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Technical and Economic Impact of Photocatalysis as a Pretreatment Process Step in Olive Mill Wastewater Treatment by Membranes

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In this work, the technical and economic benefit of using photocatalysis as a pretreatment step for a subsequent olive mill wastewater (OMW) treatment process by membranes will be discussed.

Membrane processes appear to be suitable to purify aqueous wastewater streams polluted by organic matter such as OMW, but suffer severe fouling. In order to avoid fouling, the use of operating conditions below the boundary flux are suggested. The problem is that in many cases, boundary flux values are extremely low, making the process economically not feasible. In order to overcome this limitation, pretreatment steps are necessary to increase boundary flux values accordingly. Photocatalysis appears to be capable to achieve these requirements: on one hand, the process is capable to reduce the organic load of the feedstock and on the other hand, particle size distributions of the suspended organic matter are changed. Both principles are known in literature to lead to boundary flux value changes.

In this paper, the authors report the obtained results of the experimental work concerning membrane performances with and without photocatalysis as a pretreatment step, by treating 2-phase and 3-phase olive mill wastewater streams from Spain and Italy, respectively; furthermore, the economic impact of the different design choices and the evaluation of the general process scheme will be reported in all cases.

1. Introduction

As an indication of the popularity of membrane fouling problems, the growing evolution over the last 5 years has led to more than 3000 papers published in international journals trying to satisfy these research criteria (data taken from Scopus, Dec 2016). Despite this incredible effort by researchers, the reduction of membrane fouling remains as in the past one of the main challenges of the broad applied membrane technology during the last decade (Barker, 2004). The reason for this is that fouling on membranes does not only lead to sensible investment losses, due to the need of a premature module substitution, but also gives rise to unexpected increases of investment costs during the development and design of membrane plants: therefore, engineers tend to design membrane processes with an excessive oversized capacity, up to 35% (Environmental Protection Agency, 2005).

This fact ever applied especially on wastewater purification processes (Lim and Remby, 2003). This latter situation has a great economic impact on the process since the permeate, that is purified water with a quality grade compatible with irrigation use, has limited economic value.

Field et al. (1995) introduced the concept of critical flux for microfiltration (MF), stating that there is a permeate flux below which fouling is not promptly observed. It was immediately clear that the new developed concept could be a powerful optimization tool for this kind of separation operations. Afterwards, it was possible to identify critical flux values on ultrafiltration (UF) and nanofiltration (NF) membranes systems, too (Manttari and Nystrom, 2000). Nowadays, the critical flux concept is well accepted by both scientists and engineers (Bacchin et al., 2006).

The main drawback of this concept is that the determination of critical flux values cannot be theoretically predicted, but only experimentally measured by time consuming experiments. Critical flux depends on various factors, such as hydrodynamics(Vyas et al, 2002), feed stream composition (Zhou et al., 2009) and membrane surface characteristics (Badrnezhad and Mirza, 2014).

In many cases, concerning agricultural wastewater streams, the entering feedstock quality is not constant during time. Moreover, batch membrane processes are preferred in order to limit the amount of required membrane area, and the overall investment costs, as well. Again, during the batch operation, the feedstock quality sensibly changes. As a consequence, critical flux values never remain constant, which represent a major difficulty in fine tuning optimal operating conditions.

In case of real wastewater streams Le Clech et al. (2006) noticed that operations below the critical flux may not be sufficient in order to have zero fouling rates. Therefore, it appears that membrane systems treating real wastewater streams do not exhibit a critical flux in strict way. To overcome this limitation in the definition of critical flux, in a recent paper, Field and Pearce (2011) introduced for the first time the concept of threshold flux. Summarizing briefly the concept, the threshold flux is equal to the permeate flux above which short-term fouling can be observed and below it only long term fouling is triggered.

In the past years, before the concept of the threshold flux was introduced, many papers on model (Iaquinta et al., 2009) and real olive vegetation wastewater (OVW) purification by membranes, mainly UF (Stoller and Ochando Pulido, 2012) and NF (Stoller and Ochando Pulido, 2013), always determining critical fluxes, were published by the authors. As Stoller and Ochando Pulido (2014) pointed out, Irreversible fouling arises quickly on the membranes due to the high concentration of pollutants when wastewater is purified without any pretreatment, and different pretreatment processes influence to a variable extent the critical flux values. Therefore, proper and optimal designed pretreatment processes on the given feedstock must be developed in order to maximize productivity and minimize fouling: this objective will be referred from now on as the concept of pretreatment tailoring of membrane processes.

The Authors observed in previous research works the change of the fouling regime by using olive mill wastewater (Stoller et al., 2014). Despite the applied optimization methods were based on modified critical flux measurements, before the threshold flux concept ever existed, successful fouling control was accomplished on this system, and in detail justified by means of the threshold flux in 2013 (Stoller, 2013).

In fact, critical and threshold flux concepts share many common aspects which merge perfectly into a new concept, that is the boundary flux and was introduced 2013 by the authors. Increasing the boundary flux values, thus the process productivity values without triggering severe membrane fouling, appears to be mandatory to reach the economic feasibility of the treatment process.

In case of OMW, pretreatment processes are necessary to achieve this result. Beside gridding and flocculation, on the basis of the data reported in this paper, nanotechnologies (Bavasso et al., 2016) and in particular photocatalysis appears suitable to sensibly help reach these results in liquid and soils (Gueye et al., 2016). In order to achieve economic feasibility of the process, the recovery of the catalyst has to be taken into account, since immobilized systems may not be used due to the high opacity of the wastewater. This fact restricts to operate with suspended photocatalitic particles. For this purpose, magnetic core titania particles were developed, capable to be recovered by means of a magnetic trap (Ruzmanova et al., 2013a). The produced particles have a dimension in the range of tens of nanometers, in order to maximize their efficiency due to the high surface to volume ratio they exhibit (Ruzmanova et al., 2013b). The particles were produced by means of a spinning disk reactor, and the procedure is reported elsewhere (Stoller et al., 2013).

In this work, both wastewater streams exiting 2-phase (OMW2) and 3-phase (OMW3) olive oil production processes were taking into account, and for both wastewater feed streams economic considerations will be performed to check process optimization.

2. Technical considerations

The two wastewater samples were treated by means of different pretreatment steps, always including acid flocculation by HNO_3 (AF) as proposed by Bravi and developed together with Stoller (2010), and photocatalysis by means of titania nanoparticles (PC). Other pretreatment procedures were tried in the past, such as biotech approaches (Cicci et al., 2013) and adsorption (Stoller et al., 2011), but with a lower success rate, and therefore here not considered. Biotech appears to be suitable for post treatment purposes only (Stoller et al., 2016)

The pretreated feedstreams were then processed by two different membranes in order to estimate the boundary flux values: an ultrafiltration membrane (UF) and a nanofiltration membrane (NF), both supplied by Desal Osmonics model GM and DK, respectively.

By adopting the pretreatment processes, following boundary flux values J_b were obtained for an ultrafiltration and nanofiltration membrane, respectively (Table 1).

Table 1: Boundary flux values

Feedstream	Membrane	Pretreatment processes	J_b [$l\ h^{-1}\ m^{-2}$]	TMP_b [bar]	α [$l\ h^{-2}\ m^{-2}\ bar^{-1}$]
OMW2	UF	AF	7,3	8	0,0160
OMW2	UF	AF and PC	9,4	9	0,0110
OMW2	NF	AF	10,3	7	0,0070
OMW2	NF	AF and PC	12,5	8	0,0050
OMW3	UF	AF	3,1	4	0,0239
OMW3	UF	AF and PC	7,6	6	0,0553
OMW3	NF	AF	12,2	4	0,0084
OMW3	NF	AF and PC	14,9	8	0,0191

It appears that there is a benefit in adopting additionally photocatalysis as a pretreatment process for wastewater membrane purification plants. The productivity of the plant is increased of 22.3% and 17.6% for UF and NF in case of OMW2 and of 59.2% and 18.1% for UF and NF in case of OMW3, respectively.
Concerning the value of α, the two feed streams reacts differently to the PC pretreatment: it appears very favourable for OMW2, less for OMW3 where an increase of this parameter may be observed.

3. Economic evaluation

Economics will be studied by taking into account the treatment with a total recovery of 73%, that is a recovery value of 90% for each process step, in 18h operating time T for 1000 operating cycles. All the operation will be performed below boundary flux conditions, by adopting the method and strategies described in other works.
In order to permit an economic comparison of the different systems, a simplified evaluation of the capex and opex costs was performed and based on the following assumptions:

CAPEX

- Membrane modules are of 32m^2 each, cost with membrane housing equal to 1500 Euro;
- Piping accounts for 15% of overall costs;
- Fixed capex costs are pumps, tanks, stirring systems and accessories, accounting for a fixed cost of 50000 Euro up to the investigated plant capacities.

OPEX

- Membrane modules lasts at least 1000 operating cycles;
- Electricity is available at the cost of 0,1 Euro kWh^{-1};
- Acid costs are 0,35 Euro l^{-1}; usage is 10 l m^{-3};
- Preparation of the photocatalyst costs 200 Euro kg^{-1}, and is recovered back at 98%; usage is 3kg m^{-3}.

Since membrane aging will occur, this parameter (Δw%) is taken into account by a 10% for 1000 cycles. This approximation relies on the observation performed on OMW3 values over several years, and due to the lack of data for OMW2, will be taken equally. In order to estimate the membrane area required for each process, following relationship is used as reported on the Boundary Flux Handbook (Stoller and Ochando Pulido, 2015):

$$A = F\ Y\ ((1-\Delta w\%)\ J_b(T))^{-1} \qquad (1)$$

where F is the flow rate of the wastewater stream, Y the recovery value and $J_b(T)$ the boundary flux value at the end of operation, that is:

$$J_b(T) = J_b - \alpha\ T\ TMP_b \qquad (2)$$

By adopting this approach, the target capacity requirements during the last operation cycle of the membrane are fulfilled and as a consequence, were certainly reached in all other previous operation cycles as long as the operation were performed below boundary flux conditions.
In Table 2-4, the performed economic evaluation results are reported for different plant capacities.

Table 2: Economic evaluation results referred to 1m^3 of treated wastewater, plant capacity 10m^3 d^{-1}

Feedstream	Membrane	Pretreatment processes	A [m^2 m^{-3}]	CAPEX [Euro m^{-3}]	OPEX [Euro m^{-3}]	TOTAL COST [Euro m^{-3}]
OMW2	UF	AF	33,27	6,96	4,15	11,11
OMW2	UF	AF and PC	50,74	7,07	8,23	15,30
OMW2	NF	AF	62,72	7,15	4,07	11,21
OMW2	NF	AF and PC	78,45	7,25	8,15	15,39
OMW3	UF	AF	9,19	6,81	3,82	10,63
OMW3	UF	AF and PC	10,84	6,82	7,99	14,80
OMW3	NF	AF	77,22	7,24	3,82	11,06
OMW3	NF	AF and PC	80,92	7,26	8,15	15,41

Table 3: Economic evaluation results referred to 1m^3 of treated wastewater, plant capacity 30m^3 d^{-1}

Feedstream	Membrane	Pretreatment processes	A [m^2 m^{-3}]	CAPEX [Euro m^{-3}]	OPEX [Euro m^{-3}]	TOTAL COST [Euro m^{-3}]
OMW2	UF	AF	99,82	2,46	4,15	6,61
OMW2	UF	AF and PC	152,21	2,57	8,23	10,80
OMW2	NF	AF	188,17	2,65	4,07	6,71
OMW2	NF	AF and PC	235,36	2,75	8,15	10,89
OMW3	UF	AF	27,56	2,31	3,82	6,13
OMW3	UF	AF and PC	32,52	2,32	7,99	10,30
OMW3	NF	AF	231,67	2,74	3,82	6,56
OMW3	NF	AF and PC	242,75	2,76	8,15	10,91

Table 4: Economic evaluation results referred to 1m^3 of treated wastewater, plant capacity 50m^3 d^{-1}

Feedstream	Membrane	Pretreatment processes	A [m^2 m^{-3}]	CAPEX [Euro m^{-3}]	OPEX [Euro m^{-3}]	TOTAL COST [Euro m^{-3}]
OMW2	UF	AF	166,37	1,56	4,15	5,71
OMW2	UF	AF and PC	253,68	1,67	8,23	9,90
OMW2	NF	AF	313,62	1,75	4,07	5,81
OMW2	NF	AF and PC	392,27	1,85	8,15	9,99
OMW3	UF	AF	45,93	1,41	3,82	5,23
OMW3	UF	AF and PC	54,20	1,42	7,99	9,40
OMW3	NF	AF	386,12	1,84	3,82	5,66
OMW3	NF	AF and PC	404,58	1,86	8,15	10,01

Finally, Table 5 summarizes the previous results.

Table 5: Summary of the economic evaluation results referred to 1m^3 of treated wastewater

Feedstream	Membrane	Pretreatment processes	TOTAL COSTS [Euro m^{-3}] 10 m^3 d^{-1}	30 m^3 d^{-1}	50 m^3 d^{-1}
OMW2	UF	AF	11,11	6,61	5,71
OMW2	UF	AF and PC	15,30	10,80	9,90
OMW2	NF	AF	11,21	6,71	5,81
OMW2	NF	AF and PC	15,39	10,89	9,99
OMW3	UF	AF	10,63	6,13	5,23
OMW3	UF	AF and PC	14,80	10,30	9,40
OMW3	NF	AF	11,06	6,56	5,66
OMW3	NF	AF and PC	15,41	10,91	10,01

Even simplified economic evaluation procedures were adopted, interesting conclusions can be withdrawn from this data.

It is possible to notice that opex costs are much higher than capex costs. With this insight, it is mandatory to have long lasting membranes working to keep the capex value that low. This can only be achieved by proper membrane fouling avoidance and process control (Stoller, 2016).

Moreover, the increase of plant capacity does exhibit sensible costs savings, since membrane technology is modular and such as, do not strictly follow classic scale-up rules. A plant capacity over 30m^3 d^{-1} ensures sensible capex optimization. Small plants are economically not feasible.

Finally, it appears that from an economic point of view, the use of PC is not profitable in the case of OMW2 and OMW3 treatment, almost doubling the opex costs.

4. Conclusions

In this paper the technical and economic feasibility of membrane processes treating olive mill wastewater streams was investigated.

From a technical point of view, pretreatment processes are necessary to reach usable boundary flux values. Without any pretreatment, membranes would suffer severe fouling even at low pressure values, and reach zero flux conditions within days. Operating below boundary flux conditions permit to use the membrane modules for many years.

A simplified economic evaluation of the proposed processes shows that the treatment of OMW2 and OMW3 have comparable costs, and these are mostly dependant of the used pretreatment process. In detail, the use of photocatalysis as an additional pretreatment process appears to be not reasonable, since costs are doubled. Acid flocculation appears to fully satisfy the requirements and should be adopted as a stand-alone pretreatment process for this kind of wastewater.

At the end, exceeding a minimum plant capacity of 30m^3 d^{-1}, overall treatment costs are in the range of 5-7 Euro m^{-3}, which is comparable to those paid nowadays by olive mill owners to discharge this wastewater on terrain or lagoons (7 Euro m^{-3}). These latter practices are low cost but against EU directives and are permitted by specific national legislation.

Surely, the proposed process may represent a valuable alternative to terrain discharge or lagoon practices, since environmental impact is reduced to only 26% of concentrates, suitable to biogas production, and have much lower costs than special waste discard procedures as desired by EU (30 Euro m^{-3}). Nevertheless, a critical point is yet not reached, since no cost savings can be guaranteed to the olive mill owners. Research should focus in the next future on reducing the pretreatment costs of OMW to 50%; in this case, a critical technical and economic point would be reached (total costs being 3 Euro m^{-3}) in order to promote this technology as definitively affordable.

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