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

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To cite this Article Milonjić, Slobodan K. , Vučić, Nevenka B. and Vujošević, Sofija I.(1996) 'Ultrafiltration of Hematite Sol', Separation Science and Technology, 31: 10, 1515 — 1521
To link to this Article: DOI: 10.1080/01496399608001410
URL: http://dx.doi.org/10.1080/01496399608001410

SEPARATION SCIENCE AND TECHNOLOGY, 31(10), pp. 1515–1521, 1996

TECHNICAL NOTE

Ultrafiltration of Hematite Sol

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ABSTRACT

Ultrafiltration of a laboratory-made hematite sol was studied in a batch cell with an Amicon PM 10 membrane at 298 K. The effects of hematite bulk concentrations (2 to 10 kg·m^{-3}), stirring conditions (0 and 400 rpm), and pressure (50 to 350 kPa) were investigated. The permeate flux increases with increasing pressure and stirrer speed, and decreases with increasing hematite bulk concentration. The polarization resistance increases with an increase in pressure and hematite concentration. The polarization resistance is greater under unstirred conditions.

INTRODUCTION

Over the past two decades, membrane ultrafiltration has become recognized as a viable process for the concentration or separation of moderate to high molecular weight solutes from solutions and for the concentration of colloidal dispersions. Ultrafiltration is used industrially nowadays as an alternative to conventional separation methods such as distillation, centrifugation, and extraction.

The volumetric flux obtained during ultrafiltration of macromolecular and colloidal dispersions is usually much smaller than that attained with a pure solvent. This reduction in flux has been attributed to the phenomenon of concentration polarization, i.e., the build-up of rejected solute in the boundary layer near the membrane surface. The mechanisms by which flux reduction occurs have been variously thought to be a reduction in driving force resulting from the increased osmotic pressure at the membrane surface in the case of macromolecular solutions and the formation of a gel which offers a hydraulic resistance in addition to that of the membrane in the case of colloidal dispersions.

Ultrafiltration of natural polymers, synthetic flexible and rigid polymers, surfactants, and dyes has been an object of interest and study of many researchers, but very few studies have dealt with ultrafiltration of metal oxides and metal sols (1–8). To our knowledge, there are no literature data on the ultrafiltration of colloidal hematite dispersion.

In this paper the effects of several factors (hematite bulk concentration, pressure, and stirring conditions) on hematite sol ultrafiltration are investigated.

EXPERIMENTAL

All experiments were performed using a Sartorius cell, model SM 16526, with a capacity of 200 cm^3 and an effective membrane area of 12.5 cm^2. The cell has a removable plastic jacket, so that the fluid to be ultrafiltered can be warmed or cooled by water passing from a thermostat through the jacket. The top of the cell contains a pressure relief valve and a gas inlet, while the bottom contains a permeate outlet. The cell houses an internal magnetic stirring bar suspended close to the upper surface of the membrane. An Amicon Diaflo PM-10 membrane was used. This membrane is made of polysulfone with a nominal molecular weight cut-off of 10,000 Daltons and an apparent pore diameter of 3.8 nm.

Hematite sol had been prepared by "forced hydrolysis," i.e., thermal hydrolysis of iron(III) chloride solution, similar to the method of Brusov and Usyarov (9). The colloid formed was stable (no precipitation or change in color) over 2 years. The hematite content was determined gravimetrically, the pH was measured by a glass electrode and a silver–silver chloride electrode using a Backman pH meter, model ϕ 71, and the crystalline structure of the solid phase was analyzed by a Siemens-D 500 diffractometer with CuKα Ni filtered radiation. The hematite sol obtained had a pH value of 1.82, which means that the colloid particles were positively charged (the pH < pH of hematite point of zero charge). The solid phase had the hematite crystal structure, and the hematite content in the prepared sol was 2.0 $kg{\cdot}m^{-3}$.

An experiment commenced with introduction of 100 cm^3 of distilled water or hematite sol into the cell with the membrane in position. The cell was then quickly pressurized to the operating pressure by nitrogen gas. Each experiment was performed until 8–10 cm^3 of the permeate was collected. Operating conditions were kept at 25 ± 1°C, with transmembrane pressures in the range of 50 to 350 kPa and stirring speeds of 0 or

400 rpm. The stirring speed was fixed at 400 rpm to prevent the formation of a serious vortex in the cell. The flux was measured with a Sartorius electronic balance and a graduated cylinder continuously weighing and measuring the volume of permeate, respectively.

After each ultrafiltration run of hematite sol, the membrane was removed from the cell and carefully rinsed (cleaned) with distilled water. The distilled water flux was measured both before and after each ultrafiltration of hematite sol to verify the presence of fouling phenomena.

RESULTS AND DISCUSSION

Prior to the study of ultrafiltration of hematite sol, it was necessary to determine the membrane resistance. The membrane resistance, R_m, was obtained from the distilled water ultrafiltration experiments using the basic filtration equation:

$$J = \frac{dV}{dt}\frac{1}{A_m} = \frac{\Delta p}{(R_m + R_s)\eta} \tag{1}$$

where J is the permeate flux, V is the permeate volume, t is filtration time, A_m is an effective membrane area, Δp is the pressure difference, η is the permeate viscosity, and R_m and R_s are the resistances of the membrane and of the solute, respectively.

Equation (1) for ultrafiltration of distilled water, in which R_s was taken as zero, is

$$R_m = \frac{\Delta p}{J\eta} \tag{2}$$

Water viscosity, under the experimental conditions, is $\eta = 0.87 \times 10^{-3}$ Pa·s so that, based of the data obtained by ultrafiltration of distilled water at different pressures, the membrane resistance increased linearly with Δp:

$$R_m = 1.05 \times 10^{12} + 7.5 \times 10^6 \Delta p \tag{3}$$

Presumably, the increased pressure difference caused compression of the membrane, resulting in an increase of its hydraulic resistance. The stirring conditions had no influence on the membrane resistance. Similar dependences were registered for the membranes used for ultrafiltration of silica and aluminum oxide sols (5, 6).

In Fig. 1 the cumulative permeation mass, obtained by ultrafiltration of hematite sol of a bulk concentration $C_b = 9.4$ kg Fe_2O_3/m^3, is plotted as a function of time for stirred and unstirred experiments at various pressure differences. It is evident that the amount of permeate collected at any

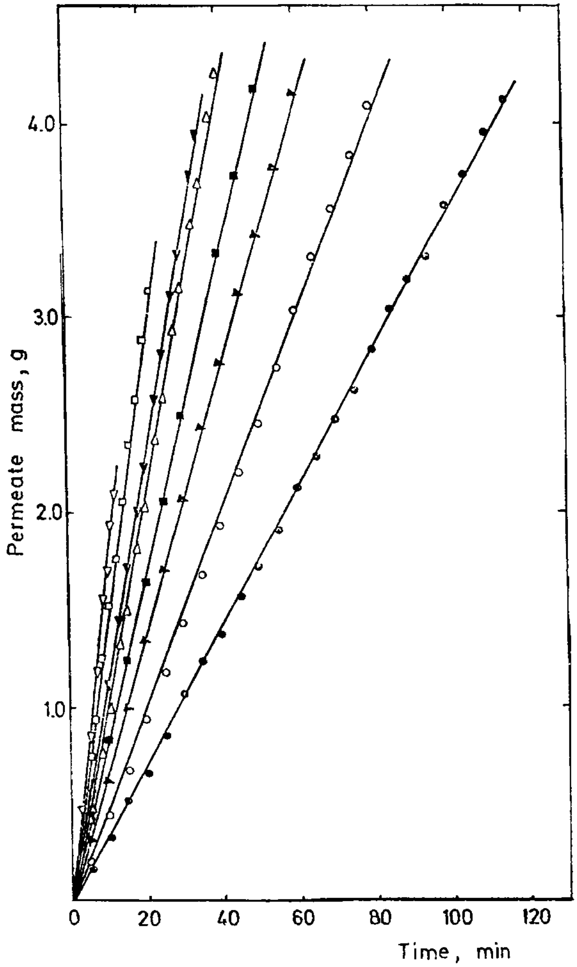

FIG. 1 Dependence of permeate mass vs time for colloidal hematite. $C_{Fe2O3} = 9.4\ kg{\cdot}m^{-3}$. (○, ●) 0.05 MPa; (△, ▲) 0.10 MPa; (□, ■) 0.15 MPa; (▽, ▼) 0.20 MPa. Open symbols: 400 rpm. Filled symbols: 0 rpm.

time increases with increasing pressure differences and stirrer speed. For all experiments the cumulative permeation mass is linearly related to the time, indicating an almost instantaneous attainment of the stationary state under these experimental conditions. Similar dependences were found for other investigated lower bulk concentrations of hematite sol, but for the sake of brevity these dependences are not presented in Fig. 1. The amount of permeate collected at any time decreases with increasing bulk concentration of hematite.

The rejection characteristic or retention coefficient of a membrane is defined by

$$R = \frac{C_m - C_p}{C_m} \tag{4}$$

where C_m and C_p denote the concentrations of solute at the membrane surface and in the permeate, respectively. Since the value of C_m is not directly obtainable by experiment, the rejection characteristic of a membrane is usually described by the observed rejection, R'_{obs}, defined as

$$R'_{obs} = \frac{(C_b - C_p)}{C_p} \tag{5}$$

where C_b denotes the bulk concentration of solute. The PM-10 membrane used rejected 84–90% of hematite particles. These rejections were almost the same in all the experiments performed.

The permeate flux was calculated using Eq. (1). To calculate the permeate volume, V, the permeate density was taken as 990 $kg \cdot m^{-3}$. Permeate flux versus applied pressure data obtained for the unstirred ultrafiltration experiments are illustrated in Fig. 2. As can be seen, the flux increases with increasing pressure and decreases with increasing bulk concentration of hematite. No limiting flux was observed even at the highest applied pressures and regardless of the time the measurement was done. This suggests an incomplete polarization. If this were true, the membrane properties would be more importance than those of the boundary layer.

The distilled water flux decreased greatly after the hematite sol ultrafiltration experiments and did not return to its initial value after membrane surface washing. It is supposed that this flux decline was caused by the plugging of membrane pores.

An overall characteristic of flux reduction during an experiment can be expressed in terms of an extra resistance, R_f, that will be added to the resistances of the membrane and solute, R_m and R_s. Introducing R_f into Eq. (1), the permeate flux is given by the following relationship:

$$J = \frac{\Delta p}{(R_m + R_f + R_s)\eta} \tag{6}$$

R_f corresponds to the fouling effect which is not removed when the pressure is released. The membrane resistance, R'_m, measured by the distilled water flux following fouling, will be the sum of R_m and R_f. Membrane

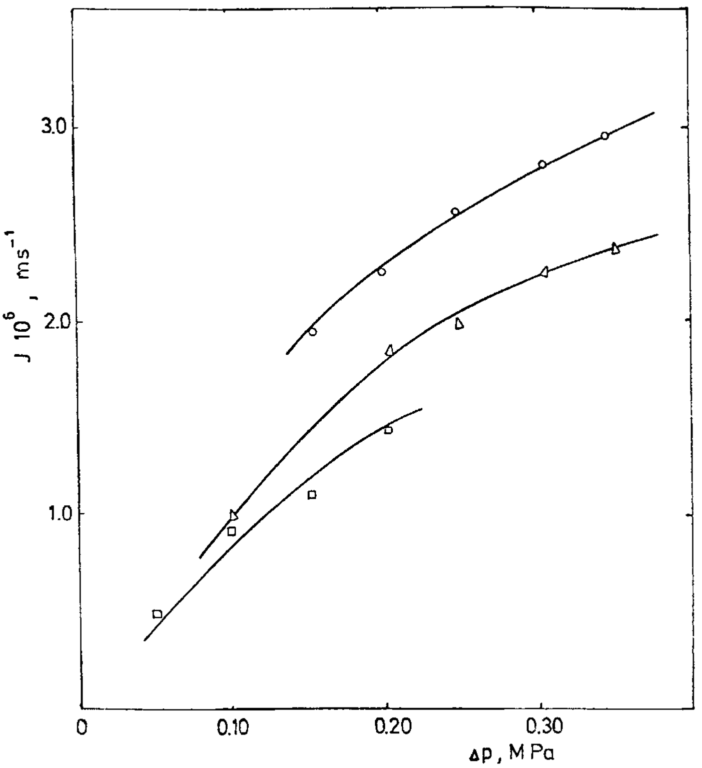

FIG. 2 Dependence of permeate flux as a function of applied pressure and bulk hematite concentration (unstirred). $C_{Fe_2O_3}$ in kg·m^{-3}: (○) 2.0, (△) 3.1, (□) 9.4.

TABLE 1

Effect of Bulk Concentration, C_b, of Hematite, Pressure Difference, Δp, and Stirring Conditions on Polarization Resistance, R_s ($R_s \times 10^{-13}$, m^{-1})

	C_b (kg·m^{-3})				
	2.0		3.1	9.4	
Δp (MPa)	400 rpm	0 rpm	0 rpm	400 rpm	0 rpm
0.05	0.07	—	—	1.22	2.41
0.10	0.21	—	—	0.84	2.89
0.15	0.21	—	—	1.94	6.29
0.20	0.27	1.55	1.90	1.76	6.54
0.25	—	—	2.40	—	—
0.30	—	—	2.40	—	—
0.35	—	2.0	2.90	—	—

fouling is a complex process involving convective deposition of aggregated materials and adsorption.

Knowing the membrane resistance R'_m (i.e., $R_m + R_f$) and permeate flux, the polarization (or gel layer) resistance, R_s, can be determined from Eq. (6). The calculated R_s values are presented in Table 1. From Table 1 it can be seen that the polarization resistance increases with an increase in pressure at constant hematite concentration, and that it increases with an increase in hematite concentration at constant pressure. It can also be seen that polarization resistance is greater for unstirred conditions.

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Received by editor September 14, 1995