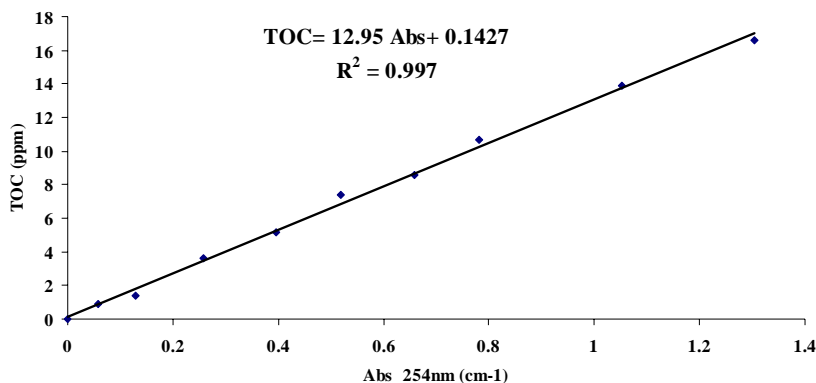


Fig. 1. Calibration curve AbsUV254nm–TOC for the synthetic water I (NOM).

Table 1
Composition of the wastewater

Compounds	Concentration (mg/L)
Beef extract	1.8
Peptone	2.7
Humic acid	4.2
Tannic acid	4.2
Sodium lignin sulfonate	2.4
NH ₄ HCO ₃	19.8
Sodium lauryle sulphate	0.94
Acacia gum powder	4.7
Arabic acid (polysaccharide)	5
(NH ₄) ₂ SO ₄	7.1
K ₂ HPO ₄	7
MgSO ₄ ·3H ₂ O	0.71

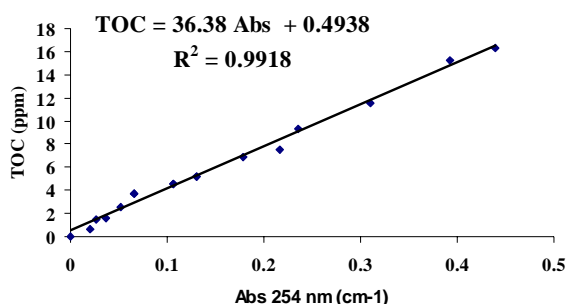


Fig. 2. Calibration curve Abs 254nm TOC for the synthetic wastewater II.

Table 2
Characteristics of the resins

Resin	Pore structure	Functional group	Matrix	Size (mm)
Lewatit VP OC 1071	Gel	Quaternary ammonium type I	Polyacrylic amide	0.55
Lewatit Mono Plus MP 500	Macroporous	Quaternary ammonium type I	Polystyrene	0.63
Purolite A500P	Macropous	Quaternary ammonium	Styrene Divinyle Benzene	0.3 — 1.2

Table 3
Characteristics of the powdered activated carbons

Specification	Norit SA UF	PAC WB
Iodine number, mg/g.min	1050	900
Ash content, %	10	6 max
Moisture content, %	3	5 max
Bulk density, kg/m ³	250	290–390
Surface area, m ² /g	1150	882
Mean pore diameter, Å	—	30.61
Micropore volume, cc/g	—	0.34
Mean diameter	10	19.71

be less expensive and/or easily regenerable. The characteristics of the resins used as well of the powdered activated carbons used are summarised in Tables 2 and 3.

Adsorption isotherms and kinetics were established by using either a mixer “Rotamix” (rotation of 8 bottles of 100 ml at 20 rpm) or the “jar test” in which six 1 L beakers containing the samples of water to be treated are agitated by a rotating blade (150 rpm).

The TOC analysis of the synthetic waters as well as the effluent was carried out by the TOC meter Bioritech in the range 1–50 ppm. UV absorbance (254 nm) was measured by the spectrophotometer HP8452 Diode Array.

However, TOC results are in fact DOC as all the samples were filtrated on Millipore membrane of 0.45 microns before analysing.

2.3. Hybrid reactor

This hybrid reactor has been used for several years in the Environmental Engineering R&D Laboratory of the University of Technology, Sydney (UTS) and described in detail elsewhere [6].

A hollow fiber microfiltration module, whose characteristics are summarized in Table 4, is immersed in the reactor of 6 L (Fig. 3).

The solution to be treated was initially put in contact with the activated carbon for pre-adsorption before the filtration step. An intense bubbling produced by porous diffusers at the bottom of the

tank ensures a good mixing and playing at the same time a beneficial role for limiting the membrane fouling.

The initial filtration flux was fixed at 36 l/m²h which corresponds to a hydraulic residence time (HRT) of 3.3 h.

The pressure–flow characteristic of peristaltic pump used resulted in decreasing permeate flux when the transmembrane pressure increased due to the fouling of the membrane.

The initial concentration of PAC was 2 g/L. 10% of the PAC was extracted daily and replaced giving a residence time of the activated carbon of 10 days.

NaOCl was added at a low dosage (10 mg/l) to avoid the formation of a biofilm on the membrane and ensure that only the physicochemical phenomena played a role. The transmembrane pressure TMP was recorded every 30 s. The operation was carried out with 60 min filtration followed by a backwash until obtaining a difference of TMP of 1 kPa during 5 s or less. The method for backwash control has been formerly described [8]. Samples were taken periodically from the reactor and the permeate for DOC measurement.

Table 4
Membrane characteristics

Material	Hydrophilic polyethylene
Nominal pore size, μm	0.1
Surface area, m ²	0.05
Inner diameter, mm	0.27
Outer diameter, mm	0.41
Membrane manufacturer	Mitsubishi-Rayon, Tokyo, Japan

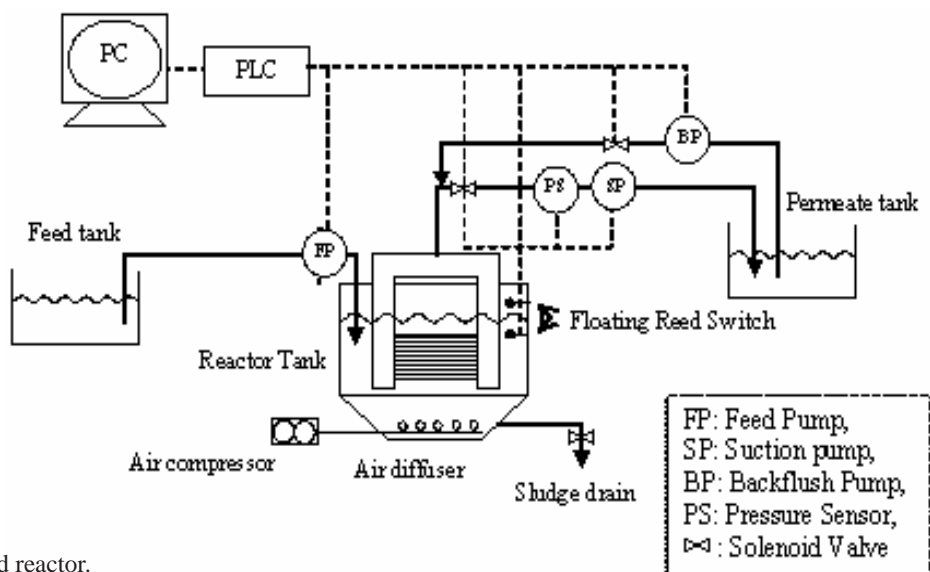


Fig. 3. Hybrid reactor.

3. Results and discussion

3.1. Adsorption/ion exchange

3.1.1. Preliminary tests

3.1.1.1. Resins

Three resins containing a quaternary ammonium functional group (supposed to be very effective for organics removal) were chosen for these tests (Table 5).

The tests of adsorption on the ion exchange resin (concentration of 5 g/L) with synthetic natural organic matter solutions (initial TOC 6.7 ppm) show that Purolite A500P (Table 5) has a larger adsorption capacity than the other resins.

This result is in agreement with those of Brian Bolto [9] and may be explained by the nature of the resin (polystyrene resin more selective than an acrylic resin) and by its structure. (the larger adsorption capacity of Purolite A500P is due to its macroporous structure whereas Lewatit VP OC is a microporous gel type). According to these results, Purolite A500P was chosen for a comparative study with PAC.

3.1.1.2. Activated carbon

Two PACs were tested. The comparison of the kinetics of adsorption of the natural organic matter (10 ppm) onto both activated carbons (concentration of 1 g/L) shows (Fig. 4) that the Norit SA UF is more effective than the PAC-WB. As for the resins, this result is due to the structure of the PAC, macroporous for Norit SA UF, microporous for CAP-WB.

As humic substances do not contain only low molecular weight fraction, the adsorption is more complete on a macroporous adsorbent.

3.1.1.3. Influence of the particle size of the adsorbents or resins

The size of the particles has a very significant role in the adsorption phenomena. Indeed by grinding a commercially available resin not only the kinetic is faster due to the decrease of diffu-

Table 5
Retention of the resins

Resin	% retention
Lewatit VP OC 1071	35.4
Lewatit MP 500	34.9
Purolite A500P	81.7

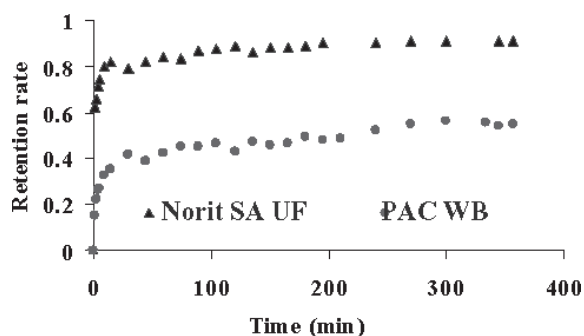


Fig. 4. Comparison of kinetics of adsorption of NOM onto PAC Norit SA UF and PAC-WB.

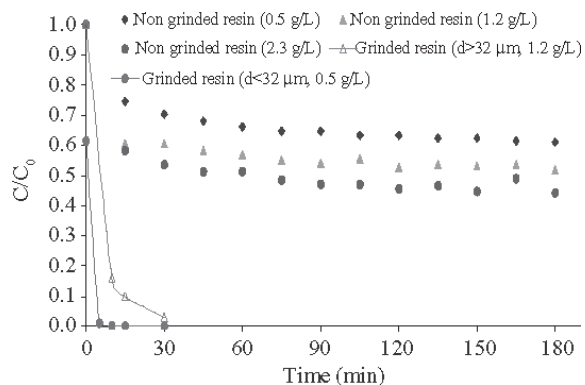


Fig. 5. Influence of resin particle size on the adsorption kinetics.

sional resistances, but the capacity of adsorption is increased by grinding (Fig. 5). This can be explained by the fact that grinding could modify the structure of the resin by creation of charged sites or eventually by making more sites accessible.

This result proves the advantage of using a combined process fine particle adsorption/membrane separation in place of the conventional process using a granular bed followed by membrane separation.

3.1.2. Comparison between activated carbon and ion exchange resin: influence of the initial concentration of organic matter

A study of the isotherms of adsorption of the natural organic matter was carried out for the activated carbon Norit SA UF as for the grinded resin Purolite A 500P (average particle size 10 micron). The results (Fig. 6) highlight the influence of the initial organic matter concentration.

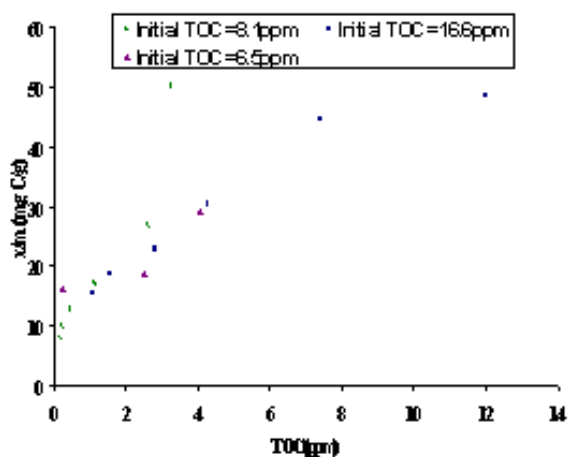


Fig. 6. Isotherm of adsorption of NOM onto PAC Norit SA UF.

Table 6
Isotherm modelling

Purolite A500P	Norit SA/UF
$\frac{x}{m} = 24.04 \left(\frac{TOC_{equi}}{M} \right)^{0.3152}$	$\frac{x}{m} = 14.37 \left(\frac{TOC_{equi}}{M} \right)^{0.279}$

With x/m — amount of organics adsorbed by gram of adsorbent (mg of C/g) and M — concentration of adsorbent (g/L).

This phenomenon already observed [10] could be explained by the electrostatic repulsions between the adsorbed or exchanged molecules and the molecules present in the solution. The isotherms thus obtained could be described by the Modified Freundlich Isotherm [11] instead of the conventional models used for single solutes (Fig. 7 and Table 6).

It can be seen that the grinded resin is as efficient as the PAC as shown in Fig. 8.

Similar results have been obtained for the adsorption of the synthetic secondary effluent on the two powder activated carbon Norit SA UF and PAC WB (Table 7 and Fig. 9). It was observed that the activated carbon Norit SA UF has a capacity of adsorption higher than that of PAC WB.

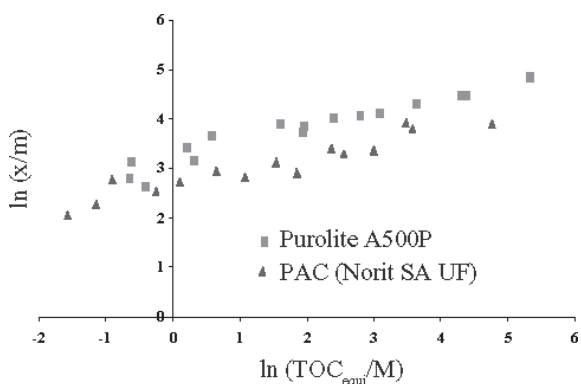


Fig. 7. Modified Freundlich isotherm.

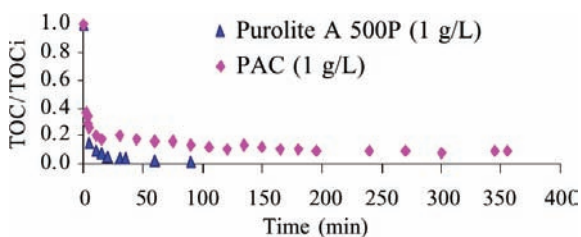


Fig. 8. Comparison of the kinetics of adsorption of NOM onto Norit SA UF and Purolite A 500P.

Table 7
Isotherm modelling

PAC WB	Norit SA/UF
$\frac{x}{m} = 3.65 \left(\frac{\text{TOC}_{\text{equl}}}{M} \right)^{0.555}$	$\frac{x}{m} = 18.05 \left(\frac{\text{TOC}_{\text{equl}}}{M} \right)^{0.2582}$

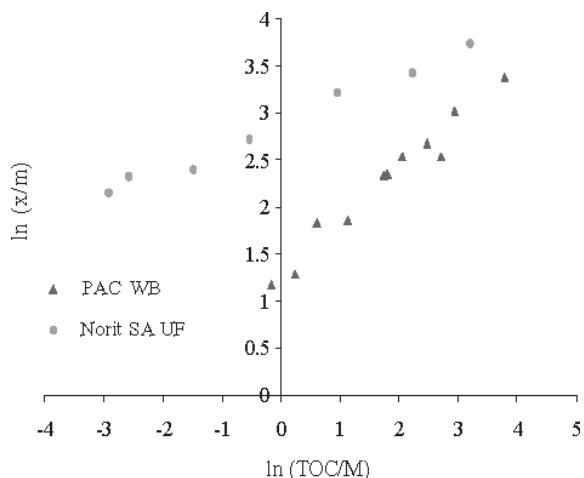


Fig. 9. Adsorption isotherm of synthetic secondary effluent onto the PAC.

3.2. Hybrid process

The first tests of the hybrid process were carried out deliberately with PAC WB (rather than with Purolite) for a better understanding of the respective roles of the adsorbent and of the membrane. The DOC of the permeate and in the reactor was measured every 12 h.

The DOC of the synthetic secondary effluent is not strictly constant: it varies between 10 and 15 ppm. It was observed (Fig. 10) that in spite of a relatively long period of operation (more than 5 days) the reactor did not reach a stationary state and that organic matter continued to accumulate. In spite of that, the membrane effectively retained the organics.

As mentioned previously, the addition of hypochlorite prevents any biological phenomena

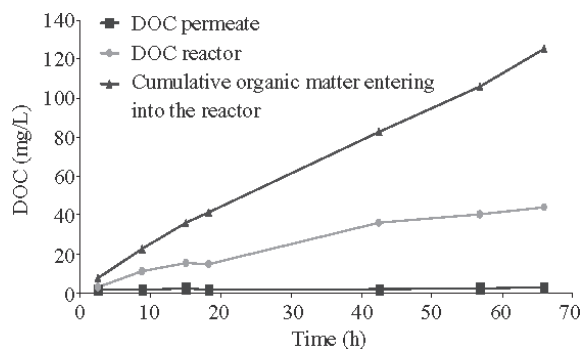


Fig. 10. Evolution of the DOC in the reactor and permeate.

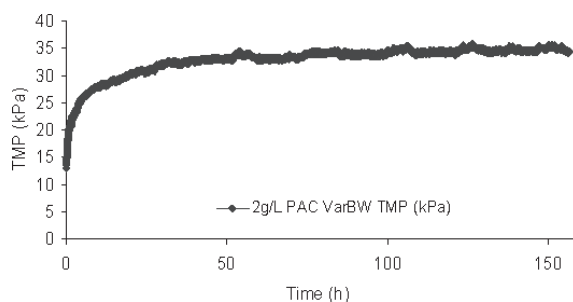


Fig. 11. Evolution of the TMP.

in order to study only the physicochemical phenomena.

Fig. 11 shows that after a few operating hours the reactor was in a quasi stationary state. However due to inverse pressure–flow characteristic curve of the peristaltic pump, the initial flow varied and progressively decreased as the membrane fouled.

The refined analysis of the data obtained during each successive sequence of filtration of one hour duration makes possible the determination of the fouling rate variation according to the flux.

The variation is due to the unsteady state operation but the tendency to stabilisation can be observed, thus allowing the determination of a critical flux of about 16 l/h.m² (Fig. 12).

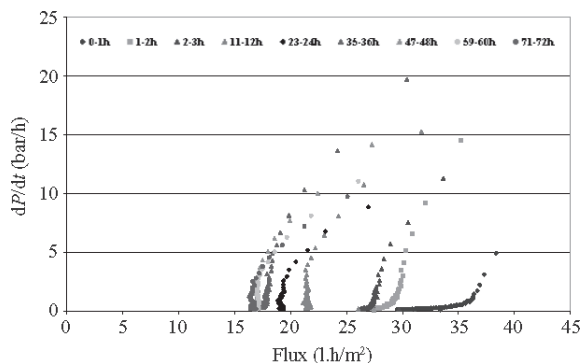


Fig. 12. dP/dt vs. flux.

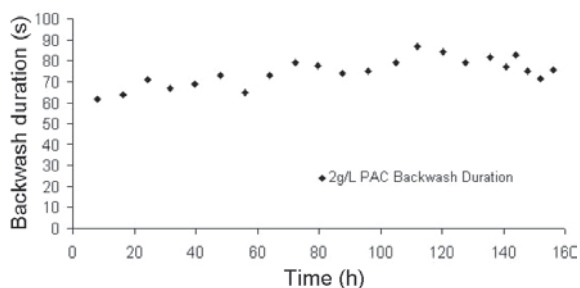


Fig. 13. Evolution of backwash duration.

The backwash duration varied between 60 and 80 s.

The optimisation of backwash duration has been studied previously [12] and the values of backwash duration (Fig. 13) in this experiment appeared to increase at a slower rate, probably due to the PAC replacement reducing the rate of concentration built up in the tank. The PAC replacement is efficient as there is less fouling leading to a decrease of the backwash duration and thus a greater production and a decreased cost.

4. Conclusion

This study resulted in the identification of a possible substitute to PAC: Purolite A 500P which has more exchange capacity. The kinetics of adsorption on the grinded resin is as fast as on the PAC.

By coupling MF and PAC it was possible to reach a retention rate of 80% of the organic matter of the secondary effluents without any biological activity and with a small consumption of adsorbent.

The phenomena of biodegradation should improve these results and allow to a certain extent bioregeneration of the adsorbent.

The permeate flux obtained is relatively low but the optimum conditions for operation have not been determined yet.

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One of the authors, Sarah Khirani, is presently involved in a double degree PhD program between UTS Sydney and INSA Toulouse France.

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