**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Ultrafiltration for the Removal of Cadmium in Waste Streams from Industrial Waste Incineration

P. Le Goff[a]; B. Benadda[a]; C. Comel[b]; R. Gourdon[a]
[a] LABORATOIRE D'ANALYSE ENVIRONNEMENTAL DES PROCÉDÉS ET DES SYSTEMES INDUSTRIELS INSA, VILLEURBANNE, CEDEX, FRANCE [b] LABORATOIRE DE CHIMIE ET ENVIRONNEMENT UNIVERSITE D'ANGERS, ANGERS, CEDEX, FRANCE

**To cite this Article** Goff, P. Le , Benadda, B. , Comel, C. and Gourdon, R.(1997) 'Ultrafiltration for the Removal of Cadmium in Waste Streams from Industrial Waste Incineration', Separation Science and Technology, 32: 9, 1615 — 1628
**To link to this Article: DOI:** 10.1080/01496399708004070
**URL:** http://dx.doi.org/10.1080/01496399708004070

SEPARATION SCIENCE AND TECHNOLOGY, 32(9), pp. 1615–1628, 1997

# Ultrafiltration for the Removal of Cadmium in Waste Streams from Industrial Waste Incineration

P. LE GOFF and B. BENADDA*
LABORATOIRE D'ANALYSE ENVIRONNEMENTAL DES PROCÉDÉS
ET DES SYSTÈMES INDUSTRIELS
INSA
20 AV. A. EINSTEIN, 69621 VILLEURBANNE CEDEX, FRANCE

C. COMEL
LABORATOIRE DE CHIMIE ET ENVIRONNEMENT
UNIVERSITÉ D'ANGERS
2 BD. LAVOISIER, 49045 ANGERS CEDEX, FRANCE

R. GOURDON
LABORATOIRE D'ANALYSE ENVIRONNEMENTAL DES PROCÉDÉS
ET DES SYSTÈMES INDUSTRIELS
INSA
20 AV. A. EINSTEIN, 69621 VILLEURBANNE CEDEX, FRANCE

## ABSTRACT

To remove Cd in waste streams from industrial waste incineration plants, a process of tangential ultrafiltration preceded by complexation was used. It was shown that the optimal pH for precipitation of metallic hydroxides was between 10 and 11, which is greater than the value (8.5) stipulated by the national standard for waste streams. A dozen products were tested in order to choose a suitable complexing agent, including Metalsorb ZT (Na-dimethyldithiocarbamate) which seemed to be the most efficient for reducing the Cd content. For additions of Metalsorb ZT from 0.25 to 2.5% in volume and in the pH 7–9 range, the Cd content was reduced by approximately 75%. The process did not seem particularly sensitive to fluctuating operating conditions.

* To whom correspondence should be addressed.

## INTRODUCTION

Environmental awareness has led the authorities to fix more severe standards concerning waste streams from industrial installations. To meet these standards, industry must not only adapt its manufacturing processes but must also take into account waste treatment. This second point is primarily concerned in the case of an industrial waste incineration plant. Air pollution control involves pollutant transfer to wastewater streams. The latter generally undergo a physicochemical precipitation or floculation treatment, which is not always efficient, especially for certain heavy metals. Although the elimination of metals from simple solutions (few complexing agents, mixture of two or three metals, . . .) does not generally present a problem, the situation is not the same for complex solutions (presence of organic matter, tens of different metals, complexed metals, . . .), as in the case of waste streams of air pollution control from industrial waste incineration.

The content of pollutants in these waste streams (either dissolved, colloidal, or in suspension) is extremely variable over time and according to the type of waste incinerated. Very diverse techniques can be used to eliminate these products: coagulation, ion exchange (1, 2), biosorption (3, 4), membrane separation, . . . .

In the case of metallic cations, the object of this study, chemical precipitation (5) is often used. However, there are certain drawbacks to this method according to the soluble reactant chosen, as shown in Table 1.

TABLE 1
Drawbacks of Chemical Precipitation

| Reactants | Advantages/drawbacks |
|---|---|
| Hydroxide | Solubility of hydroxides formed very variable according to cation and pH<br>⇒ In the case of metal mixtures, no ideal common conditions<br>Difficult dehydration of sludges<br>Formation of amphoteric compounds |
| Carbonate | Precipitation pH of metals lower than for hydroxides<br>Denser precipitate<br>The technique is not applicable to all metals |
| Sulfide | Solubility of sulfides lower than hydroxides<br>No formation of amphoteric compounds<br>Generation of potentially toxic gas $H_2S$<br>⇒ Posttreatment necessary to eliminate excess sulfide |

Although classical treatment techniques have now reached an advanced stage of optimization, thanks to the elaboration of chemical products for coagulation and flocculation and to the simplification of the treatment procedure, the growing development over the last 30 years of membrane separation techniques has made them attractive for the treatment of residual wastewater streams (6).

TABLE 2
Nature of Complexing Agents Often Use for Ultrafiltration of Cd

| Metallic ions studied | Complexing agents | pH | Ref. |
|---|---|---|---|
| $Cd^{2+}$ | PEI | Acid | 13 |
| $Cu^{2+}$ | PAA | | |
| $Fe^{2+}$ | Polyvinyl alcohol (PVA) | | |
| $Ni^{2+}$ | | | |
| $Zn^{2+}$ | | | |
| $Cd^{2+}$ | | | 14 |
| $Cu^{2+}$ | | | |
| $Cd^{2+}$ | PEI | 6 | 15 |
| $Cu^{2+}$ | AN956 (polyacrylamide) | Acid | |
| $Cd^{2+}$ | Micelles of Na-dodecylsulfate | | 9 |
| $Cu^{2+}$ | | | |
| $Cd^{2+}$ | Sulfide | 9 | 16 |
| $Co^{2+}$ | Hydroxide | 11 | |
| $Cu^{2+}$ | Diethyldithiocarbonate | 11–12 | |
| $Fe^{2+}$ | | | |
| $Pb^{2+}$ | | | |
| $Mn^{2+}$ | | | |
| $Zn^{2+}$ | | | |
| $Cd^{2+}$ | Polyacrylates with carboxyl and sulfonic functions | Alkaline | 17 |
| $Cu^{2+}$ | Copolymer of ethylenic acid with carboxyl functions | | |
| $Cd^{2+}$ | Sodium alginate | | 18 |
| $Cu^{2+}$ | | | |
| $Fe^{2+}$ | | | |
| $Pb^{2+}$ | | | |
| $Zn^{2+}$ | | | |
| $Cd^{2+}$ | Surfactants | | 10 |
| $Cd^{2+}$ | Sodium dioctylethyldicarbonate sulfonate | | 11 |

The aim of this study is to test a process associating complexation and tangential ultrafiltration to remove Cd from waste streams. It was first necessary to choose a complexing agent and then to test the process efficiency. The optimal pH for precipitation had been previously determined.

The separation process by complexation–ultrafiltration was first described by Michaels in 1968 (7), who developed an analytical technique used by biochemists. Strathmann and Koch (8) showed that ultrafiltration is technically and economically applicable to the separation of metallic ions in the presence of a macroligand which selectively complexes certain ions. Recent works have been published concerning the extraction of metals in the form of micelles by using surfactants (9–12)

Although many studies have been carried out on the extraction of such metal ions as copper and nickel by ultrafiltration, fewer studies exist for the case of cadmium. Table 2 summarizes this work (9–18).

## PRELIMINARY STUDY OF CADMIUM HYDROXIDE PRECIPITATION

Metallic cations in waste streams can be precipitated by the addition of soluble reactants (hydroxides, carbonates, and sulfides).

Although precipitation using lime is by far the most practical and most frequently used technique in industrial wastewater treatment, it is not the most efficient (1). The solubility of hydroxides formed is very variable according to the cation and the pH. In the most general case where the metals form a mixture, the conditions are not ideal and the final waste stream always contains a certain quantity of one or more pollutants. Other drawbacks of this precipitation are the difficult dehydration of the hydroxide sludges obtained as well as the growing cost of further treatment of these sludges (stabilization) before they can be used as landfill according to new French regulations.

Formation of metallic hydroxides is governed by the following chemical equilibrium:

$$Me^{2+} + 2OH^- \leftrightarrows Me(OH)_2$$

with

$$Ks = a_{Me^{2+}} \times a^2_{OH^-}$$

where $a$ = activity of ionic species
$Ks$ = solubility product

$Ks$ is $5.3 \times 10^{-15}$ at 20°C for $Cd(OH)_2$ (19).

Assuming that the waste streams are very dilute, and that no molecule or ion present influences the activity of metals, for a divalent metal we can write

$$Ks = [\mathrm{Me}^{2+}][\mathrm{OH}^-]^2$$

where $[\mathrm{Me}^{2+}]$ = concentration of ionic species in mol/L.

The minimum pH necessary in order to meet standard regulations (Cd $< 0.1$ mg/L) can be calculated for the hydroxide precipitation treatment. However, it is necessary to take all the soluble species of the same metal into accout and also the influence of complexation phenomena whenever necessary.

Cadmium is present in two main forms in aqueous solution (19), $Cd^{2+}$ and $HCdO_2^-$, with

$$\log[\mathrm{Cd}^{2+}] = 13.8 - 2\mathrm{pH}; \qquad \mathrm{Cd}^{2+} + 2\mathrm{H_2O} \leftrightarrows \mathrm{Cd(OH)_2} + 2\mathrm{H}^+$$

$$\log[\mathrm{HCdO_2^-}] = -19.5 + \mathrm{pH}; \qquad \mathrm{CD(OH)_2} \leftrightarrows (\mathrm{HCdO_2})^- + \mathrm{H}^+$$

These relations allow us to prove by calculations that it is only possible to comply with standard regulations ($[\mathrm{Cd}^{2+}] + [(\mathrm{HCdO_2})^-]) \leq 0.1$ mg/L) at pH $\geq 9.9$.

## Experimental Results

To verify the independence of pH and the initial concentration of ions in the effluent, four types of samples were treated after adjusting at pH 2. The tested effluent coming from the air pollution control facility of an industrial waste incineration plant constitutes Sample A. Sample B consists of the same effluent with a slight overload of Cu and Cd. Sample C is enriched in Cu and Cd, and Sample D is Sample C diluted 4 times.

The different samples are rendered alkaline by addition of 90 g/L lime (industrially used concentration) at pH 9, 10, and 11 (measured by combined glass electrode). The Cd in the solution is analyzed after 24 hours by atomic absorption (Perkin-Elmer 3100). The detection limit of atomic absorption is estimated to be 0.05 mg/L.

Each result is the mean value of three samples treated in the same way. The results are presented in Fig. 1. At pH 9, all the samples have cadmium contents greater than the accepted standard. At pH 10, the Cd content is less than 0.1 mg/L. The possible presence of complexing agents in the effluents does not influence hydroxide precipitation. The standard regulations specify a pH value between 5.5 and 8.5 for waste streams. It is not possible to obtain minimal Cd content within this range. Ultrafiltration is a natural candidate to overcome this problem.

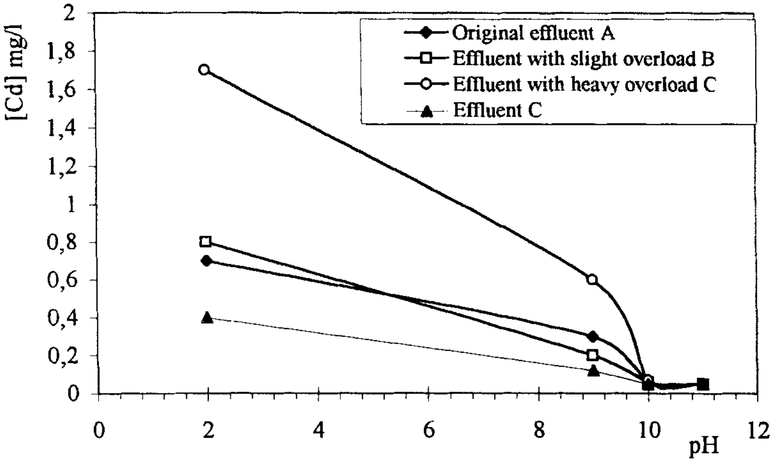

FIG. 1 Influence of pH on residual Cd content.

## CHOICE OF COMPLEXING AGENT

The cations are not retained by ultrafiltration membranes because the metallic ions are too small. Their size must therefore be increased by complexation to obtain molecules of 500 g/mol molar mass or larger than 0.001 μm. The finest ultrafiltration membranes have cut-off thresholds of 500 D.

The most used complexing agents are polyvinyl alcohol (PVA), polyethyleneimine (PEI), and polyacrylic acid (PAA) (8, 20–22). However, these products are primarily used for copper.

The most often used complexing agents for Cd (Table 2) are polyacrylamides (15) and copolymers of ethylenic acids with carboxylic functions (17). Squires (16), who patented the process associating precipitation and ultrafiltration, used sulfide hydroxides and diethyldithiocarbamate.

In our study a dozen products were tested on industrial waste incineration effluents. These effluents were enriched in Cd and other salts of Pb, Cu, and Zn to study the efficiency of complexing agents in unfavorable conditions. The complexing agent efficiency was measured after separation of the complexed or precipitated species and of the free cation. Increasing quantities of polymer were added to the enriched effluent with the pH adjusted to 8 (regulatory standard). After each addition the sample was filtered on a 3-kD membrane (after 48 hours decantation if necessary). To avoid volumes too great for the process, the volume of added polymer

TABLE 3
Cd Concentration in mg/L after Ultrafiltration on a 3-kD Membrane. Influence of Volume of Complexing Agent Added

| | Volume added, in $\mu$L, for 20 cm$^3$ of effluent | | | | | |
|---|---|---|---|---|---|---|
| Products | 50 | 100 | 500 | 1000 | 5000 | Chemical name |
| TMT15 | 20 | 15 | 12 | 4 | 3 | Trimercapto-*s*-triazine trisodic |
| Metalsorb ZT | 2 | 1.5 | 1.3 | 1.5 | 1.7 | Na-dimethyl dithiocarbamate of different molecular weights |
| Metalsorb L | 18 | 13 | 15 | 16 | 12 | |
| TE103 | 20 | 14 | 14 | 18 | 19 | Copolymer ethylenic acids with carboxyl functions |
| TE104 | 20 | 20 | 15 | 12 | 18 | |
| TE105 | 19 | 18 | 6 | 4 | 10 | |
| PVA | 19 | 17 | 16 | 15 | 15 | Polyvinyl alcohol |
| PEI | 15 | 11 | 13 | 9 | 13 | Polyethyleneimine |
| GEROPON | 19 | 13 | 11 | 8 | 15 | Polyacrylic acid (PAA) |
| AN956 | 20 | 18 | 19 | 19 | 19 | Polyacrylamides with acrylate groups |
| TELAFLOC20 0S5 | 16 | 18 | 18 | 19 | 17 | |
| TELAFLOC20 0S10 | 20 | 20 | 17 | 19 | 17 | Same, of anionic nature |

was limited to 2.5% of the effluent volume. The ultrafiltrate was analyzed by atomic absorption.

The results obtained are presented in Table 3. It can be seen that of the 12 products tested, three seem to be efficient: TMT15, Metalsorb ZT, and TE105. However, Metalsorb ZT, which is the cheapest of the three, is active after an addition of only 0.25%. This complexing agent was therefore used for ultrafiltration trials to reduce Cd content in waste streams after the addition of lime.

## TANGENTIAL ULTRAFILTRATION STUDY

### Experimental Apparatus

The experimental apparatus used is shown in Fig. 2. It is composed of a 6-bar feeding pump with an electronic variator, a Pleiade Rayflow tangential ultrafiltration module (manufactured by Tech. Sep. Inc.) with an organic membrane of 200 cm$^2$, a cooler, a flowmeter, a counterpressure

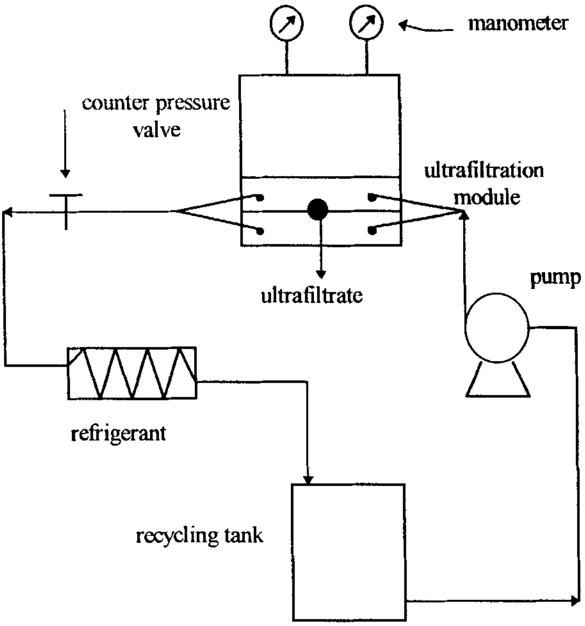

FIG. 2 Experimental apparatus for ultrafiltration.

valve, and a recycling tank. Parallel mounting was used in this study. The counterpressure valve was therefore installed at the output of the module.

The solution to be filtered flows in thin layers between the plates and the membranes of the filter module. In this study a given volume of solution was recycled continuously through the module during the experiments, with no input of fresh solution, and the ultrafiltrate was collected for analysis.

## Influence of pH and Complexing Agent Concentration on the Process Yield

Although parameters influencing a complexation–ultrafiltration process are numerous, we were interested in the parameters which could limit the extraction yield of Cd, such as the pH and the percentage of complexing agent added, in this case Metalsorb ZT. The operating conditions were as follows:

Tangential velocity: 2.2 m/s (corresponding to a flow rate of 300 $L \cdot h^{-1}$)
Counterpressure: 2 bars

Temperature: 20–25°C
"Contact" time of Cd–Metalsorb ZT: 10 minutes stirring before beginning filtration
The composition of the effluent was the same for all trials
The membranes were unclogged after each trial

The trials were carried out within the 7 to 9 pH range, corresponding to the normal pH variation in effluents from air pollution control. The quantity of Metalsorb ZT varied by a factor of 10 and was limited to 2.5%, which corresponds to a consumption of 0.5 $m^3/h$ for an output flow rate of 20 $m^3/h$ (wastewater flow rate from an incineration plant).

Ten liters of effluent were adjusted to the required pH range and then supplemented with the required amount of Metalsorb ZT. The solution was then mixed for 10 minutes. Initial Cd concentration was measured in the solution before addition of Metalsorb. Then part of the treated effluent was filtered through the ultrafiltration module. During filtration, ultrafiltrate was collected continuously in fractions of 250 $cm^3$. Cadmium concentration was then determined in each of the collected fractions. The rest of the effluent was not filtered but settled for 24 hours after addition of Metalsorb. The cadmium concentration in the supernatant was then measured.

Table 4 presents the results obtained. The rejection of the membrane *R* and the decantation yield $\eta$ are defined by

$$R = 1 - \frac{[\mathrm{Cd}]_{\mathrm{ultrafiltrate}}}{[\mathrm{Cd}]_{\mathrm{initial}}}$$

$$\eta = 1 - \frac{[\mathrm{Cd}]_{\mathrm{supernatant}}}{[\mathrm{Cd}]_{\mathrm{initial}}}$$

TABLE 4
Influence of pH and Concentration of Metalsorb ZT on the Membrane Rejection and Decantation Yield

| pH | [Metalsorb ZT] (vol%) | [Cd] Initial | [Cd] Ultrafiltrate | *R* | [Cd] after 24 hours decantation | $\eta$, decantation yield |
|---|---|---|---|---|---|---|
| 7 | 0.25 | 0.87 | 0.21 | 0.76 | 0.37 | 0.57 |
| 9 | 0.25 | 0.86 | 0.22 | 0.74 | 0.34 | 0.60 |
| 7 | 0.5 | 0.85 | 0.24 | 0.72 | 0.27 | 0.68 |
| 9 | 2.5 | 0.86 | 0.23 | 0.73 | 0.25 | 0.71 |
| 8 | 1.38 | 1.14 | 0.37 | 0.67 | 0.33 | 0.71 |
| 8 | 1.38 | 1.09 | 0.33 | 0.69 | 0.39 | 0.64 |

The results obtained allow us to observe a tendancy toward a better yield for the lower Metalsorb ZT concentrations. The pH does not seem to have an influence on the elimination of Cd during ultrafiltration.

For decantation (without addition of flocculent), a better yield is observed for higher concentrations of Metalsorb, with no influence of pH. This result tends to prove that the greater the quantity of Metalsorb, the greater the precipitate. Ultrafiltration is better for low complexing agent concentrations, whereas for high concentrations more or less the same results are obtained.

To confirm these good results obtained with low Metalsorb concentrations, further experiments were carried out on the same membrane. The results are presented in Fig. 3. The curve obtained seems to reach a maximum at a yield of 84% for an addition of complexing agent of 0.10%. Below this limit of 0.10% there is not enough complexing agent, and above this limit the formation of the complex reduces the yield.

A higher concentration of residual Cd is observed with high concentrations of Metalsorb. This can be explained, and confirmed by analysis, by the presence of Cd in the complexing agent (mixed soluble complex between Metalsorb ZT and Cd).

## Influence of Membrane Size

As the flow rate of the permeating liquid depends mainly on the pore size, a further trial was carried out at pH 8 with 0.1% of complexing agent and a microfiltration membrane of 0.2 μm instead of an ultrafiltration membrane of 20 kD. The results are presented in Table 5. A decrease in

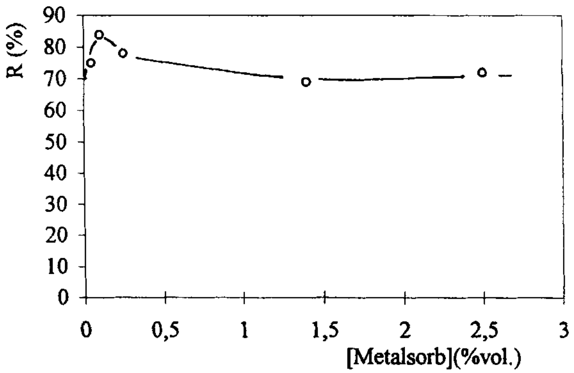

FIG. 3 Influence of Metalsorb ZT concentration on retention level at pH 8.

TABLE 5
Influence of Membrane Pore Size on the Membrane Rejection and Decantation Yield

| Membrane size | [Metalsorb ZT] (vol%) | [Cd] Initial | Ultrafiltrate | *R* | Flow rate ($L \cdot h^{-1} \cdot m^{-2}$) |
|---|---|---|---|---|---|
| 20 kD | 0.1 | 0.86 | 0.14 | 0.84 | 800 |
| 0.2 μm | 0.1 | 1.14 | 0.27 | 0.76 | 4000 |

yield can be observed, probably due to a slight amount of precipitate crossing the membrane. The Cd concentration remains similar to that obtained with higher concentrations of Metalsorb ZT. The filtrate is clear in all cases. Any Metalsorb ZT in excess crosses the 20 kD and 0.2 μm membranes (detected by its characteristic odor and acid precipitation).

## Ultrafiltration Rate and Clogging

The main problem in an ultrafiltration or microfiltration module is clogging of the membranes. For the moment it is inevitable and unpredictable, and this is why the flow rate was monitored during the trials.

The flow rate across the ultrafiltration membrane (20 kD) is about 800 $L \cdot h^{-1} \cdot m^{-2}$ whereas during microfiltration (0.2 μm) it is 4000 $L \cdot h^{-1} \cdot m^{-2}$. The clogging rate of the ultrafiltration membrane does not depend on the Metalsorb ZT content nor on the pH in the studied range, but only on the nature of the effluent. After just a few minutes the ultrafiltration flow rate falls to 200 $L \cdot h^{-1} \cdot m^{-2}$ whether it is at an initial flow rate of 300 or 700 $L \cdot h^{-1} \cdot m^{-2}$ after unclogging. After 1 hour the ultrafiltrate flow rate falls to about 70 $L \cdot h^{-1} \cdot m^{-2}$ (Figs. 4 and 5). It is therefore of no advantage to wash the membrane for a long time; it is better to wash it more often. For microfiltration, no counterpressure was applied and the flow of 300 $L \cdot h^{-1}$ was maintained. After 15 minutes in these conditions, the same flow rates were found as for ultrafiltration. However, if a counterpressure of 2 bars was applied, the flow rate increased from 90 to 500 $L \cdot h^{-1} \cdot m^{-2}$.

In the case of microfiltration, it would be necessary to program a gradual increase of the counterpressure according to the ultrafiltrate flow rate in order to optimize the system.

## Comparison of Tangential Filtration to Precipitation–Decantation

If precipitation–flocculation–decantation is compared to ultrafiltration of macrocomplexes and the microfiltration of precipitates, it is noted that:

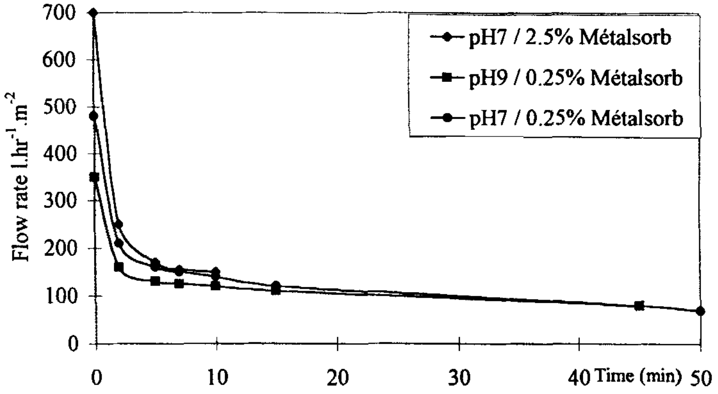

FIG. 4 Monitoring of flow rate at different pH and Metalsorb ZT concentrations during ultrafiltration.

The residence time in a precipitation–flocculation–decantation process is much longer than for tangential filtration.

The clarifier must be followed by a sand filter to equal to perfomance of tangential filtration concerning the suspended matter. According to Squires (16), clarifiers under normal conditions do not retain very small precipitates, which degrade the effluent quality. The performance of clarifiers and sand filters as compared to that of microfiltration has been tested by Cory Environnemental on effluents from the galvanoplastic industry. Microfiltration gives better results (16).

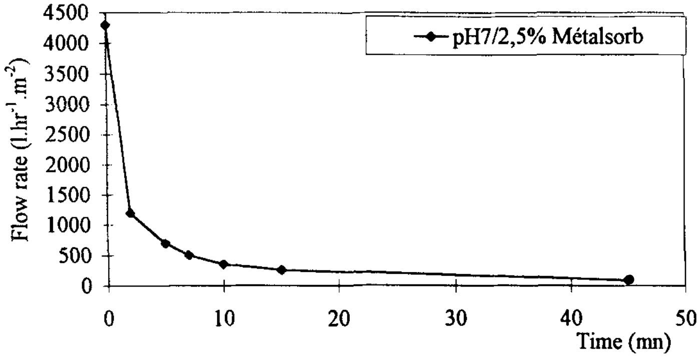

FIG. 5 Monitoring of flow rate at different pH and Metalsorb ZT concentrations during microfiltration.

Flocculent concentration must be optimized. A heavy excess can affect the treatment efficiency. If the process finishes with a tangential filtration step, the use of a flocculent can be minimized. The suspended matter retained in the filter is then eliminated when it is recycled through the flocculation–decantation system.

Tangential filtration is not subject to variations in effluent composition and produces water of constant quality.

A tangential filtration process can be completely automized and is therefore of low running cost, which counterbalances the relatively high investment cost.

Microfiltration of a precipitate is more interesting than ultrafiltration of a complex if we take into account the presence of suspended matter which involves purging retained material upstream of the process (in the precipitation–flocculation tank). A soluble complex would be in competition with the precipitation and decrease its efficiency

The use of microfiltration after flocculation–decantation is optimal because it allows recycling of the concentrate. By total elimination of the suspended matter, the filtrate can be returned to nature. Furthermore, process efficiency does not depend on fluctuations in the effluent composition, which avoids a superfluous or even harmful consumption of flocculent.

## CONCLUSION

The results obtained in this study show that tangential filtration can be usefully associated with the usual physicochemical techniques to satisfy regulatory standards concerning waste streams. In our method, hydroxide precipitation associated with tangential filtration is entirely satisfactory for reducing the Cd content in waste streams. Tangential filtration ensures a greater stability of results despite the inevitable fluctuations of flow rate, pH, and concentrations. Hydroxide precipitation alone is extremely sensitive to pH. Furthermore, tangential filtration guarantees a waste stream without suspended matter at the output, and minimizes the amount of flocculent used. The complexing agent selected after testing 12 different products is Metalsorb ZT (Na-dimethyldithiocarbamate) which removes 70 to 75% Cd with an addition of complexing agent from 0.25 to 2.5% in volume and within the pH 7–9 range.

## REFERENCES

1. A. Gouchet, *Galvano-organo-traitements de surface*, 1990, p. 981.
2. S. Mandjiny, A. I. Zouboulis, and K. A. Matis, *Sep. Sci. Technol.*, *15*, 2963 (1995).

3. R. Gourdon, P. Diard, and N. Funtowicz, *FEMS Microbiol. Rev.*, *14*, 333 (1995).
4. R. Gourdon, E. Rus, S. Bhende, and S. Sofer, *J. Environ. Sci. Health*, *A25*, 1019 (1990).
5. H. M. Freeman, *Standard Handbook of Hazardous Waste. Treatment and Disposal*, McGraw-Hill, New York, NY, 1989.
6. M. Meireles, *L'Eau, l'Industrie, les Nuisances*, 1984, p. 309.
7. A. S. Michaels, *Advances in Separation and Purification*, Wiley, New York, NY, 1968.
8. H. Strathmann, and K. Koch, *Selective Removal of Heavy Metal Ion from Aqueous Solutions by Diafiltration of Macromolecular Complexes. Recent Developments in Separation Science*, Chemical Rubber Co, New York, NY, 1978.
9. A. Hafiane, I. Issid, and D. Lemordant, *J. Colloid Interface Sci.*, *1*, 167 (1991).
10. K. W. Lee, S. H. Cho, and S. W. Park, *J. Environ. Sci. Health*, *3*, 467 (1995).
11. I. Ndiaye, M. Lo Sidy, and C. Diawara Keba, *Entropie*, *188–89*, 55 (1995).
12. M. Belkacem, H. Matamoros, C. Cabassud, Y. Aurelle, and J. Cotteret, *J. Membr. Sci.*, *106*, 195 (1995).
13. H. Strathmann, *Sep. Sci. Technol.*, *14*, 1135 (1980).
14. K. Geckeler, H. Lange, H. Eberhardt, and E. Bayer, *Pure Appl. Chem.*, p. 1883 (1980).
15. P. Sarrazin, Thèse, Institut National des Sciences Appliquées de Lyon, 1991.
16. R. C. Squires, *Water Sci. Technol.*, *10*, 55 (1992).
17. S. Niessen, V. Sciers, F. Persin, and M. Rumeau, *Rev. Gen. Electr.*, *3*, 12 (1992).
18. S. Benbrahim, Thèse, Université de Rennes 1, 1994.
19. M. Pourbaix, *Atlas d'équilibre électrochimiques à 25°C*, Gauthier-Villard & Cie, Paris, 1963.
20. K. Ennassef, M. Persin, and G. Durand, *Analusis*, *10*, 565 (1989).
21. V. Mavrov, *Desalination*, *83*, 289 (1991).
22. Q. T. Nguyen, Y. Jyline, and J. Neel, *Analusis*, *36*, 277 (1981).

*Received by editor April 9, 1996*
*Revision received September 1996*