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Separation of Humic Acids from Bayer Process Liquor by Membrane Filtration*

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ABSTRACT

Humic acids of high molecular weight were removed from spent Bayer liquor by polymeric ultrafiltration membranes. Among the commercial and laboratory-cast membranes tested, Radel-R polyphenylsulfone on a polypropylene backing material was found to be the most promising candidate for this separation. However, the maximum separation of humic acids obtained at operating conditions of 50°C and 0.34 MPa, as measured by spectrophotometric analysis, was only in the 50 to 55% range. In order to explain this limited membrane separation of humic acids in spent Bayer liquor, a synthetic alkaline solution of humic acids was treated using the same membranes. These tests indicated much higher separation of humic acids (92%). Humic substances in Bayer liquor appear to be hydrolyzed and degraded to low molecular weight fractions (molecular weight < 1000 daltons) by the combined action of the strongly alkaline Bayer liquor and high digestion temperatures. These low molecular weight fractions cannot be retained by standard ultrafiltration membranes. However, some preliminary tests with laboratory-cast Radel-R nanofiltration membranes showed improved color separation ($>70\%$) when treating spent Bayer liquor. Characterization of these new membranes, at different temperatures and pressures as well as by other factors influencing separation of humic acids from Bayer liquor, were investigated.

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INTRODUCTION

Humic substances are widely distributed in nature. They are a complex mixture of organic compounds which give surface waters a brown to yellow color. The general molecular structure for humic acids is a straight chain with numerous functional groups, and the resulting molecular weight distribution ranges from <1,000 to 200,000 daltons.

In the Bayer process, organic matter originates mainly with bauxite ore, with a small portion coming from flocculants and antifoam agents used in the process. Bauxite ores contain from 0.1 to 0.6% organic carbon in the form of humic substances. Over 50% of the organic carbon from the ore is extracted into the leach liquor during contacting of the ore with concentrated sodium hydroxide at elevated temperatures and pressures. Spent Bayer liquor still contains large amounts of usable alkali and recoverable alumina, and this stream is typically recycled to the leaching stage of the process. However, the buildup of organic carbon in this stream can lead to numerous processing problems. An important example is the inhibiting effect of the organics on hydrate precipitation, resulting in a decrease in solution productivity. Other related problems include:

Reduced purity of alumina product due to humic acid coloration of precipitated aluminum hydroxide
Generation of excessively fine aluminum hydroxide particles
Decrease of the red mud settling rate
Loss of caustic values due to the formation of organic sodium compounds
Increased liquor density and viscosity
Foaming of the liquor

The level of organic carbon in the Bayer liquor should be controlled at a specific target level or removed completely. Ultrafiltration is a simple process with the potential to be a convenient and economical method of reducing the organic carbon content of spent Bayer liquor. No chemical change is required for this separation process, thus providing an advantage over several competing processes. Membrane treatment also provides direct insight as to the molecular weight or size distribution of organic species present in spent Bayer liquor.

The purpose of the present study was to identify candidate commercial and National Research Council (NRC) of Canada developed ultrafiltration membranes capable of producing a maximum separation of colored humate species from spent Bayer liquor and suffering minimal degradation when exposed to the highly alkaline solutions. Additionally, the effect of operating variables, such as temperature, pressure, and recirculation rate, on humic acids removal was investigated.

LITERATURE REVIEW

Numerous methods to remove and/or control humic matter in Bayer liquor have been reported in the literature. These include oxidation by sodium hypochlorite or other oxidizing agents including oxygen or air at elevated temperatures and in the presence of copper ions as a catalyst (1, 2). Treatment of Bayer liquor with compounds of alkaline earths, such as magnesium, barium, and calcium, to precipitate and remove organic materials is also known (3–5). Impurity levels of organic materials such as sodium oxalate are also removed from sodium aluminate solutions by quaternary ammonium salt extraction (6) and by treatment with ethanol to cause the sodium oxalate to precipitate (7, 8). Strongly basic anion-exchange resins are capable of eliminating iron, silica, titanium, zinc, and organic acid impurities from strongly alkaline sodium aluminate solutions (9). Carbon compounds in Bayer liquor can also be removed by increasing the molar ratio of aluminum to sodium and then heating the liquor to drive off the carbon compounds as carbon dioxide (10).

The use of conventional filtration with filter cloth to separate sodium aluminate solutions from the red mud residue of a Bayer process digestion has been reported (11). The possibility of removing organic impurities by membrane filtration has also been explored. For example, results obtained using sulfonated polysulfone hollow fiber ultrafiltration modules indicated an increase in Bayer liquor whiteness of 75–90% due to the removal of colored humate species. As a result, the purity of the aluminum hydroxide product was significantly increased (12, 13). Ultrafiltration (14, 15) and reverse osmosis (16–18) have also been used in the characterization and removal of aquatic organics such as humic acid in natural waters.

Reduction of dissolved organic and inorganic impurities in an aqueous caustic solution from the Bayer process has also been achieved by electrodialysis (19–21). Electrodialysis was carried out with at least two cell pairs, consisting of a cation or an anion permselective membrane and a bipolar membrane, that produces hydroxide ions by dissociation of water, in series. The products from electrodialysis are a low organic content caustic solution which is recycled to the Bayer process and an impure organic/caustic solution which is discarded. The authors claim that this process allows spent Bayer solutions to be economically treated, yielding a recycle caustic solution with reduced impurity levels that have no effect on the Bayer process.

EXPERIMENTAL

The ultrafiltration test system is shown schematically in Fig. 1. It consists of four NRC-designed membrane test cells mounted in series, connected to a feed tank and pump. Both concentrate and permeate can be collected separately or recycled to the feed tank. Each test cell provides a usable membrane area of 14.5×10^{-4} m^2. A heating tape wrapped around the feed tank is used to control the solution temperature. This arrangement provides sufficient heating capacity to allow experiments to be carried out at temperatures up to 70°C.

Commercial polyethersulfone ultrafiltration membranes with nominal molecular weight cut-offs of 1,000, 5,000, 10,000, and 50,000 daltons (Nova Series, Filtron Technology Corporation, Northborough, Massachusetts, USA) were used in the initial phase of the test program. Nanofiltration membranes tested included a thin film composite (DS-5, Desalination Systems, Escondido, California, USA) and a polyvinyl alcohol derivative membrane (HPVD, Hydranautics, San Diego, California, USA). A sulfonated polyethersulfone coated, polyethersulfone ultrafiltration membrane (Nitto 7410, Nitto Denko Corporation of Tokyo, Japan) was also evaluated.

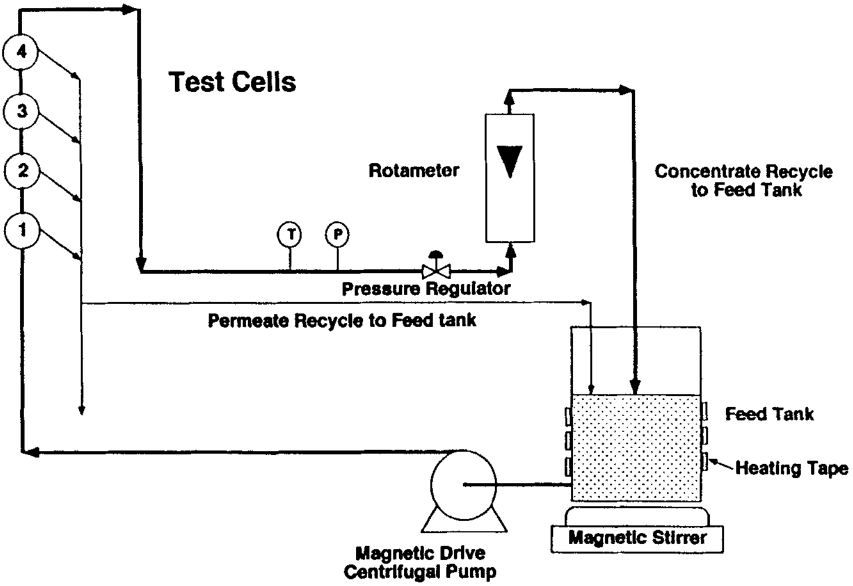

FIG. 1 Schematic diagram of four cell ultrafiltration system.

A variety of membranes was prepared in-house from Udel polysulfone and Radel-R polyphenylsulfone (Amoco Performance Products), Victrex polyethersulfone (ICI), and Ultem polyetherimide (General Electric). After the membranes were cast, circular coupons were cut and stored in distilled water for several days in order to remove residual organic solvents used during the casting procedure. Selected coupons were placed in the ultrafiltration test system and flushed with distilled water for a period of 5 hours to remove any remaining traces of the organic solvents. These membrane coupons were characterized by determining permeate flux and solute separation for 200 mg/L solutions of polyethylene glycols (PEG) of varying molecular weight (600 to 6000 daltons) at operating pressures between 0.17 and 0.69 MPa and temperatures ranging from room temperature to 70°C.

A sample of spent Bayer liquor was obtained from Alcan International in Arvida, Quebec. Analysis of the total organic carbon, alumina, and caustic contents provided by Alcan appears as Table 1. A powdered mixture of humic acids in the Na form was also obtained (Aldrich Chemical, Milwaukee, Wisconsin, USA). This material was used to prepare a synthetic solution of humic acids in alkali (0.5 g/L in 4 N NaOH) without the presence of either alumina or unknown organic compounds.

The removal of humic acids was determined based on the color of feed and permeate samples. Spectrophotometric analysis at a wavelength of 370 nm was performed using a Hewlett-Packard 8450A, UV/Visible Spectrophotometer. Total organic carbon content for a few samples was determined by coulometric titration. Samples were acidified with HCl and allowed to stand overnight to insure the removal of carbon present as carbonates. Concentrates of metal species including Fe, Mn, V, Cr, Cu, and Zn were determined by inductively coupled plasma–atomic emission spectroscopy (ICP-AES). Electron diffraction x-ray analysis (EDXA) of the surfaces of virgin and used membranes was used to identify metal species adsorbed or deposited on the membrane surface after exposure to the spent Bayer liquor feed.

TABLE 1
Analysis of Spent Bayer Liquor (as provided by Alcan International)

Element	Concentration (g/L)
Caustic (as Na_2CO_3)	181.6
Alumina	61.4
Total organic carbon	6.64

RESULTS AND DISCUSSION

Commercial Ultrafiltration Membranes

The polyethersulfone membranes obtained from Filtron Technology Corporation were used to separate humic acids from the spent Bayer liquor solution provided by Alcan International. The results are presented in Table 2. For example, for membrane FIL-1 (MWCO 1000 daltons), at room temperature (25°C) and a pressure of 0.34 MPa, the removal of humic acids based on reduction of color was approximately 50%. As expected, the permeate flux increased and percent removal of humic acids decreased as the molecular weight cut-off of the membrane under consideration increased. At higher temperatures the permeate flux increased significantly and the percent removal dropped to negligible values. This reduction in color separation is attributed to an increase of membrane pore size at elevated temperature. This increase in pore size, coupled with a reduction in feed solution viscosity, is responsible for the increase in permeate flux. Membrane characterization results using polyethylene glycols (PEG) and similar operating conditions indicated that the FIL-1 membrane separation of a 6000 daltons PEG was only about 3% at 50°C. Based on this result, large chromophoric molecules would be expected to pass through the membrane and appear in the permeate.

At elevated pH, humic acids will be dissociated and present as free anions. With this fact in mind, a Nitto 7410 membrane with surface sulfonic acid groups which will be negatively charged at elevated pHs was tested. Ionic repulsion of the negatively charged humates by these acid groups was expected to increase the rejection of these colored species. Tests carried out at room temperature gave about 25% color removal. There is an excess of Na present in the spent Bayer liquor solution, so

TABLE 2
Removal of Humic Acids from Spent Bayer Liquor by Polyethersulfone Ultrafiltration Membranes (Filtron) at 0.34 MPa (recirculation rate = 1.9 L/min)

Membrane type	Molecular weight cut-off (daltons)	Permeate flux at 25°C (kg/m^2/h)	Humic acids removal at 25°C (%)	Permeate flux at 50°C (kg/m^2/h)	Humic acids removal at 50°C (%)
FIL 1	1,000	0.55	52	2.48	0
FIL 5	5,000	4.83	27	9.38	9
FIL 10	10,000	11.0	30	17.4	5
FIL 50	50,000	35.5	19	73.1	0

that the membrane surface and humic acids are in the uncharged Na form. Room temperature characterization of the Nitto 7410 membrane using uncharged PEGs indicates that this membrane's MWCO is similar to that of the FIL-5 membrane.

The results of these preliminary tests indicate that the maximum obtainable color removal is 50% using the tightest membrane at room temperature. Since the color removal decreases as temperature increases to the desired operating temperature of 50°C, it is clear that tighter membranes are required to achieve acceptable separation of humic acids from the spent Bayer liquor.

Commercial Nanofiltration Membranes

Results for Desalination Systems DS-5 and Hydranautics HPVD nanofiltration membranes are reported in Table 3. Operating at 50°C and 0.17 MPa, the DS-5 membrane gave about 53% color removal while the HPVD membrane gave only about 21% color removal. As the test continued, membrane performance deteriorated, as indicated by the permeate flux and color removal reported after 22 hours of operation. The highly alkaline Bayer solution attacked the membrane surface, leading to increased fluxes and reduced color removal. It was concluded that these membranes were unsuitable for the caustic operating environment and further study was abandoned.

Laboratory-Cast Ultrafiltration Membranes

Results for low molecular weight cut-off laboratory-cast ultrafiltration membranes are presented in Table 4. As indicated in this table, Radel-R polyphenylsulfone membranes gave the most promising results although the color removal of 37% at 50°C was still considerably lower than the target value of 75%. At the other extreme, the Ultem membranes were

TABLE 3
Removal of Humic Acids from Spent Bayer Liquor by Commercial Nanofiltration Membranes at 50°C and 0.17 MPa (recirculation rate = 1.9 L/min)

	Initial results		After 22 hours	
Membrane type	Permeate flux ($kg/m^2/h$)	Humic acids removal (%)	Permeate flux ($kg/m^2/h$)	Humic acids removal (%)
DES 5	8.83	53	23.8	30
DES 5	10.8	54	23.0	28
HPVD	46.0	21	—	—

TABLE 4
Removal of Humic Acids from Spent Bayer Liquor Using NRC Ultrafiltration Membranes at 0.34 MPa (recirculation rate = 1.9 L/min)

Membrane type	Permeate flux at 25°C ($kg/m^2/h$)	Humic acids removal at 25°C (%)	Permeate flux at 50°C ($kg/m^2/h$)	Humic acids removal at 50°C (%)
R74	8.90	42	14.1	37
V236	0.55	20	46.0	19
U79	2.90	18	22.9	18
UL17	0.62	43	5.43	18

severely deformed as this material had no chemical resistance for the alkaline Bayer solution. Based on these results, a series of Radel-R membranes was produced using casting solutions of varying composition. Test results for these membranes appear in Table 5. This served to confirm that the tightest available Radel-R membrane had the best performance at 50°C although the maximum color removal of 43% was still much lower than the required level. Extended use of the coupons resulted in higher color separation and lower permeate fluxes. For instance, the color separation of the R64 coupon increased from 26 to 54% while the flux declined from 35.9 to 10.3 $kg/m^2/h$.

This is believed to be the result of organic molecules blocking the membrane pores. It was observed that after treating the spent Bayer liquor solution, the surface of the membrane coupons became yellow in color. EDXA analysis identified the expected major peak for sulfur, resulting from the polysulfone structure, and minor peaks of aluminum and silicon

TABLE 5
Removal of Humic Acids from Spent Bayer Liquor by NRC Cast Radel-R Ultrafiltration Membranes at 0.34 MPa (recirculation rate = 1.9 L/min)

Membrane type	Permeate flux at 25°C ($kg/m^2/h$)	Humic acids removal at 25°C (%)	Permeate flux at 50°C ($kg/m^2/h$)	Humic acids removal at 50°C (%)
R64	21.2	36	36.1	26
R70	0.62	63	4.21	35
R74	8.90	42	14.1	37
R75	6.34	51	6.00	43
R80	7.79	43	12.1	32

on both virgin and used membrane coupons. This confirms that the yellow color was not due to the presence of inorganic species.

Treatment of Synthetic Humic Acids Solution

A synthetic solution of humic acids was used in an attempt to better understand the separation of humic matter from strong alkali solutions. Color removal for this solution using membranes R75 and R64 was 92%. In order to better simulate the operating conditions of the Bayer process and their potential effect on humic acids, the solution was boiled for approximately 1 hour. This resulted in a slight decrease in color removal to 85%. The processing conditions encountered in the Bayer process cause the hydrolysis of humic acids, producing lower molecular weight organics which pass through ultrafiltration membrane pores. This result is in agreement with work done by Lever (22) to characterize humic acids in Bayer liquor. His study suggested that organic matter extracted from bauxite is continuously hydrolyzed and oxidized through the intermediate benzene carboxylic acid and phenolic acid building blocks, yielding lower molecular weight acids. In his work, these low molecular weight degradation products represented about 44% of the total organic carbon content in the spent Bayer liquor.

Laboratory-Cast Nanofiltration Membranes

Further adjustments were made in the casting procedure, allowing the production of Radel-R membranes with pore sizes in the nanofiltration range. Four identical membrane coupons were used in all experiments. Each point plotted on the figures that follow represents the mean value for these four coupons.

Figure 2 presents the molecular weight cut-off curves for the Radel-R nanofiltration membrane at temperatures of 35, 50, and 70°C and a transmembrane pressure of 0.34 MPa. This figure clearly shows the decrease in PEG separation with an increase in operating temperature. The differences are more pronounced for lower molecular weight solutes that are neither completely rejected or permeated. For example, separation for PEG 600 declines from values of 28 to 36% at 35°C to nearly zero at 70°C. On the other hand, the separation for PEG 6000 ranges from 90 to 96% for the three temperatures tested.

The effect of operating pressure on permeate flux and PEG separation at 50°C is shown in Fig. 3. Separation can be seen to increase as the operating pressure is increased from 0.17 to 0.69 MPa. This effect is most apparent for the lowest molecular weight solute, PEG 600, and essentially absent for PEG 6000. Clearly, permeate flux is significantly altered by

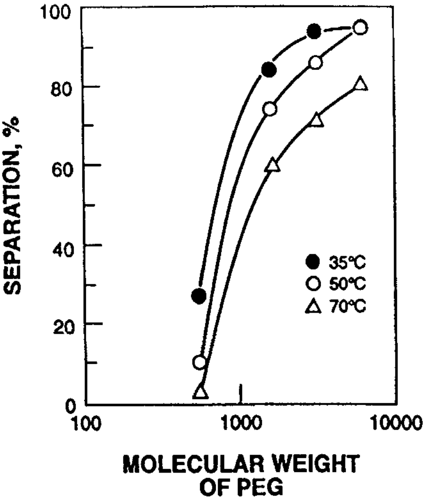

FIG. 2 Separation vs PEG molecular weight for laboratory-cast Radel-R nanofiltration membrane for ΔP = 0.34 MPa and several temperatures (recirculation rate = 1.9 L/min).

increases in both pressure and temperature. For solutes with low retentions, the increase in water flux due to higher operating pressures is greater than the increase in solute flux, with the result that separation increases. This effect is insignificant for solutes with high rejections.

The spent Bayer liquor was treated using this membrane at similar conditions to those used for the characterization tests. The results for various combinations of temperature and pressure appear in Fig. 4. In general, both permeate flux and color removal are increased by an increase in operating pressure. While increased operating temperatures generally result in reduced color removal, results obtained at 50 and 70°C are similar. At these higher operating temperatures, increasing operating pressure from 0.34 to 0.69 MPa had only a minor effect on color removal. The permeate flux is significantly greater for increases in both operating temperature and pressure. This suggests that the optimum operating conditions for removal of humic acids are an operating pressure of 0.69 MPa and temperatures between 50 and 70°C. Figure 5 indicates that at 0.69 MPa, humic acids removal is about 60% in the temperature range 50 to 70°C with permeate flux ranging from 25.5 to 41.4 kg/m^2/h.

The total organic carbon (TOC) content of permeate samples with approximately 45% color removal was determined to be 5.1 to 5.5 g/L. Based on a feed TOC content of 7.0 g/L, this represents about 24% TOC separation. Assuming proportionality between color removal and TOC separa-

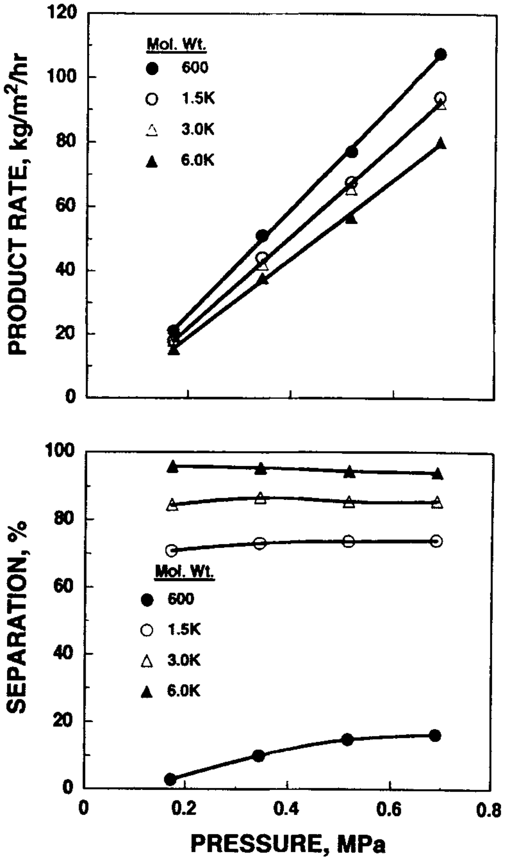

FIG. 3 Permeate flux and PEG separation for laboratory-cast Radel-R nanofiltration membrane vs operating pressure for T = 50°C (recirculation rate = 1.9 L/min).

tion, TOC separation for a permeate with 70% color removal was estimated to be 37%, essentially in agreement with the measured TOC content of 4.4 g/L. These results indicate that the majority of the carbon content of the feed is not retained by this membrane. This is due to degradation of the natural humic acids during the Bayer process, leading to the presence of low molecular weight carbon-containing compounds. In fact, a white crystalline precipitate appeared in the permeate samples after sitting for a few days. X-ray diffraction (XRD) analysis indicated that this material was sodium oxalate (ASTM No. 20-1149), confirming the presence of at least one other low molecular weight organic carbon compound.

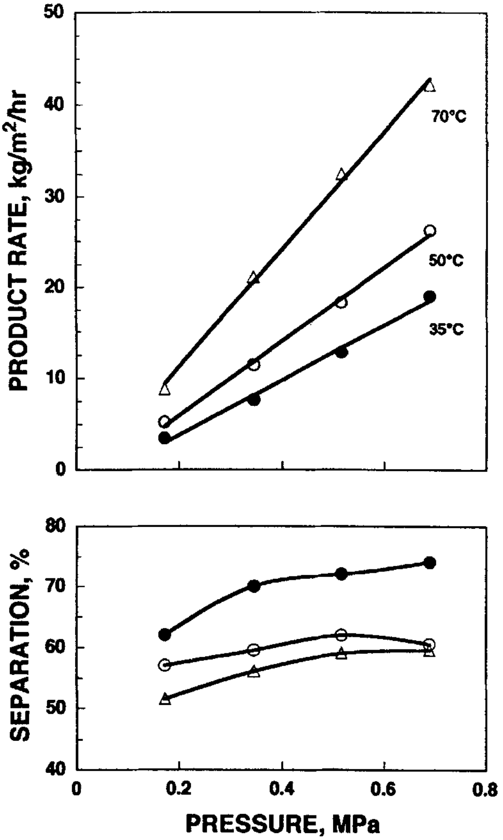

FIG. 4 Permeate flux and removal of humic acids from spent Bayer liquor for laboratory-cast Radel-R nanofiltration membrane as a function of operating temperature and pressure (recirculation rate = 1.9 L/min).

Metals analysis of feed and permeate samples revealed that with the exception of vanadium, all metals were present in trace amounts. Typical feed solution concentrations in mg/L were 1.4:<0.3:5.0:2.0:0.45:115.0 for Zn:Mn:Fe:Cr:Cu:V, respectively. Permeate metal concentrations were similar with the exception of vanadium which at 76 mg/L represented approximately 66% of the V in the feed. Among these metal species, iron can potentially interfere with the spectrophotometric method used to determine removal of humic acids. Both Fe^{2+} and Fe^{3+} impart a yellow color to an alkaline solution which absorbs at similar wavelengths as humic acids. Figure 6 presents absorbance at varying wavelengths for both va-

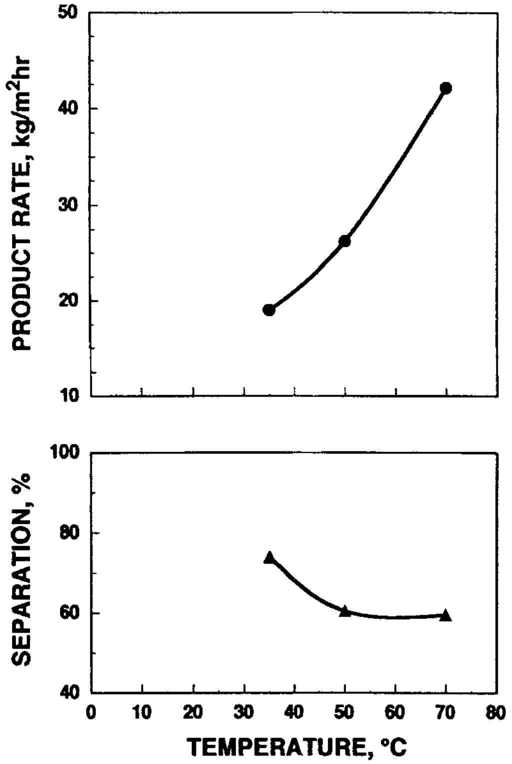

FIG. 5 Permeate flux and removal of humic acids from spent Bayer liquor for laboratory-cast Radel-R nanofiltration membrane vs operating temperature for ΔP = 0.68 MPa (recirculation rate = 1.9 L/min).

lence states of iron as 20 mg/L in 4 N NaOH and 200 mg/L in water. Comparing these absorbance curves with that for the spent Bayer liquor and permeate solutions of various color removal shown in Fig. 7, it is evident that at the selected wavelength of 370 nm, the presence of 5 mg/L Fe^{3+} will increase the absorption. This effect will be even more pronounced if a portion of the iron is present as the more highly absorbing Fe^{2+}. As a result of the presence of iron, color reduction underestimates the removal of humic acids. Assuming about 15% of the absorption at 370 nm is due to iron in the feed (based on a measured absorbance for 5 mg/L Fe^{3+} in 4 N NaOH), 50% color removal corresponds to 59% removal of humic acids. The magnitude of this underestimation increases with increasing color removal. The maximum color removal of 60% determined at 70°C is equivalent to a humic acids removal of 70%.

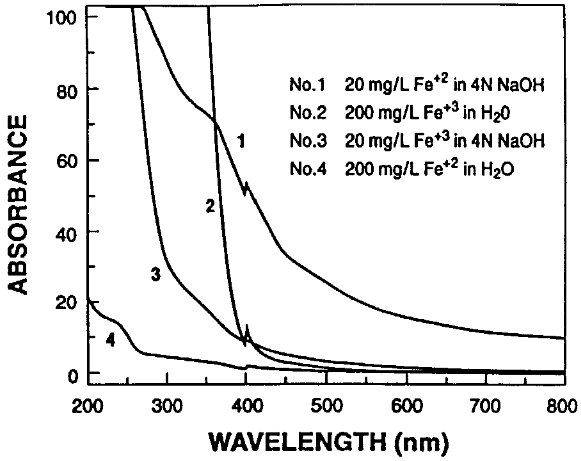

FIG. 6 Absorbance vs wavelength for Fe in various valence states.

Conceptual Process Flow Sheet

Figure 8 illustrates a modified Bayer process flow sheet for producing aluminum hydroxide from bauxite ore. In order to allow spent Bayer liquor recycle without unwanted process problems, a portion of the filtered green liquor from the overflow tank is diverted to the membrane unit for treatment at a pressure of 0.69 MPa and a temperature of 70°C. The permeate

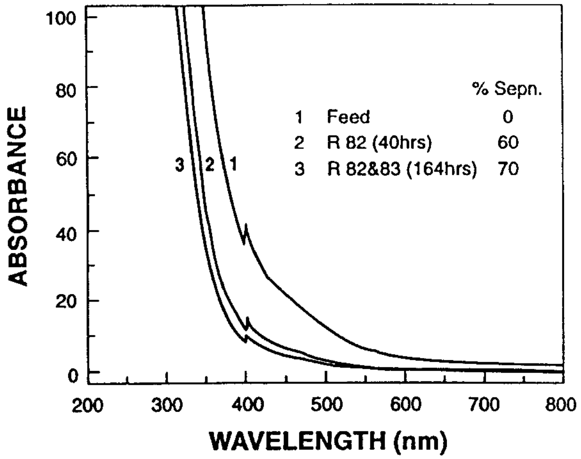

FIG. 7 Absorbance vs wavelength for spent Bayer liquor feed and permeates.

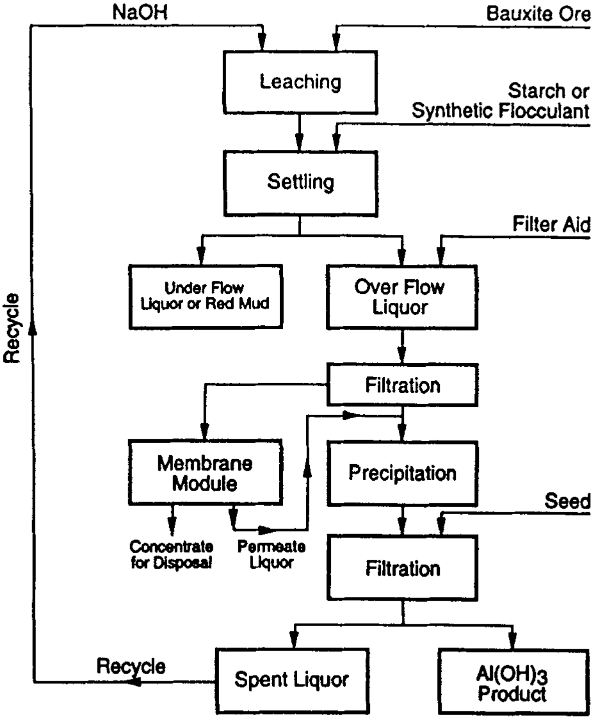

FIG. 8 Modified Bayer process flow sheet.

liquor after humic acids removal of about 75% is then returned to the precipitation tank and the smaller volume concentrate sent to disposal. Introducing membrane treatment at this point produces a higher quality aluminum hydroxide product and improves process productivity.

A conservative estimate of the treatment cost associated with the proposed flow sheet can be developed. Membranes used in industry typically cost on the order of \$100 US/m^2. While membrane cost usually represents about 20 to 30% of the system cost for aqueous membrane separation systems, it can be expected that treatment of the highly corrosive spent Bayer liquor will increase the cost of vessels, pumps, and other ancillary equipment. Assuming that membrane cost represents 15% of the system cost, capital cost of the system will be approximately \$667 US/m^2. At operating conditions of 0.69 MPa and 70°C, the permeate flux is expected to be 1000 kg/m^2/day, leading to an estimated capital cost of \$0.67 US/kg/day or \$770 US/m^3/day (based on a specific gravity of 1.15). Four major factors will contribute to production costs: energy, labor, membrane replacement, and capital cost recovery. Based on typical values for operating costs from the literature (23), energy, labor, and membrane replacement costs will be \$0.11, \$0.08, and \$0.10 US/m^3, respectively. The membrane life in this application was assumed to be 3 years. Assuming an 85% on-stream factor, amortizing the estimated capital cost for periods of 5 and 10 years at an interest rate of 10% leads to capital recovery costs of \$0.66 and \$0.40 US/m^3, respectively. Based on these figures, the total estimated cost of production will be in the range of \$0.69 to \$0.95 US/m^3 or \$2.60 to \$3.60 US/1000 gallons. These production cost estimates are slightly higher than typical values cited for brackish water treatment.

CONCLUSIONS

This study has shown that humic acids present in spent Bayer process liquor can be removed by membrane filtration. The maximum separation of humic acids obtained using ultrafiltration membranes was approximately 50%. Based on experiments with a synthetic solution of nondegraded humic acids in caustic, which gave color removals of approximately 90%, this limited separation was attributed to humic acid degradation to lower molecular weight compounds by the combined action of the alkaline Bayer liquor and elevated digestion temperatures. Although commercial nanofiltration membranes gave improved separation results, they were unstable when exposed for extended periods of time to the aggressive solution conditions.

Among the various laboratory-cast membranes investigated, Radel-R polyphenylsulfone on a polypropylene backing was the most promising candidate. A Radel-R membrane with pore sizes in the nanofiltration range gave color removals in excess of 70% at 35°C. Using this membrane, the optimum operating conditions for separation of humic acids from spent Bayer liquor were estimated to be as follows: recirculation rate of 1.9 L/min, operating pressure of 0.69 MPa, and operating temperature in the 50 to 70°C range. Permeate fluxes under these conditions ranged from 25 to 40 kg/m^2/h with humic acids removal of approximately 70%.

The percentage removal of total organic carbon was about 50% of the percentage color removal determined spectrophotometrically. Upon standing, a precipitate formed in the permeate samples. Analysis indicated that this material was sodium oxalate. It was concluded that a significant portion of the feed and permeate organic carbon content was due to the presence of low molecular weight compounds.

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