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Decontamination of polluted discharge waters from surface treatment industries by pressure-driven membranes: Removal performances and environmental impact

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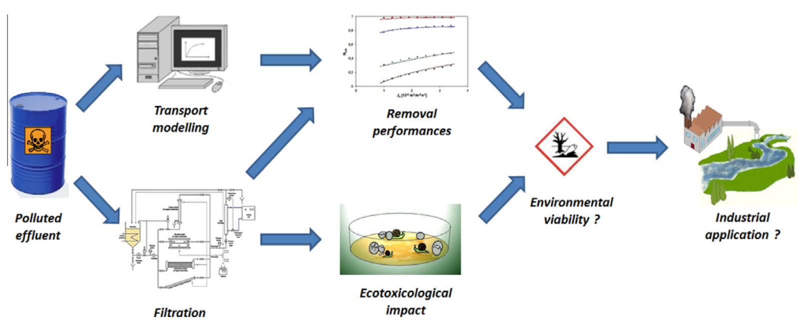
HIGHLIGHTS

- Nanofiltration allows very high rejection of heavy metals and micro-pollutants.
- Discharge water can have a noxious effect even at low pollutant concentrations.
- Eco-toxicity of synthetic metallic solutions mainly disappears after NF treatment.
- Significant toxicity remains after NF treatment of real discharge waters.
- Rejection of metal ions is governed by steric, electric and dielectric exclusions.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the feasibility of implementing a pressure-driven membrane process to remove toxicity from industrial discharge waters was investigated. Several kinds of membranes from reverse osmosis (RO) to tight ultrafiltration (UF) were tested and nanofiltration (NF) was found to be the most relevant process for such a problematic. The performances of heavy metals removal by a NF membrane was thoroughly analyzed firstly for synthetic solutions and afterwards for a real effluent from French surface treatment industry. The removal performances were found to be higher than 90% irrespective of the solution investigated. Numerical simulations have shown that steric exclusions alone cannot explain such removals, and electric and dielectric contributions also contribute to separation performances. Finally, the environmental impact of a NF step was examined through two bioassays. These ecotoxicological tests have shown that metallic synthetic solutions fully lose their toxicity after NF treatment whereas industrial discharge water led to a non-negligible detrimental influence, in spite of the noteworthy rejection of metal ions. This toxicity could probably be attributed to other non-metallic pollutants. To investigate their contribution to this residual toxicity, an analysis of organic micro-pollutants (PAHs, VOCs and APs) present in the effluent has therefore been carried out before and after filtration but their amount in the permeate stream was not sufficient to explain its residual toxicity.

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Nomenclature

A_k	porosity of the active layer
c_i	concentration of ion i within the pore (mol m^{-3})
$C_{i,p}$	permeate concentration of ion i (mol m^{-3})
$C_{i,r}$	bulk concentration of ion i (mol m^{-3})
$C_{i,w}$	wall concentration of ion i (mol m^{-3})
$D_{i,\infty}$	molecular diffusion coefficient of ion i at infinite dilution (m^2 s^{-1})
F	Faraday constant (96487 C mol^{-1})
j_i	ionic flux of ion i (mol m^{-2} s^{-1})
J_v	volumetric permeation flux (m^3 m^{-2} s^{-1})
$K_{i,c}$	ionic hindrance factor for convection (dimensionless)
$K_{i,d}$	ionic hindrance factor for diffusion (dimensionless)
L_p	water permeability (m^3 m^{-2})
P	pressure (Pa)
R	universal gas constant (8.314 J mol^{-1} K^{-1})
r_i	Stokes radius of ion i (m)
$R_{i,m}$	real rejection of ion i (dimensionless)
$R_{i,obs}$	observed rejection of ion i (dimensionless)
r_p	average pore radius (m)
T	temperature (K)
V	solvent velocity (m s^{-1})
x	axial position within the pore (m)
X_d	effective membrane charge density (mol m^{-3})
z_i	valence of ion i (dimensionless)

Greek symbols

$\gamma_{i,pore}$	activity coefficient of ion i in the pore side of the interface (dimensionless)
$\gamma_{i,sol}$	activity coefficient of ion i in the solution side of the interface (dimensionless)
ΔP	applied pressure (Pa)
ΔW_i	solvation energy barrier (J)
Δx	membrane thickness (m)
$\Delta\psi_D$	Donnan potential (V)
$\Delta\pi$	osmotic pressure difference (Pa)
ε_0	permittivity of free space (8.85419 10^{-19} C)
ε_b	bulk dielectric constant (dimensionless)
ε_p	pore dielectric constant (dimensionless)
η	dynamic viscosity (Pa s)
ϕ_i	steric partition coefficient (dimensionless)
ψ	electrical potential within the pore (V)

1. Introduction

The treatment of industrial wastewaters and discharge waters is currently a major environmental concern since the polluted wastewater volumes released by the industries are increasingly significant, irrespective of their field of activity. Moreover, due to the growing stress in many places of the planet, population has recently become aware of health and environment issues, so that industries are now faced to increasingly drastic European standards concerning the acceptable concentrations of noxious substances in their discharge. These restrictions have led industries to focus on new depollution processes to treat their wastewaters. In this framework, decontamination of multi-contaminated solutions appears to be an overriding challenge and especially for Surface Treatment (ST) industries [1–3]. As a consequence, ST industries are strongly affected by the presence in their effluents of heavy metals but also organic micro-pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs), Volatile Organic Compounds (VOCs), and possibly some endocrine disruptors (*e.g.*, Alkylphenols (APs)). Indeed, these compounds have a deleterious impact on environment [4–6] and a toxic effect on living organisms [7–9], even in trace amounts. Many technologies are available for wastewaters treatment [10,11] viz. coagulation-flocculation [12], precipitation [13], oxidation [14], sorption [15–17] (on activated sludge, charcoal or non-conventional material [18]), but among them, membrane processes, and especially pressure-driven membranes, have demonstrated a great potential for the decontamination of aqueous solutions [19–21]. Membrane technologies are indeed particularly attractive due to their respect of the treated solutions and environment, as they require neither temperature rise nor chemical adjuvant. For these reasons, they found applications in several fields such as waters from biotechnology [22], agrifood [23–25], pharmaceutical [26,27], or textile [28,29] industries as well as groundwater for drinking water production [30,31]. Nonetheless, despite their strong potential for decontamination, the use of membrane processes is still rather limited for industrial purposes, probably due to some drawbacks, such as fouling, lifetime or chemical resistance, despite the fact that most of them can be avoided [32]. In this context, nanoporous membranes exhibit suitable properties since their narrow pore size, close to nanometer, and their electrical charge allow the rejection of ions or small molecules such as organic micro-pollutants. In this study, it is thus proposed to investigate the possibility of purifying multi-contaminated discharge waters from a French ST industry by a final step of membrane treatment. Various kinds of membranes, in terms of both porosity (from dense reverse osmosis to tight ultrafiltration) and material (namely organic or ceramic), have been studied in this project, so that further investigations have been conducted on the most appropriate membrane.

Even though the performances of pollutant remediation, in terms of rejection, are of prime importance, the impact of the treatment on environment and health is also primordial. Consequently, the environmental benefits of such a process should be investigated on various bioassays. Many ecotoxicological tests can be implemented to analyze the pollution influence on human, animal or plant populations [33,34]. Here, the environmental impact of effluents before and after membrane treatment is studied by two biological indicators: the hatching of snail eggs through a liquid phase bioassay [35,36] and the mobility inhibition of an aquatic crustacean *Daphnia magna* [37,38].

Finally, the separation performances obtained in this study are investigated theoretically with a knowledge model to investigate how heavy metals are remediated by the membrane. The model used for this purpose is called Pore Transport Model [39] and was initially developed to describe multi-ionic separation by nanofiltration membranes but its use on real solutions could be very useful to understand the mechanisms governing the selectivity between ionic metals and small target molecules.

Although many studies have been dedicated to depollution by membrane processes, the originality of the proposed study lies in the coupling between four different but complementary approaches, viz. technological, chemical, biological, and numerical approaches.

Firstly, a brief description of the model used for the numerical discussion is provided. Then, materials and various experimental protocols used for membrane treatments and bioassays are accurately detailed. Afterwards, performances in terms of pollution remediation and eco-toxicological impact are discussed for both synthetic solutions and real industrial waters.