**Electrochemical microfluidic reactors combined with nanofiltration for wastewater treatment – kinetics and modeling studies**

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**Highlights**

* Firs time combination between nanofiltration and micro-reactors for MWWTPs
* Optimal interelectrode gap related to maximal mass transfer
* Non-linear increase of decay rate constants with electrolyte concentration
* Increase of faradic yield with the number of nanofiltration cycles

**1. Introduction**

The continuous increase of water demand along with the raise of water scarcity due to climate change make water a very precious resource all over the world. To face this issue, it is considered to reuse treated wastewater within the same process or for a secondary purpose such as irrigation and even drinking water. In the aim at succeeding in the water reuse perspective, there are several scientific and technological obstacles to overcome. Numerous studies highlighted the presence of hazardous organic micropollutants (pesticides, pharmaceuticals residues, personal care products,…) in the water bodies at trace levels (from pg/L to µg/L), at the outlet of municipal wastewater treatment plants (MWWTPs). In this context, advanced physico-chemical treatments have been developed. Advanced oxidation technologies produce reactive radicals (e.g. hydroxyl radicals) [1]. Compared to chemical technologies that require the addition of chemicals, emerging electrochemical advanced oxidation processes (EAOPs) implement a clean reagent (e.g. electron) that allows producing *in situ* and continuously the oxidizing species, leading to higher removal yields [2]. Furthermore, the application of microfluidic reactor within the framework of EAOPs has spurred the capability of wastewater treatment. The average ionic conductivity of effluent of MWWTPs (~1 mS cm-1) is apparently too low for conventional macroreactor of EAOPs in–which the distance between electrodes is in the range of 1-4 cm [3]. Hence, supporting electrolyte reagent is very often added to compensate the low value of conductivity as to avoid huge ohmic drop in-between electrodes. In parallel, membrane filtration has been widely applied to produce clean water. It does not require the addition of chemicals and its efficiency has been well established. However, membrane is technically a filter. It is prone to fouling and concentrated effluent containing organics and very likely toxic compounds are separated in the retentate stream that need to be disposed then.

Thus, in this research work, synergy between nanofiltration and EAOPs is investigated. To date, the application of EAOPs to treat the concentrate of membrane separation techniques has already been reported in literature. However, no report has been found on the coupling of nanofiltration with microfluidic reactor moreover to treat the effluent of MWWTPs. As prevalently acknowledged, the efficiency of degradation of organics by EAOPs depends on various parameters and they behave differently in microfluidic reactors relatively to the macros. Therefore, throughout this study, the influence of different initial concentration of pollutant, inorganic matrix, applied current density, interelectrode distance and flow rate is particularly investigated. Experimental results of degradation and mineralization of representative pharmaceutics are accompanied with mathematical modelling taking into consideration the enhancement of mass transfer of organics, of kinetic of the redox reactions at electrodes and of flow behavior with microfluidic reactor.

**2. Methods**

A flow-by cell was used in a batch recirculated mode. The cathode was a piece of graphite felt or stainless steel while the anode was in stainless steel or a BDD coated on Niobium. The cathodes and anodes had the same geometric surface area of 50 cm2. The interelectrode gap was varied using polytetrafluoroethylene (PTFE) spacers of different thicknesses. The current intensity was applied using a power supply. When synthetic solution was used, representative inorganic salts (Ca2+, Mg2+, Na+, K+, NH4+, NO3-, PO43-) where added at concentrations similar to those found at outlet of MWWTPs. Real MWWTPs effluent were also used for comparison. The nanofiltration cell was a stainless steel cross-flow filtration unit using polyamide thin film (6.0 × 7.5 cm2) NF 90 membrane. The applied transmembrane pressure was varied from 3 to 15 bars.

**3. Results and discussion**

Varying the inter-electrode distance from 50 to 1000 µm highlight the existence of an optimal mass transfer coefficient at 500 µm (Figure 1a). At too short gap, the gas bubbles increase the mass transfer limitation. Interestingly, increasing the electrolyte concentration make increase non-linearly the acetaminophen decay rate constants (Figure 1b).



**Figure 1.** influence of inter-electrode distance on mass transfer (a) and electrolyte concentration on paracetamol decay rate constant (b).

**4. Conclusions**

The possibility of performing electrolysis at 1 mS cm-1 – the average conductivity in municipal WWTP outlets – could be considered in microfluidic reactors. Further results will be presented on the synergy between nanofiltration and electrochemical micro-reactor, i.e. relation between faradic yield and concentration factors.

**References**

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