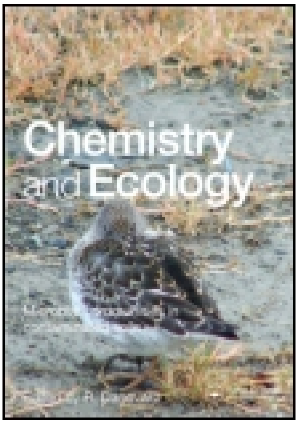

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gche20

Optimisation of batch membrane processes for the removal of residual heavy metal contamination in pretreated marine sediment

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To cite this article: M. Stoller, L. Di Palma & C. Merli (2011): Optimisation of batch membrane processes for the removal of residual heavy metal contamination in pretreated marine sediment, Chemistry and Ecology, 27:S1, 171-179

To link to this article: http://dx.doi.org/10.1080/02757540.2010.534083

Chemistry and Ecology
Vol. 27, Supplement, February 2011, 171–179

Optimisation of batch membrane processes for the removal of residual heavy metal contamination in pretreated marine sediment

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(*Received 24 November 2009; final version received 19 October 2010*)

In this article, an innovative process that uses membranes to purify marine sediments contaminated with heavy metals is presented. The proposed process is composed of a centrifugation step, performed with a hydrocyclone, followed by a batch membrane step. The initial separation of sand from the raw stream appears to be very efficient and is important to avoid plugging the membrane separation step. The remaining stream, called silt, is then processed by a batch membrane separation step, capable of separating organic and inorganic pollutants from the purified water. Pilot tests were carried out to estimate membrane performance, including the maximum recovery value achievable, typical rejection values, the permeate and critical fluxes.

Keywords: marine sediment; heavy metals; purification; contamination; membrane; fouling

1. Introduction

In the past, marine coasts have been severely polluted with many types of industrial contaminants, leading to a severe environmental emergency. The most common pollutants are heavy metals, widely known to be toxic to human and aquatic life. The presence of these pollutants is likely to persist for a long time because soil-adsorbed metals are washed into rivers, lakes or other aquifers such as the groundwater, where they accumulate and reach concentrations toxic to animals, plants and humans. Therefore, research efforts have been aimed at developing technologies for the purification of metal-contaminated soils and sediments [1].

This type of contamination is mainly encountered in marine sediments, deposited by gravity in a thin, superficial layer. This layer can be easily dredged from the sea using pumping systems and treated successfully [2]. Mechanically dredged marine sediments typically have a solid content comparable with that of *in situ* sediments, up to 50% by weight for most fine-grained sediments. By contrast, hydraulically dredged marine sediments are characterised by a smaller amount of solids, typically in the range of 10–20% by weight [3]. Therefore, both streams are composed mainly of contaminated seawater, which needs to be purified of all the pollutants originating in the sediments.

Several methods have been proposed for the remediation of heavy metal-contaminated soils. These methods are based on two principles: (1) immobilisation of the metal, by increasing its

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ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540.2010.534083
http://www.informaworld.com

retention in the soil or decreasing its rate of mass transfer; or (2) removal of metals from the soil matrix [4].

In the case of soil or marine sediments, previous studies have demonstrated that heavy metals (and other pollutants) mostly adsorb onto the fine fractions of solid matrices [5–7]. Therefore, separation of the fines from the coarse fraction of the soil and water is normally sufficient for proper purification. The main challenge is to separate purified seawater from contaminated fine sediments at the end of the process. This final step can be performed by ultrafiltration membranes.

Fouling of the membranes is one of the main challenges in the recent widespread application of membrane technology. Fouling decreases productivity and shortens membrane life. Critical flux determination seems to be the best method to identify process conditions that minimising fouling. At the critical flux point, the forces of drag on particles depositing on the membrane surface are equal to the dispersive forces, leading to a quasi-stationary layer. Under these conditions, only reversible fouling, which can be periodically soft-cleaned, takes place.

Field et al. [8] introduced the concept of critical flux with respect to microfiltration (MF), stating that it is the maximum permeate flux below which fouling is not observed. It was immediately clear that the new concept is an effective criterion for the optimisation of a membrane separation operation. Critical flux has also been defined for ultrafiltration (UF) and later for nanofiltration (NF) operations [9].

Currently, critical flux values cannot be predicted theoretically, but may only be evaluated experimentally or extrapolated from permeate flux–time data. Critical flux depends on, among other factors, hydrodynamics and the nature of the feed stream [10]. Similar hydrodynamic conditions may be attained at different scales if the same mean velocity over the membrane surface is applied.

Feedstock quality is a crucial parameter in respect to critical flux changes: this is particularly true for batch processes, which are characterised by a change in the pollutant concentration due to differences in batch concentrations. The chemical composition of both solvent and solute in the bulk are correlated to the solution phase change profiles, which are very important in understanding fouling issues [11]. Moreover, Sethi and Wiesner [12] noticed that the performance of UF membranes was strictly correlated to the particle size of the solutes in the solution. A study on critical flux changes was performed by introducing uniform polystyrene particles of known size, from 0.1 to 10 μm [13]. The observed trend, that is a minimum critical flux value for 0.2 μm particles, was explained theoretically by Harmant and Aimar using the coupling of different mechanisms between critical flux, surface interactions and diffusion [14].

Copper is one of most frequent contaminants in Italian marine sediments and was therefore taken as key contaminant during this research. In this study, a purification treatment process was developed to decontaminate different marine sediments of heavy metals, especially copper. The proposed process involved a preliminary size-based separation by centrifugation and a subsequent batch membrane separation process. The first step is performed using a high-performance hydrocyclone to separate the finest possible sediment grains by this technique. It should be possible to discharge the separated fraction, poor of contaminants, safely and inexpensively into the municipal sewer system. By contrast, the outgoing slurry is sent to a batch membrane operation step, where large quatities of purified seawater, which could be discharged back into the sea, are finally produced. The final fraction, i.e. the volume-reduced concentrate rich in fine sedimets and metal ions, needs to be disposed of.

To be economically feasibile, the process should avoid disposal and as far as possible produce outlet streams that are in compliance with the municipal sewer system and/or direct discharge limit.

The objective of this study was to carry out experiments on typical contaminated sediments in order to check whether the developed process is capable of producing high quatities of outlet streams compatible with a safe and cheap discharge.

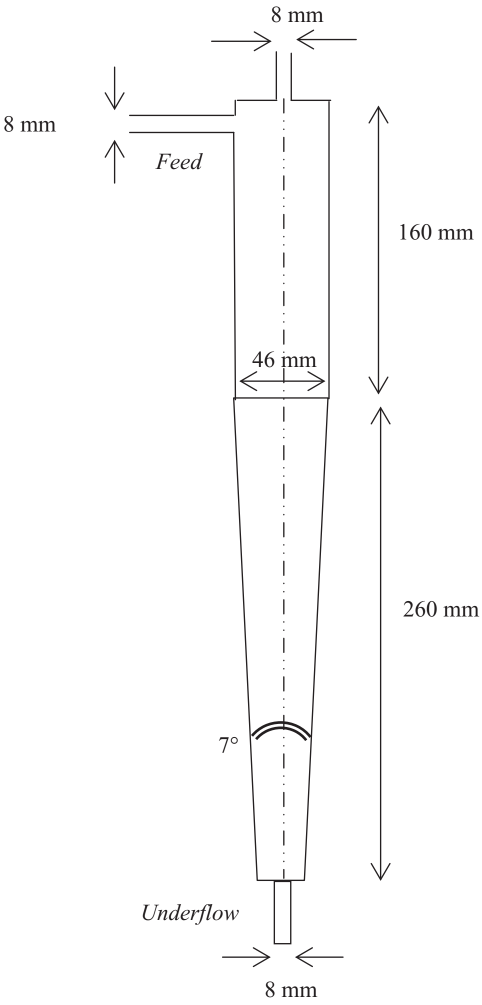

Figure 1. Scheme and dimensions of the adopted hydrocyclone.

2. Materials and methods

Artificial sediment mixtures were used for the experiments. Concerning the hydrocyclone separation step (Figure 1), different feedstocks were prepared to simulate sediments different in terms of both total solids concentration (TSC) and composition. Different amounts of sand and fines were mixed: the sand, defined as the fraction having particles $>0.63\,\mu$m, was collected from the Italian coast near Rome, whereas the fines were supplied by the CWR (Pero, Italy) in the form of clay [8]. The obtained solid mixtures were analysed by sieving. The data for the adopted feedstock are reported in Tables 1 and 2.

The sediment was artificially polluted with copper chloride. The contamination was carried out so as to obtain a concentration higher than the Italian regulation limit for copper at an industrial site, which is 600 mg Cu per kg of soil.

The sediment was spiked by mixing for 48 h at 120 rpm in a Hobart-type mixer together with a saturated aqueous solution of dihydrate copper chloride. After mixing, the sediment was air dried by exposure to ambient air for 90 days before metal analysis. Six 1 g samples of sediment were

Table 1. Sieving analysis results for the solid fractions used.

Material	>500 µm	500–63 µm	63–45 µm	<45 µm
Sand	42.5%	49.1%	8.4%	–
Clay	–	–	3.6%	96.3%

Table 2. Characteristics of the feedstock.

Name	Sand (%)	Clay (%)	TSC ($g \cdot L^{-1}$)
FSA1	100	0	4.2
FSA2	100	0	12.6
FSA3	100	0	21.1
FSA4	100	0	50.7
FSB1	80	20	10.0
FSB2	80	20	50.0
FSB3	80	20	150.0
FSB4	80	20	250.0
FSC1	70	30	10.0
FSC2	70	30	50.0
FSC3	70	30	150.0
FSC4	70	30	250.0
FSD1	20	80	5.0
FSD2	20	80	20.0
FSD3	20	80	40.0
FSD4	20	80	70.0

then processed by acid digestion according to the EPA3050B method: the leachate was analysed with a Philips PU9200 atomic absorption spectrophotometer to determine total metal content, after filtration through a Whatman membrane filter (0.45 µm).

The average Cu concentration was ~900 $mg \cdot kg^{-1}$ with a standard deviation of ±78 mg. Table 3 summarises the typical values and legal limits in Italy for reference purposes.

Table 3. Limits of Italian legislation for soil contamination.

	Maximum allowed heavy metal concentrations ($mg \cdot L^{-1}$)
Emission to aquifers	0.1
Emission to sewer systems	0.4
Potable water	0.02

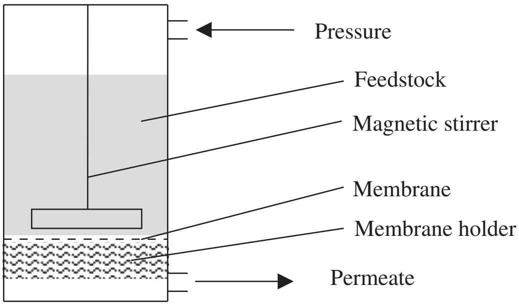

Figure 2. Schematic diagram of the membrane cells.

Table 4. Characteristics of the adopted membranes.

Name	P (Pa × 10^6)	Pore size (nm)	W Flux (L·hm^{-2}·bar^{-1})
MW	2.1	15.0	>600
EW	3.4	6.0	525
JW	3.4	5.0	400
GE	20.7	0.1	5

Membrane cells, supplied by Berghof, Germany (Figure 2), were used to analyse the performance of four different ultrafiltration membranes, all supplied by Osmonics. The characteristics of the different membranes, such as operating pressure, corresponding water permeability and typical pore size, are given in Table 4. The permeates were analysed for copper concentrations using flame spectroscopy (Philips PU9200 FLAAS). All the analyses were performed three times and the standard deviation calculated in each test was in the range between 0.6 and ~3.5%. Permeate fluxes were determined by weighing.

3. Results and discussion

Table 5 reports all the results obtained using the hydrocyclone on the different feedstock: ΔTSC is the percentage reduction in mass in the clarified solution compared with the initial TSC value, whereas the cut-off size is equal to the size of the largest particle found in the clarified solution with at least 15% wt. compared with the initial solution.

As expected, the reduction in suspended solids in the stream achieved by the hydrocyclone depended mainly on the percentage fines content of the feedstock. An increase in fines reduced the performance of the hydrocyclone. This can be justified by the cut-off value of the adopted hydrocyclone, which appears to be 45 μm, and the high quantity of particles below this value contained in the clay.

A quick analysis of various samples of the coarse particles separated by the hydrocyclone demonstrates that only very small to immeasurable amounts of copper were separated, well below the potable water common standards. Moreover, heavy metals, depending on the pH value,

Table 5. Results of the hydrocyclone experiments.

Name	Flow rate (L·h^{-1})	ΔTSC (%)	Cut-off size (μm)
FSA1	0.37	99.7	63
FSA2	0.37	99.9	45
FSA3	0.36	99.9	45
FSA4	0.36	99.8	45
FSB1	0.34	100.0	–
FSB2	0.33	89.7	–
FSB3	0.32	97.5	–
FSB4	0.30	95.8	–
FSC1	0.37	95.6	–
FSC2	0.36	80.8	–
FSC3	0.32	88.1	–
FSC4	0.31	92.2	–
FSD1	0.36	82.9	–
FSD2	0.35	55.7	–
FSD3	0.34	59.4	–
FSD4	0.34	51.1	–

solubilise in water at a maximum of 10 mg·L^{-1} (in the case of copper this is 5 mg·L^{-1}): because the maximum amount of seawater in the downstream is 4%, the maximum concentration of heavy metals is 0.4 mg·L^{-1}. Therefore, it appears that the coarse sediment recovered using this method could safely be sent into the sewer system as long as the water content remains below 4%, which maintains a heavy metal concentration that is in accordance with Italian Environment Regulation Limits [15]. Safe and legal discharge into the sewer system reduces the costs of cleaning up the environment.

However, the upstream has a heavy metal concentration well above legal limits, with heavy metals adsorbed onto fines and solubilised in seawater. Membrane treatment is therefore necessary to clean the permeate from fines and solubilised heavy metals. To meet cost-efficiency requirements, a highly permeable membrane should be chosen which is good enough to meet the legal requirements for sewer discharge.

The feedstock for these tests was the upstream of FSD3, which is the most representative feedstock in Italy. As a consequence, the initial TSC value is 16.24 g·L^{-1}. The results of the membrane tests in terms of permeability (permeate flux J_p) and copper concentration of the permeate ($c_{\mathrm{P,CU}}$) are reported in Table 6, as a function of the recovery factor Y and operating pressure P.

As expected, tabulated values of pure water flux were not obtained in the real case experiments, becaused the fines led to heavy fouling on the membranes. Increased fouling on the membranes reduces the longevity of the modules and, as a consequence, dramatically increases the costs. The advantage of fouling is that the additional layer on the membrane may lead to greater rejection values. At first glance, although the MW membrane appears to have the best permeability and selectivity in the tests, this is caused by excessive fouling. By contrast, the GE membranes appear to be too tight, with permeability values below measurable limits: the productivity of this membrane appears to be too low for this treatment process.

One method to evaluate fouling issues is to determine the decrease in the permeate flux rate over time [16]. The data points can be fitted using a logarithmic equation, such as:

$$J_\mathrm{p}(Y) = (m\,TMP - J_\mathrm{c})\,\mathrm{e}^{-BY} + J_\mathrm{c}, \tag{1}$$

where m is the permeability, *TMP* is the transmembrane pressure, B is the fouling factor and J_c is the critical flux. Because the critical flux value was not measured, a best fit was performed on parameters m, B and J_c, using the hypothesis of osmotic pressure = 0 (which applies on almost every ultrafiltration system), a constant critical flux (valid due to the short operation time of the

Table 6. Results obtained by membrane experiments.

Membrane	Y (%)	P (bar)	J_p (L·hm^{-2}·bar^{-1})	$c_{\mathrm{P,CU}}$ (mg·L^{-1})
MW	33	2.1	71.43	0.037
MW	66	2.1	34.95	>0.035
MW	99	2.1	26.00	>0.035
EW	33	3.4	27.88	0.283
EW	66	3.4	20.76	0.100
EW	99	3.4	15.12	0.107
JW	33	3.4	21.18	0.077
JW	66	3.4	15.35	0.070
JW	99	3.4	13.05	0.097
GE	33	8	<2	<0.001
GE	66	8	<2	<0.001
GE	99	8	<2	<0.001

Table 7. Estimated critical flux and fouling factor values.

Membrane	m	B	J_c (L·hm^{-2}·bar^{-1})
MW	60.0	0.023	15.0
EW	18.0	0.010	2.0
JW	14.0	0.015	8.0
GE	–	–	–

experiments), a constant value of m and the following constraint:

$$J_c \leq J_p(Y = 99\%), \tag{2}$$

The results of the fitting ($R^2 > 0.99$) are reported in Table 7.

A lower value of B corresponds to reduced fouling formation: in the examined case, it appears that the EW-type membrane suffered the least fouling. However, the critical flux of this membrane looks very low. This may be justified by the different membrane materials compared with the JW and MW membranes, which may interact more strongly with the suspended solids.

Because it is advisable to operate membrane processes below the critical flux, the MW membrane appears to be the best choice even though it is more prone to fouling in supercritical conditions due to the higher B value. In the subcritical condition, little fouling formation is achieved (as consequence of very low B values). This result was expected, because the particle size of the fines is much higher than the pore size of the membranes, above a ratio 1 : 10, and thus not capable of promoting fouling [17]. However, special care is needed and a optimised operation mode for the batch is strictly required [18].

At optimised operation, only 13.3% of the required EW membrane surface is needed compared with the MW membrane to obtain the same permeate fluxes, which corresponds to a reduction of 85% in membrane costs. Moreover, this membrane is preferred in respect to the selectivity. In Table 8, the final concentrations of copper in the permeate tank ($c_{\mathrm{P,CU}}$ FINAL) are reported.

The MW membrane ensured a total permeate stream quality well below Italian Environment Regulation Limits, permitting direct discharge to aquifers in the case of more heavy metal-concentrated streams also [15].

The purification of the seawater can be justified by the adsorption of the fines depositing on the membrane surface during the operation more than by the very limited capability of a loose ultrafiltration membrane to separate metal ions such as MW, EW or JW. In fact, the fines separated by the membrane quickly form a loose cake on the surface, and thus a secondary filtering layer capable of capturing additional dissolved metal ions from passing seawater. Because the thickness of this cake depends on the operating conditions and especially on the permeate flux, the MW membrane gave the maximum fines layer thickness of the analysed membranes, and thus the greatest dissolved metal ion rejection value. Only the GE membrane, with pore dimensions similar to those of a loose nanofiltration membrane, was capable of physically rejecting the copper ions, thus eliminating the dissolved metal ions with great efficiency, but with very small permeate fluxes.

Table 8. Final copper concentrations in the permeate tank at $Y = 99\%$.

Membrane	$c_{\mathrm{P,CU}}$ FINAL (mg·L^{-1})
MW	0.026
EW	0.163
JW	0.081
GE	<0.001

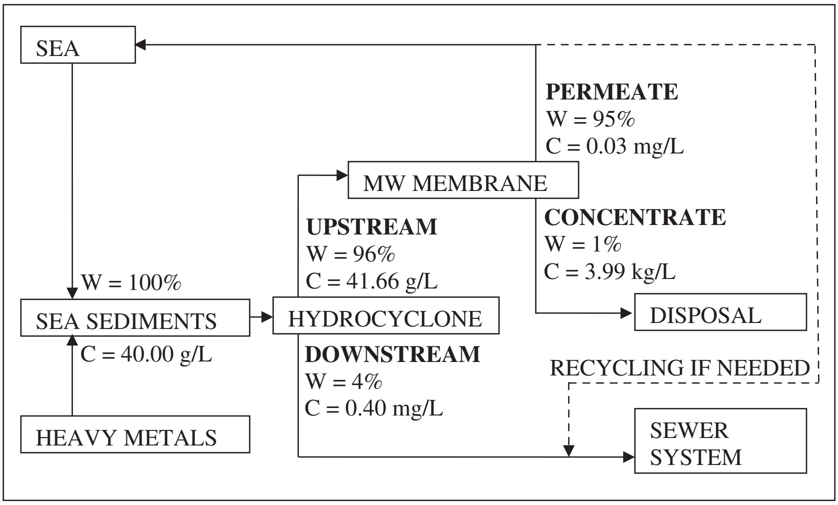

Figure 3. Proposed process for treatment of marine sediment.

Therefore, the fines depositing on the membranes functionalise the membrane surfaces with an additional dissolved metal ion-adsorption layer, which permits concentration targets to be met without sacrificing high permeate fluxes.

Finally, a scheme of the proposed process is reported in Figure 3. After the hydrocyclone, the downstream is treated using a MW membrane. The concentrate containing the polluted fines must be disposed of. The permeate is sent back to the sea or can be legally used as dilution medium because it comprised of a recycled stream from purified waste water. This recycling allows adjustment, if needed, of the heavy metal content of the downstream in order to permit safe sewer discharge; this depends mainly on the heavy metal dissolved in the starting feed stream and the fraction of seawater contained in the downstream.

In Figure 3, for all streams, typical values of the water flow rate (expressed as percentage of the starting volume, 'W') and copper concentration (expressed as copper concentration, 'C') are reported. At the end, only 0.046 mg of the initial quantity of copper per litre of feedstock, equal to 40 g, is not separated by the process and escapes into the sewer system or is returned to the sea.

4. Conclusions

Heavy metals mostly adsorb onto fine solids and/or solubilised in water. Purifying marine sediments consists of separating fines and solubilised metal ions from coarse solids and water. The proposed purification process developed here consisted of a hydrocyclone and a batch membrane process. The first step separated water and fines from coarse solids, whereas the second step separated clean water from the contaminated fraction. The latter can be achieved at subcritical operating conditions by selecting a membrane with a proper pore size. Using this method, it is possible to recover 95% of the polluted seawater.

References

[1] C. Bertin and A.C.M. Bourg, *Trends in the heavy metal content (Cd, Pb, Zn) of river sediments in the drainage basin of smelting activities*, Water Res. 29 (1995), pp. 1729–1736.

[2] M. Fukue, T. Nakamura, Y. Kato, and S. Yamasaki, *Degree of pollution for marine sediments*, Eng. Geol. 53 (1999), pp. 131–137.

[3] US Environmental Protection Agency, *Assessment and Remediation of Contaminated Sediments. ARCS Remediation Guidance Document*, EPA 905-B94-003, US EPA, 1994.

[4] C.N. Mulligan, R.N. Yong, and B.F. Gibbs, *Remediation technologies for metal-contaminated soils and groundwater: an evaluation*, Eng. Geol. 60 (2001), p. 193.

[5] R.C. Sims, J.L Sims, D.L. Sorensen, J. McLean, R. Mashmood, and R.R. Dupont, *Review of In-place Treatment Techniques for Contaminated Surface Soil 1*, EPA-540/2-84003a, US Environmental Protection Agency, Cincinnati, OH, 1985, p. 85.

[6] G. Chakrapani and V. Subramanian, *Heavy metal distribution and fractionation in sediments of the Mahanadi River bassin, India*, Environ. Geol. 22 (1993), pp. 80–87.

[7] T.C. Young, M.R. Waltman, T.L. Theis, and J.V. DePinto, *Studies of heavy metal sorption by Trenton Channel (Detroit River) sediments*, Hydrobiology 235/236 (1992), pp. 649–660.

[8] R.W. Field, D. Wu, J.A. Howell, and B.B. Gupta, *Critical flux concept for microfiltration fouling*, J. Membr. Sci. 100 (1995), pp. 259–272.

[9] M. Mänttäri and M. Nystörm , *Critical flux in NF of high molar mass polysaccharides and effluents from the paper industry*, J. Membr. Sci. 170 (2000), pp. 257–273.

[10] P. Bacchin, P. Aimar, and R.W. Field, *Critical and sustainable fluxes: theory, experiments and applications*, J. Membr. Sci. 281 (2006), pp. 42–69.

[11] P. Bacchin and P. Aimar, *Critical fouling conditions induced by colloidal surface interaction: from causes to consequences*, Desalination 175 (2005), pp. 21–27.

[12] S. Sethi and M.R. Wiesner, *Performance and cost modelling of ultrafiltration*, J. Environ. Eng. 121 (12) (1995), pp. 874–883.

[13] P. Harmant and P. Aimar, *Coagulation of colloids in a boundary layer during cross flow filtration*, Colloids Surf. 138 (1998), pp. 217–230.

[14] P. Bacchin, D. Si-Hassen, V. Starov, M.J. Clifton, and P. Aimar, *A unifying model for concentration polarization, gel-layer formation and particle deposition in cross-flow membrane filtration of colloidal suspensions*, Chem. Eng. Sci. 57 (2002), pp. 77–91.

[15] http://www.camera.it/parlam/leggi/deleghe/06152dl.htm, accessed 20 April 2009.

[16] M. Stoller and A. Chianese, *Optimization of membrane batch processes by means of the critical flux theory*, Desalination 191 (2006), pp. 62–70.

[17] M. Stoller, *On the effect of flocculation as pre-treatment process for membrane fouling reduction*, Desalination 240 (2009), pp. 209–217.

[18] M. Stoller, *Technical optimization of a dual ultrafiltration and nanofiltration pilot plant in batch operation by means of the critical flux theory: a case study*, Chem. Eng. Process. J. 47(7) (2008), pp. 1165–1170.