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S. K. Thampy[a]; P. K. Narayanan[a]; D. K. Chauhan[a]; J. J. Trivedi[a]; V. K. Indusekhar[a]; T. Ramasamy[b]; B. G. S. Prasad[b]; J. Raghava Rao[b]
[a] CENTRAL SALT & MARINE CHEMICALS RESEARCH INSTITUTE, BHAVNAGAR, INDIA [b] CENTRAL LEATHER RESEARCH INSTITUTE, MADRAS, INDIA

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Concentration of Sodium Sulfate from Pickle Liquor of Tannery Effluent by Electrodialysis*

S. K. THAMPY, P. K. NARAYANAN, D. K. CHAUHAN,
J. J. TRIVEDI, and V. K. INDUSEKHAR
CENTRAL SALT & MARINE CHEMICALS RESEARCH INSTITUTE
BHAVNAGAR 364002, INDIA

T. RAMASAMY, B. G. S. PRASAD, and J. RAGHAVA RAO
CENTRAL LEATHER RESEARCH INSTITUTE
MADRAS, INDIA

ABSTRACT

An electrodialysis technique using indigeneously prepared interpolymer membranes and a laboratory-scale electrodialysis unit having an effective area of 25 cm × 12 cm with 20 pairs of ion-exchange membranes was used for the concentration of sodium sulfate of pickle liquor by the recycling method. In the first stage the sodium sulfate in the effluent was concentrated three and half times with respect to the original effluents, thereby rendering the concentrate usable in the tannery process. The diluate of first stage solution was further subjected to electrodialysis in a once through pass system, and the total dissolved solids content of the second stage diluation was brought down to less than 1000 ppm. This process offers the possibility of either reusing the water or safely discharging it. The parameters voltage, flow rate, and change of concentration with fresh effluent were investigated. The energy requirement and current efficiency were also calculated.

INTRODUCTION

Tannery wastewater management has assumed global importance in recent years. It is now established that typical composite tannery wastewaters contain significant quantities of neutral salts in the form of sodium

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chloride and sodium sulfate, heavy metal ions in the form of chromium and aluminum salts, and organic wastes which include also proteins. Through the use of conventional end-of-pipe treatment methodologies suited to tannery wastewater, it is difficult to comply with the limits set up by environmental regulatory agencies, particularly with respect to dissolved solids. Therefore, in-plant control measures to contain the neutral salt and toxicity budget have become important. A recovery and recycle approach in the form of segregated sectional waste streams in leather processing seems more attractive, particularly for containing dissolved solid problems in tannery wastewaters. In this regard, the management of pickle and spent chrome tannery liquors in the leather industry is of vital importance. Electrodialysis lends itself as a powerful technique to recover and recycle sodium sulfate in leather processing and to the containment of dissolved solids in the tanning industry.

Ion-exchange membranes have been the subject of worldwide research and development since 1950. For more than four decades, ion-exchange membranes have been well established for the production of fresh water from salt water or for concentrating seawater, as in Japan (1, 2). Electrodialysis is also used for the purification through demineralization of solutions of widely varying natures encountered in the food, chemical, and pharmaceutical industries (3–5).

In India, where electrodialysis is used to treat brackish water, it is only logical to exploit the process for other applications like the separation, concentration, and recovery of chemicals, and the reuse of water (6–8). The separation process is carried out at ambient conditions so it can be applied wherever thermally labile chemicals have to be handled. Electrodialysis has the advantage of linking the energy expended to the quantity of electrolytes removed, and energy consumption is low in compared to thermal processes. It also allows low ion concentrations to be raised to higher levels. It is beneficial both for economy of raw materials and for reducing pollution as evidenced by plants operating in Japan and other countries (9, 10). The equipment is modular in nature, offering the possibility of designing plants of varying capacities. Such variable parameters as flow rate and current density are amenable to automatic control.

All separation processes require a selective barrier for the separation of components. In the case of the selective transport of electrolytes, two types of separation barriers are needed, one each for the selective transport of cations and anions, and these are called cation- and anion-exchange membranes, respectively. In an electrodialysis stack these membranes are arranged alternately between two end electrodes to form cells with the help of gaskets and spacers.

Such chemical processing operations as metal pickling, rayon manufacture, and tanning regularly generate aqueous salt streams as effluents (11). Conventional methods to recover and reuse the chemicals are costly due to high energy consumption. The stringent pollution controls which are operative in developed countries are increasing in developing countries. All these aspects converge toward use of the membrane processes to dispose of waste effluent or to reuse the effluent water treated.

Sodium sulfate is a pollutant widely used in tanning. Most sodium sulfate streams are currently discharged into lakes, rivers, and oceans. Strict environmental regulations focusing on waste minimization prohibit discharging such effluents without processing. Electrodialysis can be used to minimize sodium sulfate waste if not eliminate it totally (12).

Spent pickle liquor has a high dissolved solid contents and a considerable amount of chemical oxygen demand. Since pickling involves the use of 8 to 10% sodium salt with a quantity of sulfuric acid which depends on the pelt being tanned, pickle liquor contributes significantly to the dissolved solid load. The recovery and reuse of water and sodium salts are necessary options to contain the problem of dissolved solids in composite tannery wastewaters. The present research was directed to obtain sodium sulfate in concentrated form for reuse with or without the addition of a further quantity of the salt and to produce a fresh water stream for make up or washing purposes.

EXPERIMENTAL

A laboratory electrodialysis unit containing 20 cell pairs of cation- and anion-exchange membranes having an effective cross-sectional area of 300 cm^2 was used to study the separation of sodium sulfate from spent pickle liquor. The electrode housings were prepared from rigid PVC sheets with built in flow distributors and outlets. A stainless steel 316 sheet and platinum-coated titanium were used as the cathode and anode, respectively. Interpolymer-type membranes based on a process developed by the Central Salt & Marine Chemicals Institute were packed alternately between the electrodes (13). The electrodialysis (ED) stack was packed to obtain parallel cum series flow.

The pickle-liquor-tannery effluent, after filtration and passage through an activated carbon column to remove suspended particles and some organics, was taken into aspirator bottles of 10 L capacity kept at an elevated point to facilitate gravity flow. Pumps were used to move the outlet streams from ED stacks to the respective bottles for recirculation. The electrode chambers were flushed with dilute sodium sulfate solution separately. The flow rates of the diluate concentrate, and electrode wash were 50, 30, and 5 L/h, respectively. A dc power source was applied at constant voltage. All three streams were recirculated, and the sulfate content of both the diluate and concentrate streams were estimated. In the first stage of our experiments when the sulfate content of the diluate stream had reached about 6 g/L, the diluate was replaced by another lot of original effluent. The schematic flow diagram is given in Fig. 1.

For further demineralization the diluates of the first set of experiments were subjected to electrodialysis. A single pass system was adopted for both streams using various voltages and flow rates to bring the total dissolved solids (TDS) content of the diluate down to less than 1000 ppm.

RESULTS AND DISCUSSION

The electrodialysis technique is so flexible for recycling or for single pass depletion of the concentration of salts that a single stack or multiple stacks can be used. As the volumes treated were very small and salt

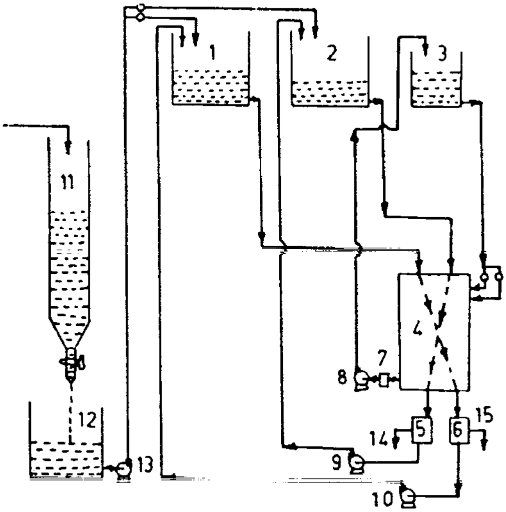

FIG. 1 Schematic diagram of concentration of sulfates from pickle liquor of tannery effluent. (1) Aspirator bottle for diluate; (2) aspirator bottle for concentrate; (3) aspirator bottle for electrode wash; (4) electrodialysis unit; (5) receiver for concentrate; (6) receiver for diluate; (7) receiver for electrode wash; (8, 9, 10, 13) pump; (11) activated carbon column; (12) pickle liquor; (14) concentrate for reuse; (15) diluate for reuse/discharge.

content was large, additional recycling systems were adopted. In the first stage a pickle liquor containing 22 g/L sulfate was used in both the diluate and concentrate compartments. When the sulfate content of the diluate was reduced to 6 g/L, the experiment was discontinued. In the second stage the concentrate of the first stage was used for further build up whereas the original effluent was taken up for further depletion. When the sulfate content of the diluate stream was around 6 g/L, the experiments were discontinued.

Three sets of experiments were carried out at different voltages. The results obtained are presented in Table 1.

In the first stage the sulfate content of the concentrate stream had gone upto 45 g/L and in the diluate it had come down to around 5 g/L. This order of difference enhances diffusion and water transport, which in turn leads to further desalination. This phenomenon of water transport was also observed in seawater desalination (14). The difference in concentration between the two streams at this stage was about 8.5 times that in the first stage and about 10.6 times that in the second stage when 20 V was applied. However, the difference in the current ratio goes up when the voltage is raised to 25, contributing about a 10.5 times increase in the first stage and a 12.7 times increase in the second stage. The same trend in the difference in concentration is also observed at 30 V: a 16 times concentration difference between the concentrate and diluate in the first stage and about 20 times in the second stage.

The power consumption was of the order of 0.67 kW·h/kg of sodium sulfate removed with 61.5% current efficiency in the first stage when 20 V was applied. At this voltage in second stage the power consumption was 0.76/kg of Na_2SO_4 removed and the current efficiency was 60%. Water transport for first and second stages was 7 and 9%, respectively.

When the voltage was increased to 25 (second set), the power consumption was 0.77 kW·h/kg Na_2SO_4 removed and current efficiency was 73.5% for an 8% water loss. In the second stage the power consumption was 0.77 with 65% current efficiency and a 11% water transport.

At 30 V (1.5 V per cell pair) the power consumption calculated was 0.75 in the first stage and 0.88 in the second stage. The current efficiencies were 67.5 and 63%. The water transport observed was 9 and 13% in the first and second stage, respectively.

From the data presented we notice the increase of water transport when the voltage and concentration gradient increase. In all these experiments the current efficiency realized was 65%. This is partly due to monovalent and divalent ions transport. However, the current efficiency can be improved if the cell geometry of the stack is altered to reduce cell thickness.

TABLE 1
Concentration of Sulfate of Pickle Liquor (tannery effluent) by the Electrodialysis–Recirculation Method

	Set I		Set II		Set III	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
Initial volume (L):						
Treated	9.5	9.0	10.5	10.5	11.5	11.5
Concentrated	5.5	4.5	5.0	5.5	6.0	6.0
Final volume (L):						
Treated	8.8	8.1	9.7	9.4	10.6	10.2
Concentrated	6.2	5.5	5.8	6.7	7.0	7.0
Voltage (V)	20	20	25	25	30	30
Current (A)	1.2–0.8	1.25–0.9	1.5–0.9	1.55–1.0	1.65–0.6	1.75–0.8
Initial TDS (g/L):						
Treated	33.45	32.45	33.26	33.11	22.06	24.49
Concentrated	33.45	59.33	33.26	69.47	22.06	53.70
Final TDS (g/L):						
Treated	7.98	10.69	5.733	5.07	3.30	3.72
Concentrated	59.33	83.73	70.31	94.80	55.37	79.96
Initial sulfate (g/L as SO_4):						
Treated	21.78	21.78	24.50	24.50	19.06	21.78
Concentrated	21.78	44.93	24.50	55.85	19.06	46.30
Final sulfate (g/L as SO_4):						
Treated	5.44	6.12	5.40	6.12	3.05	3.34
Concentrated	44.93	65.30	55.85	77.65	49.01	68.03
Initial chloride (ppm as Cl):						
Treated	1,254	627	523	627	767	557
Concentrated	1,254	2,880	523	—	767	1,417
Final chloride (ppm as Cl):						
Treated	69	82	52	74	260	26
Concentrated	2,919	4,008	2,875	—	2,091	2,963
Initial sodium (ppm as Na^+):						
Treated	6,900	6,900	6,900	6,900	6,325	6,785
Concentrated	6,900	13,800	6,900	16,100	6,325	13,800
Final sodium (ppm as Na^+):						
Treated	1,150	2,070	803	575	690	345
Concentrated	14,950	23,000	16,100	23,000	14,375	25,300
Initial acidity (ppm as H_2SO_4):						
Treated	2,493	3,567	3,478	3,387	3,656	3,834
Concentrated	2,493	7,580	3,478	7,580	3,656	871
Final activity (ppm as H_2SO_4):						
Treated	2,318	2,586	1,605	3,032	3,160	9,140
Concentrated	7,580	—	8,482	9,988	10,032	12,708
Initial pH:						
Treated	3.23	3.15	3.10	3.15	2.38	2.34
Concentrated	3.23	2.60	3.10	—	2.38	2.20

TABLE 1 Continued

	Set I		Set II		Set III	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
Final pH:						
Treated	2.67	2.77	2.92	2.71	3.16	3.78
Concentrated	2.44	2.25	2.45	2.41	2.12	2.10
Power (kW·h/kg), Na_2SO_4 removed	0.67	0.76	0.74	0.77	0.75	0.88
Power (kW·h/m^3), Na_2SO_4 removed	16.2	17.8	21.5	21.2	25.5	28.0
Current efficiency (%)	61.5	59.5	73.5	65.0	67.5	63.0

Based on these sets of experiments, the results obtained at 25 V seem to be advantageous as we get very near the concentration of spent liquor used in tanneries.

The diluates of Stages 1 and 2 of all three sets were mixed together and further removal of salt was attempted by using a single pass system. The flow rates of the diluate and concentrate streams were adjusted to a 3:1 ratio. From Table 2 it can be seen that the TDS of the diluate was brought down to less than 1000 ppm, and this could be used as a washwater and

TABLE 2
Results of Single Pass System by Electrodialysis

Flow rate (L/h):									
Treated	5.5	5.5	5.5	7.8	7.8	7.8	12.0	12.0	12.0
Concentrated	1.8	1.8	1.8	2.4	2.4	2.4	3.0	3.0	3.0
Voltage applied (V)	25	30	35	25	30	35	25	30	35
Current (A)	225	250	275	250	275	300	275	300	325
TDS (ppm):									
Treated	896	828	800	1,260	1,208	1,164	1,376	1,300	1,228
Concentrated	6,784	6,896	7,164	5,340	5,635	6,520	5,280	5,572	6,160
pH:									
Treated	3.18	3.15	3.12	3.16	3.14	3.10	3.14	3.12	3.10
Concentrated	2.44	2.38	2.32	2.42	2.40	2.39	2.40	2.36	2.35
Power (kW·h/kg), salt removed	0.75	0.94	1.19	0.8	0.99	1.22	0.64	0.78	0.91
Power (kW·h/m^3), salt removed	1.02	1.36	1.75	0.8	1.05	1.34	0.57	0.75	0.94
Current efficiency (%)	75.02	70.8	65.7	70.2	68.0	63.75	87.4	86.6	84.4

also be discharged into streams. The concentrate could be taken for further concentration. At a 5.5 L/h flow rate, the TDS of the diluate could be brought down to well within the reusable or dischargeable limit. Thus, in all sets the concentrate stream could be reused in the pickling bath and the diluate stream could be reused for washing purposes or for safe discharge.

The power consumption was 0.75 kW·h/kg, and the sodium sulfate removed with 70% current efficiency.

CONCLUSION

Electrodialysis can be gainfully employed to treat pickle liquor. The sodium sulfate recovered by concentration can be reused in a pickle bath. The diluate stream can be reused as washwater or discharged. Power consumption for the recovery of sodium sulfate is of the order of 75 kW·h/kg of sodium sulfate removed. With commercially available indigenous membranes, three to four times the concentration of pickle liquor seems to be possible and economically viable.

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