

## Application of Cross-Flow Electro-Microfiltration in Chromium Wastewater Treatment

C. VISVANATHAN

*CEFIGRE International Training Centre for Water Resources Management, P.O. Box 13, Sophia Antipolis, 06561 Valbonne Cedex (France), Tel.: 93-743100, Telex: 461 311 F*

R. BEN AIM

*Laboratoire de Genie Chimique, CNRS, Chemin de la Loge, 31078 Toulouse (France), Tel.: 53958025, Telex: 572767 F*

and

S. VIGNESWARAN\*

*Environmental Engineering Division, Asian Institute of Technology, G.P.O. Box 2754, Bangkok (Thailand), Tel.: 66 2-5290100 (ext. 2635 or 2910), Telex: 84278 TH, Telefax: 66 2-5296374*

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### SUMMARY

Cross-flow microfiltration (CFMF) was experimentally studied for the separation of precipitates of chromium hydroxide. Although this process enables one to obtain chromium-free filtrate, a disadvantage is that the filtration flux declines rapidly due to membrane fouling. In order to avoid this fouling problem and increase the filtration flux, an electric field was applied across the membrane as an antifouling technique (cross-flow electro-microfiltration — CFEMF). The surface charges of the precipitates were modified by adding a dispersant. The experimental results indicate that this modified process of CFEMF is highly effective in reducing the membrane fouling, which eventually leads to a remarkable filtration flux increase. The application of this antifouling technique of CFEMF is cited only for the suspensions containing charged particles and colloids. Nevertheless, the process of modification of surface charge with a dispersant permits us to use this technique with a wide variety of suspensions.

*Keywords:* cross-flow electro-microfiltration, chromium wastewater, dispersant, antifouling, electric field, filtration flux, surface charge, laboratory-scale experiments.

### INTRODUCTION

In recent years increasing attention has been given to the presence of heavy metals (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Pb and Zn) in the aquatic environment,

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\*Author to whom all correspondence should be addressed.

mainly due to their toxicity to the ecological system. Some of these metals are known to be highly toxic to man, while the others are more lethal to the aquatic microorganisms, fish and plants. The lethal effect of heavy metals on aquatic organisms and humans depends predominantly on the type and concentration of the metal present in the water stream. The industrial effluents are known to be the major source of heavy-metal pollution. As the presence of these metals, even in minute quantities, leads to detrimental effects on the ecological systems, most of the developed and developing countries have established stringent standards on their presence in industrial effluents. In order to meet these effluent standards industries have to adopt an effective effluent treatment system.

Selection of an appropriate treatment process usually depends on (a) the concentration of the metal in the suspension to be treated and its form, and (b) the volume of the suspension to be treated. In industrial wastewaters, metals are found in different forms, namely: soluble, insoluble, organic, reduced, oxidized, free metal, precipitated, adsorbed and complex.

#### *Treatment process for chromium wastewater*

In most industrial effluents, chromium is present in the soluble form either as hexavalent chromium [Cr(VI)] or trivalent chromium [Cr(III)]. The discharge of hexavalent chromium into the aquatic environment comes mainly from industries such as metal finishing, paint manufacturing, dyeing, etc. It is highly toxic to aquatic organisms. Cr(III) is considered to be relatively less toxic, and industries such as textile, ceramic, tanneries, photographic, etc., are the primary sources of this pollutant.

The separation of Cr(VI) consists of two steps, namely the reduction of Cr(VI) with a reducing agent at an acidic pH and then precipitation of the reduced compound. These precipitates are then allowed to settle down in a settling tank for a period of 6–8 h. The effluent usually contains 5–20 mg/l of suspended solids, mostly in the form of precipitates of Cr(III) [1]. In order to accomplish total elimination of chromium and attain the required effluent standards, the settling tank effluent has to be filtered through a sand bed filter (see Fig. 1). Meanwhile, the sludge produced in the settling tank is dewatered by using a filter press or vacuum filter.

The application of cross-flow microfiltration (CFMF) has been intensively studied as an alternative separation process for precipitates of Cr(III) [2]. In the conventional chromium separation process, CFMF can be used in two possible modes: (a) direct filtration of precipitates without the settling tank, and (b) filtration of settling tank effluent. In the CFMF system, when the recirculating slurry attains a concentration of 10–15% solids, it is usually sent to the sludge dewatering system.

In spite of the advantages like better quality of treated effluent and the pos-

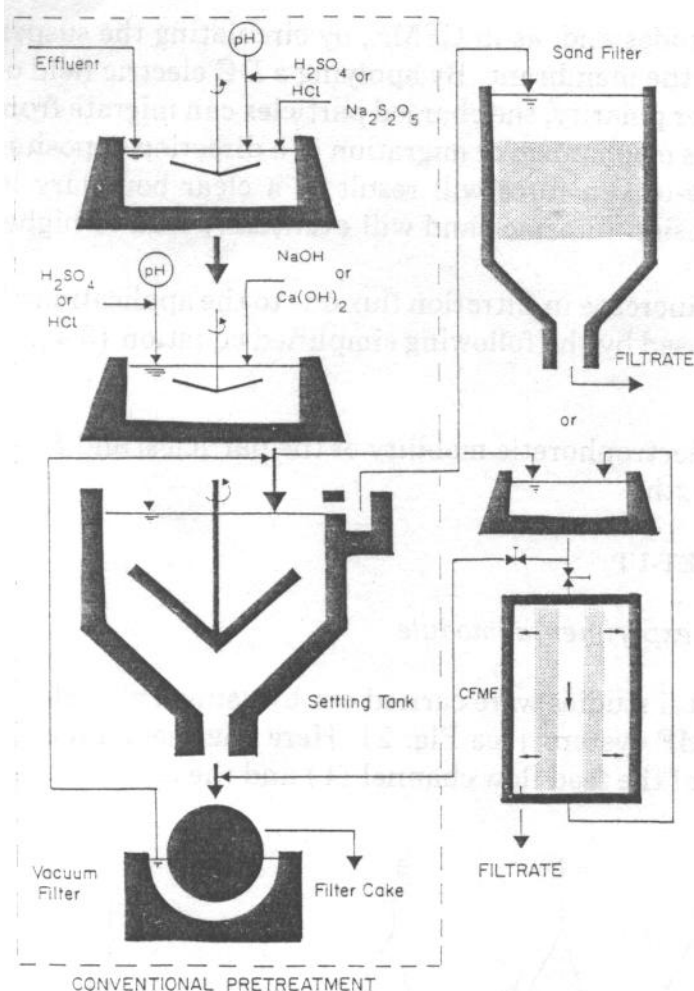


Fig. 1. Separation of hexavalent chromium in the form of  $\text{Cr}(\text{OH})_3$  precipitates.

sibility of installation in most of the conventional treatment systems, at present the CFMF process has been confined to very few industrial applications. In this technique there exists a deposition of precipitates at the membrane-suspension interface, which is generally named as membrane fouling. This membrane fouling leads to an increase in resistance and an eventual reduction of filtration rate. So, the effectiveness of a CFMF system is primarily limited by such membrane fouling problems.

The primary objective of this study is thus to examine a process modification, which will lead to either elimination or reduction of this membrane fouling problem in the conventional CFMF. In this respect, we have used an antifouling technique called “cross-flow electro-microfiltration” (CFEMF).

#### *Cross-flow electro-microfiltration*

This method is a hybrid physical operation which combines CFMF and electrophoretic separation techniques. CFEMF is achieved by placing a membrane

between two electrodes and, as in CFMF, by circulating the suspension to be treated parallel to the membrane. By applying a DC electric field of sufficient strength and proper polarity, the charged particles can migrate from the membrane surface. This mechanism of migration in a direction opposite to the conventional pressure-driven force will result in a clear boundary layer at the membrane-suspension interface and will eventually lead to higher filtration flux.

In CFEMF, the increase in filtration flux due to the application of an electric field can be expressed by the following simplified equation [3,4]:

$$J_{ep} = U_{ep} \cdot E \quad (1)$$

where  $U_{ep}$  is the electrophoretic mobility of the particles, and  $E$  is the applied electric field strength.

#### EXPERIMENTAL SET-UP

##### *Description of the experimental module*

The experimental studies were carried out by using a plexiglass plate and a frame-type CFEMF system (see Fig. 2). Here the membrane (2) is placed between one side of the feed flow channel (1) and the filtrate collection cham-

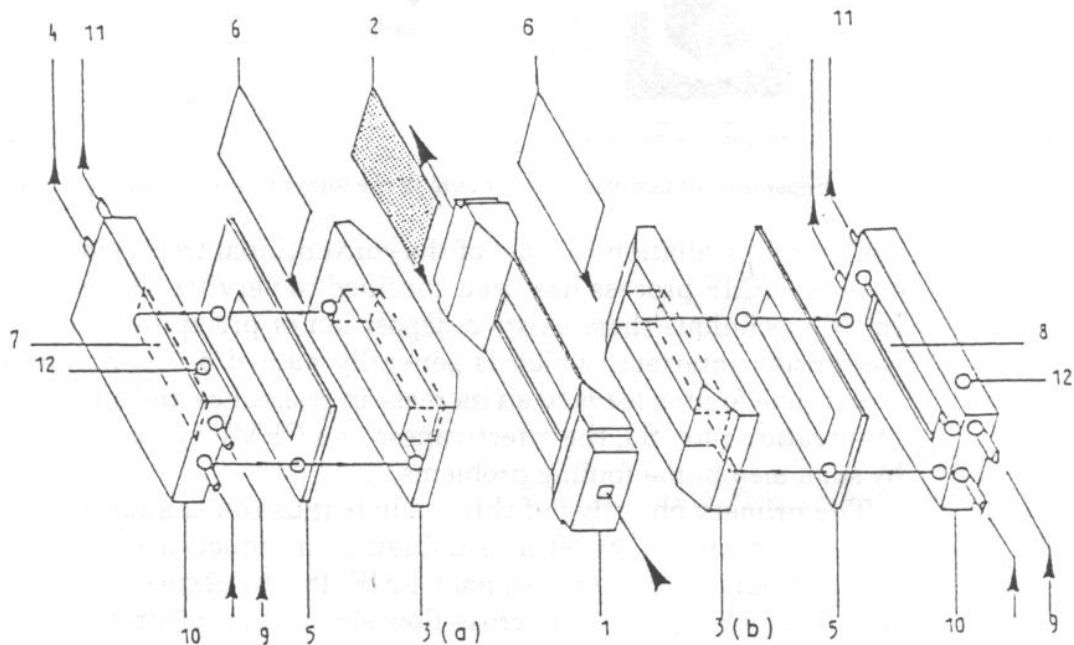


Fig. 2. Cross-flow electro-microfiltration cell assembly. (a) Feed flow channels; (2) microfiltration membrane; (3a) filtrate collection chamber; (3b) supporting spacer; (4) filtrate outlet; (5) intermediate spacer; (6) ion permeable cellulose membrane; (7) cathode; (8) anode; (9) electrolyte inlet; (10) electrode supporting plate; (11) electrolyte outlet; (12) electrode connection.

ber (3a). The depth, width and length of the feed channel are 0.5, 4 and 20 cm, respectively. The other side of this flow channel consists of an ion-permeable cellulose membrane, which permits the separation of the feed suspension and the electrolyte. Another ion-permeable cellulose membrane (6) is placed between the intermediate spacer (5) and the filtrate collection chamber (3a) in order to separate the electrolyte and filtrate. Platinum-coated titanium electrodes (7 and 8) are fixed to the electrode supporting plate (10). In this arrangement, the electrodes do not make any direct contact either with the filtrate or the feed solution. The ion-permeable membrane permits the physical separation of filtrate and feed suspension from the electrolyte. At the same time, it allows the passage of ions on applying a DC electric field.

All the experiments were carried out by using a Versapor-200 acrylic copolymer membrane (Gelman Science) with a pore diameter of  $0.2 \mu\text{m}$  and a filtration surface area of  $80 \text{ cm}^2$ . The cross-flow velocity in all experimental runs was fixed at  $1.3 \text{ m/s}$ , which corresponds to a Reynolds number of 11,544. In Fig. 3 is presented the schematic representation of the experimental set-up. The detailed description of the experimental procedures was summarized elsewhere by Visvanathan [5].

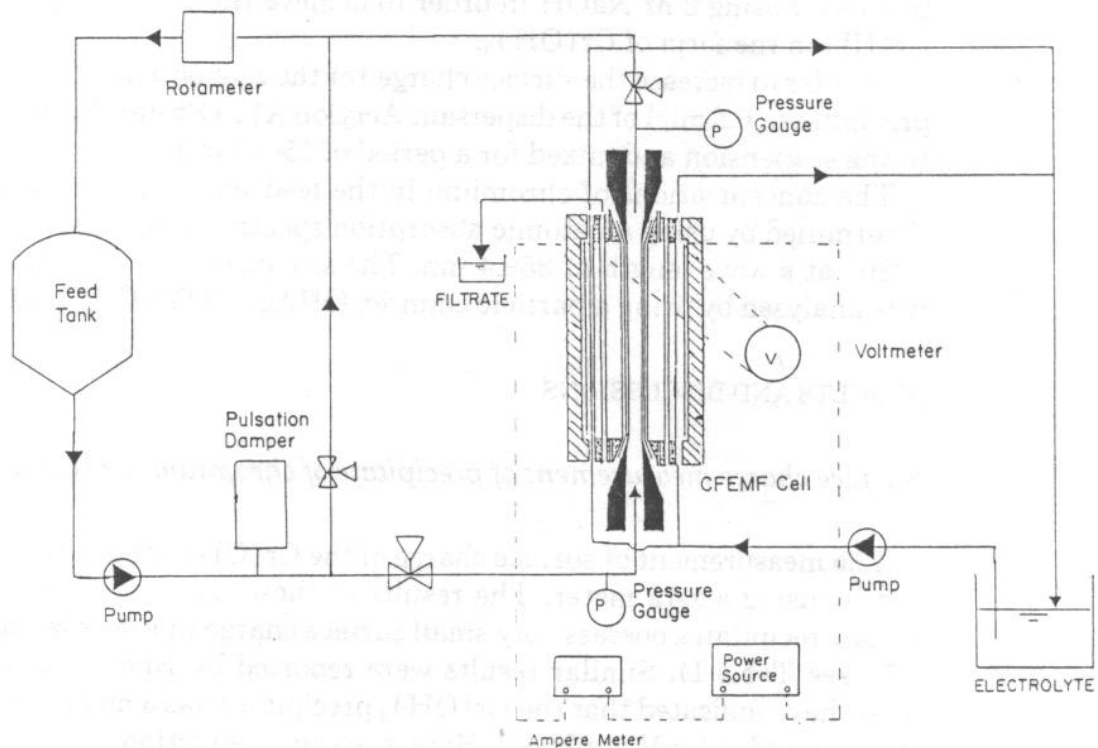


Fig. 3. Schematic representation of the experimental set-up.

### *Preparation of synthetic chromium wastewater*

The synthetic Cr(VI) suspension for the experimental study was prepared in the following manner [6,7].

A suspension of 150 mg/l of chromium was prepared by dissolving a known amount of  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (RP Normapur, Prolabo) in water. The feed suspension was made from water obtained from a MilliQ (Millipore) system (with a resistivity of 18 M $\Omega$  cm and free of organic matter, particles and colloids) and 125 mg/l Ludox (Du Pont de Nemours) silica colloids with an average diameter of 12 nm. In CFMF, the presence of colloids in the feed solution plays an important role in creating excess external membrane fouling [4]. In all practical applications, the industrial wastewaters contain a combination of colloids and particles (or precipitates). Hence, in order to make a feed suspension which represents real industrial feed suspension, the silica colloids were added to the feed water which was free from pure colloids. The pH of the feed suspension was adjusted to the range of 2–2.5 by using 1 M  $\text{H}_2\text{SO}_4$ .

An amount of 0.5479 g/l of sodium metabisulfite (Normapur, Prolabo) was added to the feed solution for the complete reduction of Cr(VI) to Cr(III). The suspension was mixed for 15–30 min. The pH of the suspension was adjusted to 6.5–7.0 using 2 M NaOH in order to achieve the complete precipitation of Cr(III) in the form of  $\text{Cr}(\text{OH})_3$ .

In order to increase the surface charge (or the zeta potential) of the  $\text{Cr}(\text{OH})_3$  precipitates, 0.5 ml/l of the dispersant Acrylon A11 (Protex, France) was added to the suspension and mixed for a period of 15–30 min.

The concentrations of chromium in the feed solution and the filtrate were determined by using an atomic absorption spectrophotometer (Perkin-Elmer 3030) at a wave length of 359.4 nm. The size distribution of the precipitates was analysed by using a particle counter (HIAC/ROYCO-PC 320).

## RESULTS AND DISCUSSIONS

### *Surface charge measurement of precipitate of chromium hydroxide*

The measurement of surface charge of the  $\text{Cr}(\text{OH})_3$  precipitates was carried out by using a zeta meter. The results of these measurements indicate that these precipitates possess very small surface charge in the order of 1 mV at pH 7.5 (see Table I). Similar results were reported by Bhattacharya et al. [7]. They have indicated that the  $\text{Cr}(\text{OH})_3$  precipitate has a maximum zeta potential value of +4 mV at pH 8.0. Here, the small reduction of the zeta potential of the precipitates may be due to possible absorption of the negatively charged silica colloids on the precipitate's surface. This small surface charge leads to a notable reduction of the particle–particle repulsion and consequently permits



TABLE I

Relation between zeta potential of  $\text{Cr}(\text{OH})_3$  precipitates and dispersant concentration

Dispersant concentration ml/l)	Zeta potential (mV)
	+0.92
.2	-46.76
.4	-46.26
.5	-46.93
.8	-50.78
.0	-46.76

the formation of particle clusters. This results in rapid settling of these precipitates in the settling tank.

Nonetheless, the effective performance of the CFEMF process is directly related to the zeta potential (or electrophoretic mobility) of the particles (Eqn. 1). So in the conventional process, the application of CFEMF for the separation of  $\text{Cr}(\text{OH})_3$  is not very promising. Considering this point in our experimental series, we have modified the surface charge of these precipitates, which will enable us to use the CFEMF process.

#### *Modification of surface charge of $\text{Cr}(\text{OH})_3$ precipitates*

A suspension containing particles can be maintained in a stable state (without settling of particles) by destructing the agglomeration of the particles by increasing the inter-particle repulsion. This can be achieved by using a dispersant [8]. The dispersants are generally composed of organic or mineral polymers (with relatively small molecular weight) consisting of a negative charge placed uniformly along the length of the molecule. When we add this dispersant to the suspension, it will get adsorbed perfectly on the particle surface resulting in an increase in surface charge of the particles. This phenomenon will lead eventually to a higher inter-particle repulsion which avoids the formation of particle clusters. This technique of surface charge modification by using a dispersant does not change the surface tension of the suspension.

The theory of surface charge modification by using a dispersant is relatively complex, and at present few fundamental studies have been carried out in this field. At this moment, the optimal performance of a dispersant is usually determined by using the empirical relations derived from the systematic experimental studies.

In our experimental studies we used the dispersant Acrylon A11 (Protex). Table I presents the surface charge of the precipitates as a function of the dispersant concentration. Here we noted a significant improvement of surface

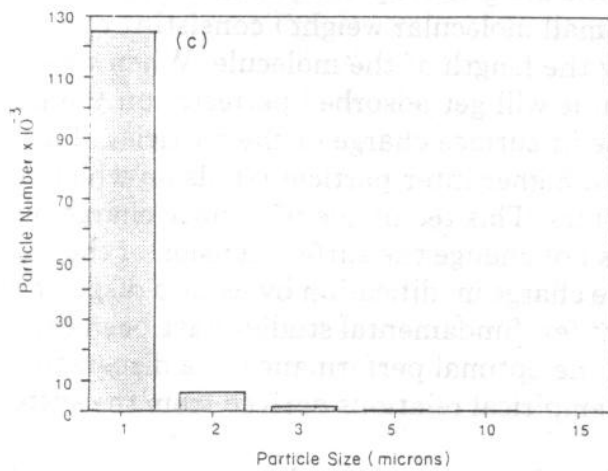
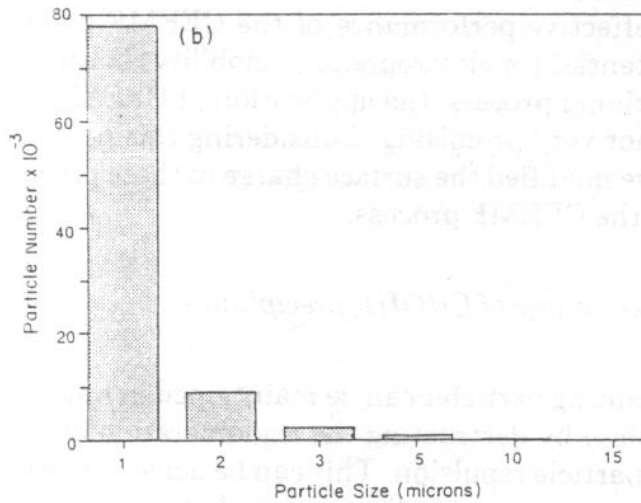
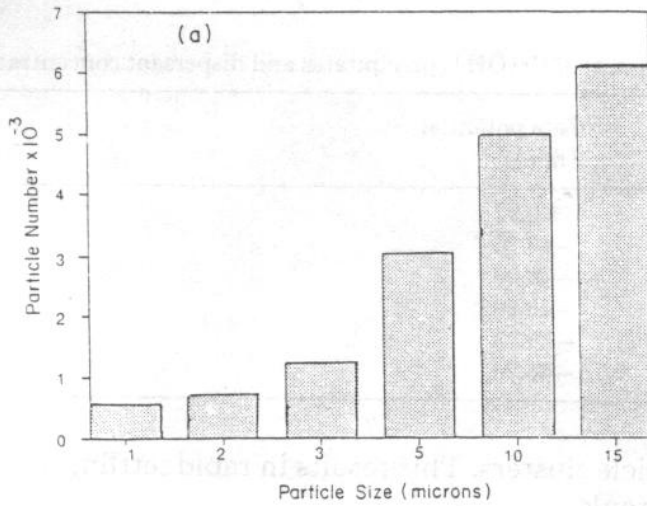


Fig. 4. (a) Particle size distribution of the suspension  $\text{Cr}(\text{OH})_3$  without the addition of dispersant. (b) Particle size distribution of the effluent obtained after 6 h of settling. (c) Particle size distribution of the suspension  $\text{Cr}(\text{OH})_3$  with the addition of dispersant.



charge after addition of the dispersant to the suspension. Nevertheless in our concentration range of the dispersant (0.2–1.0 ml/l), we did not note any significant change in the zeta potential value. In addition we did not notice any indicative change in zeta potential of the precipitate in our experimental pH range of 6.5–7.0.

#### *Particle size distribution of the precipitates*

Fig. 4a presents the particle size distribution of the suspension of  $\text{Cr}(\text{OH})_3$  without the addition of dispersant. Here, we can note that most of the precipitates had a relatively large size (more than  $5 \mu\text{m}$ ). Later, this suspension was mixed and allowed to settle in a 1-l conical flask for a period of 6 h. Then, the effluent water was analyzed for its particle size distribution, and the result is presented in Fig. 4b. This result indicates that the effluent contains more particles of about  $1 \mu\text{m}$  when compared to the original suspension. At the same time, this effluent contains 16 mg/l chromium which reveals the importance of the final treatment of this effluent using conventional sand filters or CFMF.

Fig. 4c presents the particle size distribution of a suspension of  $\text{Cr}(\text{OH})_3$  precipitate with 0.5 ml/l of dispersant. This figure illustrates that the suspension has a majority of particles of about  $1 \mu\text{m}$ . This is due to the creation of inter-particle repulsion resulting from the modification of surface charge which prevents the small monoparticles from coagulating into multiparticle floc.

#### *CFMF and CFEMF processes for the separation of $\text{Cr}(\text{OH})_3$ precipitates*

Fig. 5 illustrates the relation between filtration flux and electric field strength. For a suspension containing 0.5 ml/l of dispersant, the filtration flux increases linearly with the electric field strength. This reveals that the CFMF filtration flux (at  $E=0 \text{ V/cm}$ ) can be improved to a notable level by the CFEMF process. Nevertheless, in our study, due to the practical limitations of the module, we could not further increase the electric field strength.

Meanwhile, we have noted that during the CFMF process at  $E=0 \text{ V/cm}$ , the filtration flux of a suspension which does not contain the dispersant is higher than that of a suspension containing the dispersant. It is due to the influence of different particle size distributions of these two suspensions in the microfiltration process. Here, the addition of dispersant creates fine particles of about  $1 \mu\text{m}$ , which leads to the formation of a particle deposition layer at the membrane–solution surface. The permeability of this layer is relatively small in comparison to that formed by the suspension which does not contain the dispersant (whose particle size is relatively large). In addition, in CFMF for a given flow conditions, the fine particles tend to accumulate more easily at the membrane surface than do the larger ones [9].

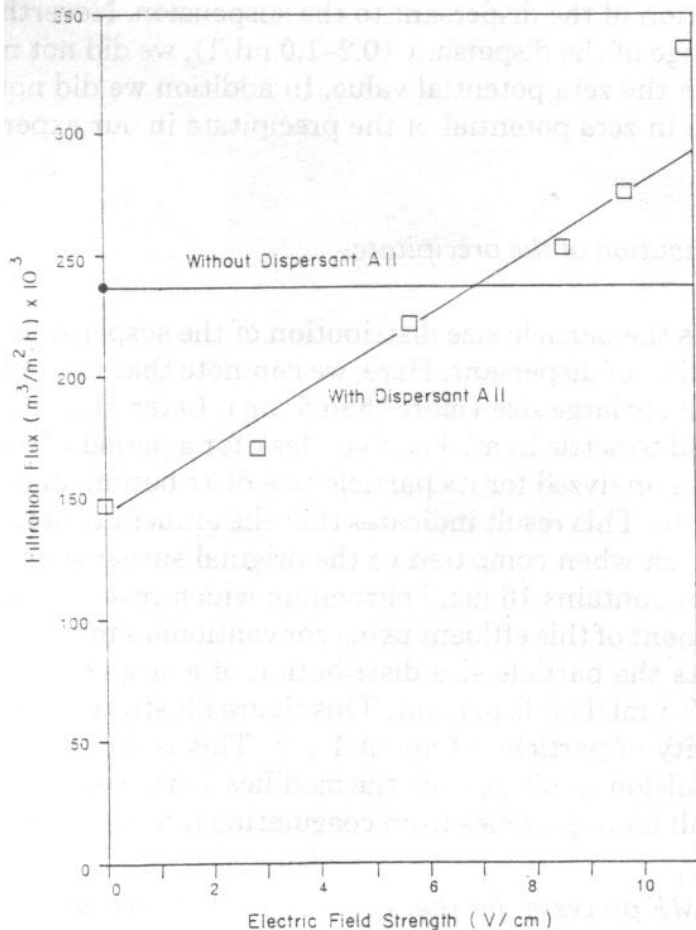


Fig. 5. Evolution of filtration flux with electric field strength at pressure = 0.2 bar.

### *Filtration and concentration of $\text{Cr}(\text{OH})_3$ precipitates in the CFEMF process*

In addition to the earlier experimental work, we have carried out work on the separation of  $\text{Cr}(\text{OH})_3$  in a CFEMF process, in two stages:

**Stage I:** In this stage, the filtration of the suspension was carried out for a period of 60 min. Here, the concentration of the suspension remained approximately constant by returning the filtrate to the feed tank. Here, even though there exists a particle polarization at the membrane, the amount of solute present at this polarized layer is relatively small in comparison to that present in the total feed suspension volume (10 l).

**Stage II:** Following stage I, the process of concentration was realized for a period of 2 h. In this case, the filtrate was collected separately which resulted in an augmentation of concentration of  $\text{Cr}(\text{OH})_3$  in the feed suspension.

Fig. 6 represents the results of the two stages of operation. These results prove that the filtration flux obtained at the stages of filtration and concen-

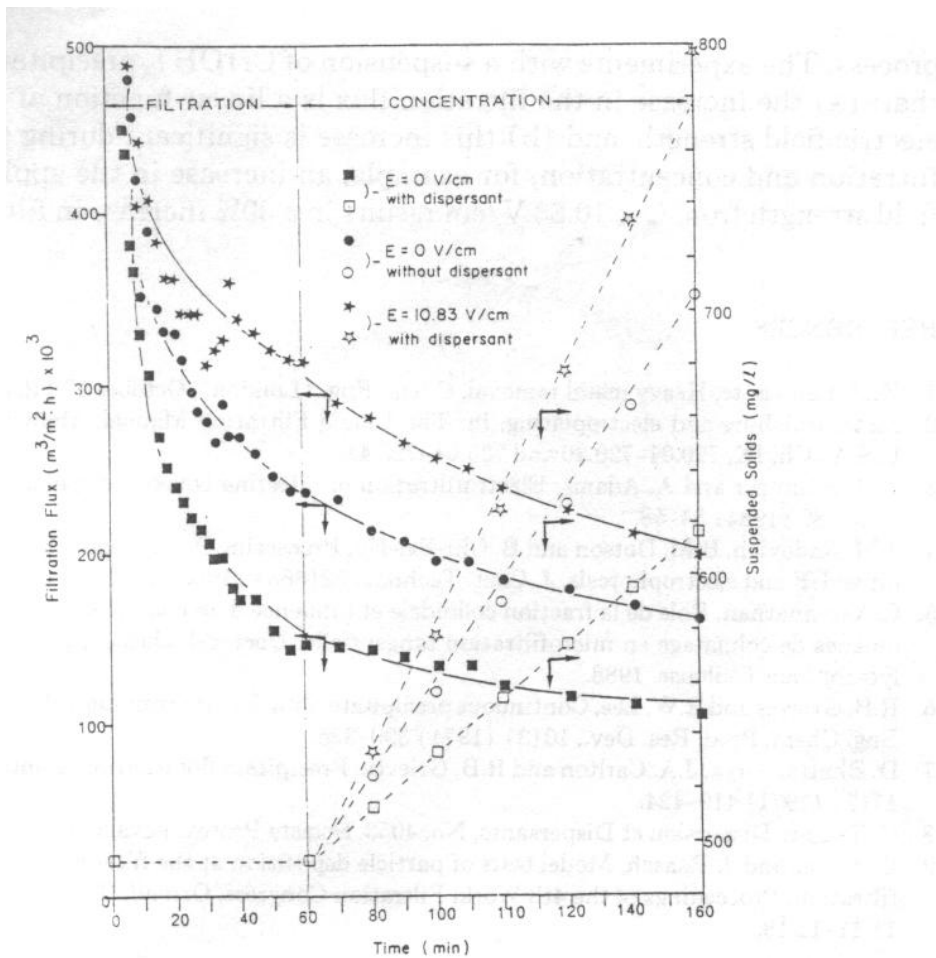


Fig. 6. Relation between filtration flux, suspended solids and time, for three different operating conditions at pressure = 0.2 bar.

tration is relatively high in comparison to the conventional CFMF process. However, it is noteworthy to point out that at the concentration stage, the concentration of  $Cr(OH)_3$  (in terms of suspended solids) treated by the CFEMF is relatively higher than that treated by CFMF.

## CONCLUSION

As the effectiveness of the CFEMF process depends primarily on the surface charge of the particles, its application is limited only to suspensions containing charged particles. However, we have shown that it is equally possible to apply this technique to suspensions such as precipitates of  $Cr(OH)_3$  with relatively negligible surface charge. In such situations, it is necessary to increase the surface charge by addition of a dispersant.

This technique of surface charge modification with the help of a dispersant permits us to use a wide variety of suspensions which can be treated in a CFEMF

process. The experiments with a suspension of  $\text{Cr}(\text{OH})_3$  precipitates indicate that: (a) the increase in the filtration flux is a linear function of the applied electric field strength, and (b) this increase is significant during the stage of filtration and concentration, for example, an increase in the applied electric field strength from 0 to 10.83 V/cm results in a 30% increase in filtration flux.

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