



159159



G00002

Improvements to membrane filtration

The present invention relates to improvements to membrane filtration of effluents, especially water, containing suspended matter for the purpose of reducing or preventing the membranes from clogging and of improving the filtration capacity of the latter.

It is known that filtration (micro-, ultra-, nano- or hyperfiltration) membranes are sensitive to clogging by various types of substances: dissolved substances, such as organic materials, substances in the colloidal state, such as metal hydroxides, or, in general, substances in suspension (suspended matter or SM). Clogging results in a very substantial reduction in the filtration capacity of the membrane, the reduction in capacity not always being reversible, the effectiveness of membrane cleaning depending considerably on various factors, such as the effective residence time of the fouling product on the membrane, its relative solubility in the cleaning products and the chemical or physico-chemical interactions between the said fouling product and the surface of the membrane, the latter factor being eminently variable according to the chemical composition of the polymer constituting the membrane.

It is also known (see especially "Mémento Technique de l'Eau [Water Technical Memorandum]", Volume 1, Chapter 3.1 and Chapter 4.1, published by DEGREMONT, 1989) that coagulation makes it easier to remove the suspended and colloidal matter. In particular, a person skilled in the art knows that coagulation by metal salts makes it possible to destabilize the colloids and to precipitate certain organic materials after adsorption, for example on metal hydroxides. There are several approaches for characterizing this phenomenon:

. by a coagulation-flocculation test in a laboratory beaker with various doses of metal salt and

estimation, for example, of the settling rates;

5 . by measuring the zeta potential (ZP) and especially the variation in the said ZP as a function of the doses of metal salt added, until that dose which makes the ZP zero, and which therefore corresponds to the required level of treatment for obtaining optimum coagulation, is determined.

10 These two approaches lead to a definition of a coagulant dose called the "optimum coagulation dose" which, from the experience gained by those skilled in the art, is the dose which allows the best clarification treatment of the water being treated and which, consequently, will ensure the optimum working
15 conditions of the membrane (that is to say the least fouling conditions).

The drawback of such a treatment involving this optimum coagulation dose is that this dose is relatively high
20 and has repercussions on the operating cost of the clarification treatment and also on the cost of investing the corresponding equipment.

Moreover, it should be noted that most membrane
25 suppliers and suppliers of nanofiltration and reverse osmosis equipment insist, for fear of loss of the guarantees associated with the membranes, on feeding them' only with water having a zero, or at the very least a very low, content of heavy metals as divalent
30 or trivalent ions, in particular such as ferric ions.

Thus, in the literature there are many publications mentioning the use or the injection of one or more metal salts upstream of the membrane treatments. It
35 should be emphasized that these publications mention doses close to that making the ZP zero or, at the very least, high doses, close to 30% and more of the said optimum dose for making the said ZP zero.

The present invention has the objective of providing a process making it possible to minimize, or at the very least reduce, the clogging of membranes and to improve their filtration capacity, while making the process
5 more economic. To achieve this result, the technical problems to be solved are the following:

. how to substantially increase the specific production flux ($l.h^{-1}.m^{-2}$ of membrane);

. how to produce the least sludge (of hydroxides
10 for example) resulting from the clarification treatment and, above all:

. how to reduce the area of the membranes to be fitted, in order to treat the same volume of water.

15 The Proprietor has observed, in a really surprising manner for one skilled in the art, that a dose of coagulation reactant very much less than the dose which makes the zeta potential of the water to be treated zero allows the filtration capacity of the membrane to
20 be considerably improved.

The subject of this invention is therefore improvements to the membrane filtration, especially micro-, ultra-, nano- or hyperfiltration, of effluents, especially
25 water, which concentrate suspended matter, so as to reduce clogging of the membranes and improve the filtration capacity thereof, characterized in that they consist in adding to the effluent to be filtered, before it passes over the membranes, a dose of a
30 coagulation reactant which destabilizes the colloidal matter in suspension, which is around 30 to 80 times less than the dose making the zeta potential zero.

According to an advantageous method of implementing the
35 process according to the invention, the said dose of coagulation reactant is around 40 to 60 times less than that making the zeta potential zero.

The field of application of the invention is

particularly wide. This is because it can be used especially for the membrane treatment of water coming from various sources, such as for example:

5 - municipal waste water, after a biological treatment and a separation allowing less than 20 mg/l of SM to be obtained;

 - water not requiring the prior removal of organic matter and having a total organic carbon (TOC) content of less than 2 ml/g; and

10 - raw surface water, having a low TOC, a high colloidal concentration and containing less than 200 mg/l of SM.

The process according to the invention gives excellent
15 results when it is applied to membranes of different shapes (capillary, tubular, planar and spiralled membranes) with an internal or external skin, having various configurations (in a casing, without a casing and immersed in a basin). The invention is also
20 suitable for applications involving the spraying of recreational areas, the reutilization of waste water in factories and, more generally, the upstream pretreatment of reverse-osmosis desalination plants.

25 Further features and advantages of the present invention will become apparent from the description given below with reference to the appended drawing and to the illustrative examples given below. In the drawing:

30 - Figure 1 is a schematic view illustrating the injection of coagulating reactant, for example a metal salt, especially an iron salt, upstream of a membrane in a casing into the flow; and

 - Figure 2 is also a schematic view illustrating
35 the injection of the coagulating reactant upstream of an immersed membrane without a casing.

In both figures, identical or similar elements are denoted by the same reference numbers.

In the method of implementation shown in Figure 1, the coagulating reactant is injected at 2 into the water 1 to be treated and the water to be treated/coagulating reactant mixture is filtered over the membrane in the casing 4. The system includes a recirculation loop 5. The reference number 3 denotes the outflow of the treated water.

In the example of implementation illustrated in Figure 2, the coagulating reactant 2 is injected into the water 1 to be treated, the mixture then being filtered over the membrane 6, without a casing, immersed in a basin containing the water to be treated. The treated water 3 is discharged by means of a pump.

Given below are two numerical examples of implementation so as to make the technical aspects and advantages afforded by the present invention clearly apparent.

Example 1: Treatment of municipal waste water

A biological treatment test was carried out on municipal waste water coming from a fabric-membrane bioreactor, such as the one described in FR-A-2 775 911.

The quality of the water output by the reactor was the following:

Total COD:	40 mg/l
Total BOD ₅ :	<10 mg/l
SM:	5 mg/l
TOC:	6 mg/l.

The dose which makes the zeta potential (ZP) zero was found by laboratory trial to be 140 mg/l of FeCl₃ (expressed as pure FeCl₃). The optimum dose of coagulating reactant, determined by in-beaker

flocculation, to reduce the organic matter (measured by UV absorption at 254 nm) was 110 mg/l.

5 The output of treated water from the fabric-membrane reactor was 1 m³/h. The steady flux through the capillary ultrafiltration membrane was 32 l.h⁻¹.m⁻². When a small amount of coagulating reactant was used, by injecting into the line 3 mg/l of FeCl₃ (expressed as pure FeCl₃), the steady flux was 100 l.h⁻¹.m⁻².

10

The backwashing was carried out with 5 mg/l of chlorine for 30 seconds every 30 minutes and, from time to time, for example once a month, with ammoniacal citric acid. The backwashing water was returned to the top of the fabric-membrane bioreactor.

15

In this example, to treat 1 m³/h without a coagulating reactant, 35 l.h⁻¹.m⁻² was obtained and a membrane area of 28.5 m² was therefore required. In contrast, by injecting 3 mg/l of FeCl₃, 100 l.h⁻¹.m⁻² was obtained and the membrane area required was then 10 m². This represents an improvement in flux of 285% and a saving of 18.5 m², i.e. 65%, of membrane at least.

20

25 Sludge production was measured to be about 8 mg/l with 3 mg/l of FeCl₃ instead of 5 mg/l without the addition of a coagulating reactant; however, this remained very much less than the amount which would be produced with 125 mg/l of FeCl₃, i.e. more than 90 mg/l of sludge formed.

30

It is clear that the experiment reported above and the results that it provides go counter to the experience of a person skilled in the art and the teaching that he can extract from the prior art. This is because:

35

- the increase in flux through a membrane, by incomplete clarification (with a coagulant dose markedly less than the optimum clarification dose), and
- the use of coagulating agents (especially

ferric salt) in small amounts, but nevertheless very much greater than the contents normally prohibited by most membrane manufacturers and suppliers, are completely contradictory to the commonly accepted routine use of membranes.

Example 2: Treatment of surface raw water

The trial was carried out on raw water from the Seine, the characteristics of which were the following:

Turbidity	15 NTU
Organic matter	5 mg/l O ₂ (KMnO ₄ oxidizability)
TOC	3 mg/l
UV	8 mg/l.

In laboratory testing, the dose which made the ZP equal to zero was 55 mg/l of FeCl₃.

The output of treated water was 150 l/h. The steady flux through the capillary ultrafiltration membrane was 80 l.h⁻¹.m². When a small quantity of coagulating reactant was used, by in-line injection of 2 mg/l of FeCl₃ (expressed as pure FeCl₃), the maximum steady flux improved by 30%.

The backwashing was carried out with 5 mg/l of chlorine for 30 seconds every 30 minutes.

In this example, in which a surface raw water was pretreated with the objective of treating it downstream by reverse osmosis, a major saving in membrane area was also found. All the TOC was not eliminated, but the flux was improved.

It follows from reading the description given above that the invention does actually limit clogging of the membranes, by considerably improving the filtration capacity of the latter. This results in very substantial economic advantages; especially a reduction

in the area of membrane to be installed in order to treat the same volume of water.

Of course, it goes without saying that this invention
5 is not limited to the examples of implementation and/or application mentioned and/or described here, rather it encompasses all variants thereof.

CLAIMS

1. Improvements to the membrane filtration, especially micro-, ultra-, nano- or hyperfiltration, of
5 effluents, especially water, which contain suspended matter, so as to reduce clogging of the membranes and improve the filtration capacity of the latter, characterized in that it consists in adding to the
10 effluent, before it passes over the said membrane, a dose of a coagulation reactant which destabilizes the colloidal matter in suspension, which is around 30 to 80 times less than the dose of coagulating reactant making the zeta potential zero.
- 15 2. Improvements according to claim 1, characterized in that the said dose is around 40 to 60 times less than that making the zeta potential zero.