Environment Canada Environnement Canada

Canada

Colloids and Dissolved Organics: Role in membrane and depth filtration

BY:

G. Leppard, J. Buffle

NWRI Contribution No: 05-182

NATIONAL WATER RESEARCH INSTITUTE
INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX

05-182

Colloids and dissolved organics: Role in membrane and depth filtration

Gary G. Leppard and Jacques Buffle

Abstract

Filters are important for water purification and as a research tool for the isolation of environmentally significant colloids and soluble organic molecules. The design of filters must become increasingly more sophisticated to make them more versatile in nature and more adaptable to new applications. This brief but comprehensive overview on the interactions between filters, colloids and dissolved organics was prepared, at the request of The Encyclopedia of Water, to feature the nature of filter/water interactions relevant to improved filter design. Noted is recent NWRI research on the use of nanotechnology to identify nano-scale biofoulants on membrane filters.

NWRI RESEARCH SUMMARY

Plain language title

The nature of interactions between filters, colloids and dissolved organics

What is the problem and what do scientists already know about it?

Filters are important for water purification and as a research tool for the isolation of environmentally significant colloids and soluble organic molecules. The design of filters must become increasingly more sophisticated to make them more versatile in nature and more adaptable to new applications. Much is known but the search for improvements is ongoing.

Why did NWRI do this study?

Dr. Leppard was requested to prepare this brief overview by The Encyclopedia of Water Editor-in-Chief, with the approval in principle by AEMRB.

What were the results?

A highly condensed, yet comprehensive, overview is the result.

How will these results be used?

These results will guide those who consult The Encyclopedia of Water.

Who were our main partners in the study?

NSERC, the University of Geneva (Switzerland), McMaster University (Hamilton, ON) and the Fonds National Suisse were the main partners.

Les colloïdes et les matières organiques dissoutes : leur rôle dans la filtration sur membrane et la filtration en profondeur

Gary G. Leppard et Jacques Buffle

Résumé

Les filtres sont importants pour la purification de l'eau et comme outils de recherche pour la mise ne évidence des colloïdes et des molécules organiques solubles qui présentent une importance pour l'environnement. La conception des filtres doit se perfectionner de façon à les rendre plus polyvalents et plus adaptables à de nouvelles applications. Ce survol, bref mais complet, des interactions entre les filtres, les colloïdes et les matières organiques dissoutes a été préparé à la demande de *The Encyclopedia of Water*, dans le but d'expliquer la nature des interactions filtre-eau pertinentes pour l'amélioration de la conception des filtres. On note particulièrement la recherche récente sur l'utilisation de la nanotechnologie pour identifier les bioencrasseurs à nanoéchelle présents sur les membranes filtrantes.

Sommaire des recherches de l'INRE

Titre en langage clair

La nature des interactions entre les filtres, les colloïdes et les matières organiques dissoutes

Quel est le problème et que savent les chercheurs à ce sujet?

Les filtres sont importants pour la purification de l'eau et, en tant qu'outils de recherche, pour isoler les colloïdes et les molécules organiques solubles qui présentent une importance pour l'environnement. La conception des filtres doit perfectionner de façon à les rendre plus polyvalents et plus adaptables à de nouvelles applications. On en connaît beaucoup sur le sujet, mais la recherche d'améliorations est une activité permanente.

Pourquoi l'INRE a-t-il effectué cette étude?

M. Leppard a préparé ce bref survol à la demande du rédacteur en chef de *The Encyclopedia of Water*, avec l'approbation de principe de la Direction de la recherche sur la gestion des écosystèmes aquatiques.

Quels sont les résultats?

Il en résulte un survol très condensé, mais complet.

Comment ces résultats seront-ils utilisés?

Ce survol guidera les personnes qui consulteront *The Encyclopedia of Water*.

Quels étaient nos principaux partenaires dans cette étude?

Le CRSNG, l'Université de Genève (Suisse), l'Université McMaster (Hamilton, Ontario) et le Fonds national suisse sont les principaux partenaires de ce projet.

For: **THE ENCYCLOPEDIA OF WATER** (section on Water Quality Control)

Colloids and dissolved organics: Role in membrane and depth filtration

Gary G. Leppard and Jacques Buffle

National Water Research Institute, Environment Canada, Burlington, Ontario, Canada L7R 4A6.
Tel. (905) 336-4787; FAX (905) 336-4420; E-mail Gary.Leppard@ec.gc.ca
and
CABE (Analytical and Biophysical Environmental Chemistry) University of Geneva, 30 Quai Ernest Ansermet, CH-1211-Geneva 4, , Switzerland.
Tel. +41 (0)22 37 96431; FAX +41 (0)22 37 96069; E-mail Jacques.Buffle@cabe.unige.ch

1. Introduction

A colloid is operationally defined as any particulate with a least dimension in the range of 1.0 to 0.001 μm, a range which includes macromolecules, but not conventional dissolved substances which tend to be smaller (Buffle et al., 1998; Leppard & Buffle, 1998). For environmental scientists, aquatic colloids are being re-defined as any particulate that provides a molecular milieu into and onto which chemicals can escape from the bulk water, and whose movement is not significantly affected by gravitational settling (Gustaffson & Gschwend, 1997). In practice, colloids and dissolved substances are often defined by a filter operation (Droppo, 2000; Buffle et al., 1992). Living microbes, when sufficiently small, can also be considered colloids, albeit colloids capable of very complex behaviour (Leppard & Buffle, 1998).

Filtration for water scientists is the separation of particulates from a liquid, achieved by passing a suspension through a porous solid. Through the application of membrane filters and/or depth filters, filtration protocols are commonly used (a) to concentrate or remove particulate matter, and (b) to separate suspended particulates into size classes for subsequent biological, chemical or physical analyses. In water treatment, one discriminates between membrane filters, which are porous membranes that concentrate particulates at or close to the upper filter surface, and depth filters. The latter are relatively inexpensive filters with high collection efficiencies and flow rates; they allow for entrapment of particulates within the filter interior.

Filters for use in the analysis of aquatic samples may be separated into three categories:
(i) filters made of a random assembly of fine fibres;

(ii) filters made of an impermeable material, which has discrete cylindrical holes traversing it, and which acts as a true sieve;
(iii) "depth filters" which have a spongy structure.

These three categories of filter and their relationships to applicable size ranges and to standard sieves and dialysis membranes are featured in Figure 1. The various filters in use are complementary in terms of pore size ranges, pore size distributions and chemical nature, thus providing versatility in attempts to minimize sample perturbation by filters.

[IMAGE NUMBER 1] + [CAPTION]

2. Practical advantage of a better understanding

Understanding better, for practical advantage, the roles of colloids and dissolved organics in the intended course of a filtration process, is particularly useful when considering the following goals:

(i) understanding the processes of fouling and biofouling as they relate to water treatment filters (Flemming et al., 1996; Liao et al., 2004);

(ii) optimizing the design of filters for improved performance in specific situations (Buffle et al., 1992; Flemming et al., 1996), with a focus on filters designed to be cleaned *in situ;*

(iii) improving the quality of size fractionations for limnologists and oceanographers, with a focus on capturing and analyzing natural microbiological consortia with minimal artifact (Cole, 1999).

Some specific concepts and advances are noteworthy. The biofouling of filters is an unwanted progressive deposition of microorganisms and their consequent formation of biofilms, which clog filter pores and eventually establish an additional (but different) filter at the upper surface of a membrane filter. The economic consequences of this process are considerable (Flemming et al., 1996). New technology is leading to the identification of specific nano-scale organic entities which microorganisms produce to facilitate their attachment to filter surfaces (Liao et al., 2004);

such research may lead to better methods for cleaning filters *in situ*. In general, fouling may also result from purely physico-chemical interactions between organic and inorganic colloids and a membrane surface, leading to colloid coagulation (Buffle et al., 1992); in such cases, controls over the flow rate and physico-chemical conditions are essential.

With an increasing realization of the many biogeochemical processes dominated by certain abundant living colloids in the oceans, the need to analyze isolated important biological species grows in importance (Cole, 1999). To isolate these microbes, and separate them according to size (and then possibly according to dominant species), for subsequent characterization and assessment of their biogeochemical roles, there is a requirement for well-controlled filtration procedures. An additional and valuable consideration is filter selection according to filter compatibility with various techniques of analytical optical microscopy for studying fresh isolates and their minimally-perturbed natural consortia while they sit on filters.

3. Abundant colloids and dissolved organics

In natural waters, the most commonly encountered colloids are fractal aggregates of fulvic and humic acids, living cells of colloidal size, viruses, fibrils (linear aggregates of biopolymers rich in polysaccharide), refractory skeletal fragments of organisms, clay minerals, and oxyhydroxides of iron and manganese (Leppard, 1992). Three major groups enable one to describe colloid coagulation properties: inorganic (compact) colloids; the fibrillar (rather rigid) large biopolymers; and the small size (nanometers) fulvic acids (Buffle et al., 1998). Fulvic and humic acids are at the borderline between dissolved and colloidal organics, while organic metabolites emanating from leaky cells or lysing cells or excreta are usually in the dissolved state. In engineered aquatic ecosystems, such as water treatment facilities, the same colloids and dissolved organics tend to be present but in different relative amounts. These colloids and dissolved organics can have an

impact on the biological activities and clarity of both natural and engineered waters, through their influences on flocculation (Ferretti et al., 2003; Leppard & Droppo, 2004); the impact on filtration processes of the most abundant ones can be considerable, leading to defective filter performance and misleading information (Buffle et al., 1992).

4. Kinds of filters and their application: general considerations

An *in depth* review of the various kinds of filters, used currently for water treatment and for the size fractionation of aquatic particles and colloids, is beyond the scope of this article. Water treatment plants and their apparatus are evolving towards greater cost-effectiveness through design changes which are adaptations to the specific properties of the water being received. Thus, different sites are likely to have different kinds of membrane filters and use different flow rates, with changes being made continually. General considerations are found in Buffle et al. (1992) and in Droppo (2000); general research needs are outlined well in a 1998 Committee Report of the AWWA. For water treatment, there is a strong research effort to develop plastic filters with well-controlled properties, an ongoing work which is progressing well. Coupled to this are considerable interests in developing filters which can be cleaned *in situ*, and improved filters for removing waterborne pathogens. Filtration can be used in conjunction with chemical aids, such as flocculants, for the purpose of minimizing fouling; this is a research topic which is likely to expand quickly.

5. Bio-physico-chemical interactions between filters and colloids/dissolved organics

As stated earlier, and revealed by a consideration of Figures 1 and 2, the various types of filters are complementary with regard to their properties. The nature of filtration problems, however,

varies from one filter type to another, in particular because flow rates through the various membrane types are different.

[IMAGE NUMBER 2] + [CAPTION]

Filters with a large pore size (>0.1 μm) are used for sieving and filtration (Figures 1 and 2); with them, a large solution flow rate can be achieved, even with a rather low pressure applied to the filter. At a large flow rate, the concentration of colloids at the filter surface may become orders of magnitude larger than in the bulk solution (the so-called concentration polarization effect), leading to instantaneous coagulation (Figure 3) and consequent clogging of the filter (Buffle et al., 1992). Under such conditions, the nature of the membrane is not very relevant. The way to minimize clogging is to use minimum flow rates; while very low flow rates are usually required to avoid surface coagulation, they cannot be so low as to permit bulk coagulation (Figure 3).

[IMAGE NUMBER 3] + [CAPTION]

Filtration membranes with pore sizes in the range 1-100 nm are used for ultrafiltration. A high pressure (1-4 atm) must be applied to the membrane, because of the small pore size, but flow rates are never large. When the effective hole size is of the same order of magnitude as the molecule size, dialysis or reverse osmosis occurs, whereby the solvent does not move through the membrane. With such membranes and techniques, clogging due to surface coagulation is small or negligible, and it decreases with the membrane pore size. On the other hand, when molecules and pore sizes become more and more similar, interactions between the solute (the organics especially) and the membrane body become increasingly important (Figure 3). In such cases, the chemical nature of the membrane plays an important role. Thus it must be realized that the problems encountered in sieving and filtration are rather different from those occurring in

ultrafiltration, dialysis and reverse osmosis. Detailed descriptions of the various types of interactions are given in Buffle et al. (1992). The concept of the optimal flow rate window is illustrated in Figure 3.

In addition to the aforementioned physico-chemical interactions between membranes, suspended colloids and dissolved organics, biological effects may play an important role. In particular, once microorganisms will have been collected onto the membrane filter, some of them will secrete adhesive organic macromolecules (as cell attachment devices) directly onto membrane surfaces, an event leading to the development of a biofilm (an attached consortium of individual colloid-size cells enmeshed in a porous matrix of their extracellular biopolymers). Attempts to identify specific important bio-adhesives are receiving an impetus from transmission electron microscopy examinations of colloid/filter associations, using fouled membrane filters (Liao et al., 2004).

6. Size fractionation

Various sequential size fractionation procedures have been subjected to comparative analysis. In analytical applications, one can use either washing (also called diafiltration) or concentration techniques and, for each case, either sequential (also called cascade) or parallel filtration. In the concentration technique, the solution is pushed through the membrane by applying a pressure. In the washing technique, a constant volume is maintained over the filtration membrane by compensating with synthetic solution. It has been found that the washing technique is more reliable because it avoids concentrating the particles in the retentate, thus minimizing coagulation problems. In a sequential filtration procedure, the same solution is filtered successfully through a series of membranes of decreasing pore size, the filtrate of one cell being filtered on the following membrane. The proportion of colloids in each size fraction is obtained by analysis of the various filtrates. In the parallel procedure, aliquots of the same sample are filtered through several

membranes of different pore size. The proportions of colloids in the size fractions are obtained, based on the analysis of the filtrates and calculations. Because the reproducibility of filtration is not better than 5-10% error, the accumulation of errors becomes exceedingly large over five filtration steps in all cases, but sequential filtration is preferred because it minimizes aggregation problems. Indeed, the rate of coagulation increases with particle concentration and heterogeneity.

7. Optimization

The factors which affect the retention of colloids are summarized by Figure 3. At large flow rates ($>3 \times 10^{-3}$ cm/s), a large concentration polarization occurs and retention is due mostly to surface coagulation, which often leads to clogging. At very low flow rates, such surface coagulation is not important, but coagulation in the bulk solution becomes an important factor (for flow rates $<10^{-4}$ cm/s), due to the fact that filtration times can be exceedingly long (days). For this reason, in chemical analysis, it is also preferable to avoid dialysis for which very long equilibration times are required. At intermediate flow rates ($10^{-4} - 3 \times 10^{-3}$ cm/s), the separation of colloids is effectively based on sieving and depends on membrane pore size.

The aforementioned limiting values of flow rates are valid for stirred conditions with a diffusion layer thickness (δ) of 10 μm. However, surface and bulk coagulation strongly depend on hydrodynamic conditions, which influence the value of δ (and thus surface coagulation), and on the bulk coagulation rate. Thus, both surface and bulk coagulation depend on the filtration mode (batch filtration with stirring, cross-flow filtration, pulsed filtration, filtration on rotatory cylinders or discs, hollow fibre filtration). Decreasing δ below a few micrometers, to minimize surface coagulation, is very difficult; thus the schematic curves of Figure 3 can be seen as the upper limits for both surface and bulk coagulation. It is interesting to note that the actual pore size

of a membrane filter might not play a direct role in particle retention; the actual pore size might only influence the flow rate, and thus the coagulation efficiency.

8. New vistas

In the last few years, novel chemical treatments have been applied to both porous and nonporous surfaces for the purpose of creating modified surfaces which kill bacteria on contact (Borman, 2002). The treatments are expected to be especially advantageous since they are not anticipated to exacerbate the problem of growing bacterial resistance to antibiotics. In practice, an antibacterial chemical (which disrupts drastically the integrity of the bacterial surface to kill bacteria before they can establish a biofilm) is bonded to the surface of interest such that it can neither be washed away nor modified upon interaction with oncoming bacteria. The treatments are currently applicable to glass surfaces, polymer surfaces and carbohydrate-based porous materials; can their use with membrane and depth filters be far behind? Considering the explanations given in section 5, this membrane treatment should be combined with a physico-chemical means to minimize "cake" formation at the surface of filters by surface coagulation.

An interesting complementary idea is the creation of living filters in which a biofilm is purposely formed at the surface of pores of a filter. Even though the concept needs considerable development, it can be envisioned that such a filter could be used (a) to selectively extract certain valuable substances from water for recovery, or (b) to selectively degrade organic contaminants which become bound within the biofilm matrix (and thus subject to enzymatic activities of nearby microorganisms).

Acknowledgements

The authors thank the Fonds National Suisse and the Natural Sciences and Engineering Research Council of Canada, for generous long-term support.

References

AWWA (1998), American Water Works Association Membrane Technology Research Committee, Committee Report: Membrane Processes, Jour. AWWA, 90(6), 91-105.

Borman, S. (2002), Surfaces designed to kill bacteria, C&EN, **80**(23), 36-38.

Buffle, J., K.J. Wilkinson, S. Stoll, M. Filella and J. Zhang (1998), A generalized description of aquatic colloidal interactions: the three-colloidal component approach, Environ. Sci. Technol., **32**, 2887-2899.

Buffle, J., D. Perret and M. Newman (1992), The use of filtration and ultrafiltration for size fractionation of aquatic particles, colloids, and macromolecules, In: Environmental Particles, Vol. 1, Buffle, J. and H.P. van Leeuwen, Eds., Lewis Pubs, Chelsea, MI, pp. 171-230.

Cole, J.J. (1999), Aquatic microbiology for ecosystem scientists: New and recycled paradigms in ecological microbiology, Ecosystems, **2**, 215-225.

Droppo, I.G. (2000), Filtration in particle size analysis, In: Encyclopedia of Analytical Chemistry, Meyers, R.A., Ed., John Wiley & Sons, Chichester, pp. 5397-5413.

Ferretti, R., S. Stoll, J. Zhang and J. Buffle (2003), Flocculation of hematite particles by a comparatively large rigid polysaccharide: schizophyllan, J. Coll. Interf. Sci., **266**, 328-338.

Flemming, H.-C., T. Griebe and G. Schaule (1996), Antifouling strategies in technical systems – A short review, Wat. Sci. Tech., **34**(5-6), 517-524.

Gustaffson, O. and P.M. Gschwend (1997), Aquatic colloids: Concepts, definitions, and current challenges, Limnol. Oceanogr., **42**, 519-528.

Leppard, G.G. (1992), Evaluation of electron microscope techniques for the description of aquatic colloids, In: Environmental Particles, Vol. 1, Buffle, J. & H.P. van Leeuwen, Eds., Lewis

Pubs., Chelsea, MI, pp. 231-289.

Leppard, G.G. and J. Buffle (1998), Aquatic colloids and macromolecules: effects on analysis, In: The Encyclopedia of Environmental Analysis and Remediation, Vol. 2, Meyers, R.A., Ed., John Wiley & Sons, New York, pp. 349-377.

Leppard, G.G. and I.G. Droppo (2004), Overview of flocculation processes in freshwater ecosystems, In: Flocculation in Natural and Engineered Environmental Systems, Droppo, I.G., G.G. Leppard, T.G. Milligan & S.N. Liss, Eds., Lewis Pubs./CRC Press, Boca Raton, FL, pp. 25-46.

Liao, B.Q., D.M. Bagley, H.E. Kraemer, G.G. Leppard and S.N. Liss (2004), A review of biofouling and its control in membrane separation bioreactors, Water Environ. Res. **76**: 425-436.

Figure captions

FIG. 1. Size ranges for sieving and filtration, including depth filters, and for application of the most important filter types. Reproduced with permission from Buffle et al. (1992).

FIG. 2. Schematic representation of size ranges where important filtration secondary effects are expected to play a significant role. The thickness of hatched zones reflects the relative importance of the corresponding factors. The word "compound" designates any component different from water, be it particulate or colloidal or dissolved. Reproduced with permission from Buffle et al. (1992).

FIG. 3. Semi-quantitative representation of the change in retention with flow rate, and with aggregation in the filtration cell, revealing the flow rate window of minimal artifact. Reproduced with permission from Leppard and Buffle (1998).

NOTE: Regarding Figures for insertion into text – these currently exist only as hard copies which the publishing house wants to convert into electronic documents at their publication site. The hard copies which I elected to have reproduced come from other publishers who have been cited and referenced fully in this manuscript. I will deliver hard copies of the 3 Figures by hand to your mailbox.

PRINTED IN CANADA
IMPRIMÉ AU CANADA
ON RECYCLED PAPER
SUR DU PAPIER RECYCLÉ

National Water Research Institute
Environment Canada
Canada Centre for Inland Waters
P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre
11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

NATIONAL WATER RESEARCH INSTITUTE
INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX

Institut national de recherche sur les eaux
Environnement Canada
Centre canadien des eaux intérieures
Case postale 5050
867, chemin Lakeshore
Burlington, Ontario
L7R 4A6 Canada

Centre national de recherche en hydrologie
11, boul. Innovation
Saskatoon, Saskatchewan
S7N 3H5 Canada

Environment Canada Environnement Canada

Canada