

Composite Cation Exchangers

PADMA VASUDEVAN,* and N. L. N. SARMA, *Department of Chemistry,
Indian Institute of Technology, New Delhi-110 029, India*

Synopsis

Sulfonated phenol formaldehyde resins containing different amounts of sulfonated sawdust were prepared. The thermal and chemical stabilities, scientific weight capacity, and apparent capacities for the exchange of Na^+ , Ca^{2+} , and Mg^{2+} at different concentrations were determined for both H^+ and Na^+ forms of resins. Composites containing up to 30%–50% of sawdust, while being very much cheaper, are comparable in their properties to the pure polymeric resin. Thus, cheaper exchangers can be prepared by substituting part of the polymer by sawdust.

INTRODUCTION

Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification, separation of radioisotopes, and so forth, and find large-scale applications in water treatment and pollution control.^{1,2} The principles of ion exchangers are well established, and various commercial exchangers having a polymeric base (styrene, acrylic, phenol formaldehyde, etc.) with cationic or anionic units as the points of exchange have been in use over several decades. In the present context of the rising cost of polymers, the need exists for either preparing new, cheaper exchangers or finding a cheaper substitute that can at least partly replace the polymeric content without losing such desirable properties as thermal stability and good exchange capacity. The present work is an attempt in this direction.

Work on the preparation of composites with sulfonated coals³ was promising, although the composites were of low capacity. Based on this, it was proposed that different kinds of organic materials, such as coconut shells and sawdust, should be used, since they can be carbonized and subsequently sulfonated. Phenol formaldehydes were chosen as the polymeric matrix, since it is easier to blend such resins with the cheaper substitutes and to test the properties as a function of the composition of the composite. Such composites will be relatively cheap. Besides, in recent years interest has been revived in phenolic resins, because they can be prepared, under suitable conditions, with high porosity and surface area. Vasudevan et al.⁴ have shown that under certain conditions, macroreticular resins based on phenol formaldehyde that were comparable to those based on styrenes could be prepared. Khose and Dasare⁵ have reported the preparation of highly porous resins.

* To whom correspondence should be addressed.

EXPERIMENTAL

Materials. Phenol (BDH reagent), formaldehyde (BDH reagent); concentrated sulfuric acid (sp. gr. 1.82), sawdust, and coconut shells.

Sample Preparation. Phenol sulfonic acid was prepared by adding conc. sulfuric acid to phenol, heating it in a water bath for 3–4 hr, and storing it overnight. Sulfonated sawdust was prepared by adding conc. sulfuric acid to sawdust, heating it in a water bath for 6 hr, washing it free of acidity, and drying at 70°C overnight. The sawdust is thus carbonized and sulfonated. Calculated quantities of sulfonated sawdust were added to phenol-sulfonic acid and polymerized with formaldehyde containing varying percentages of sawdust (S-1 to S-5) (Table I).

Similarly, coconut-charcoal-based resins were prepared by burning the coconut shells and adding conc. sulfuric acid to coconut charcoal (sample CC-1). This was added to phenol-sulfonic acid and polymerized with formaldehyde to get a 50% resin (sample CC-2).

All the above preparations were done with no attempt at purification, since on an industrial-scale use will probably not involve very pure substances.

Measurement of Physical Properties. The densities of dry samples were determined in toluene and those of wet in water by simple pycnometry.² For determining particle size, each sample was sieved and separated into particles of three sizes: >150, <150, and <105 μ . Percentage swelling, α_m , was determined gravimetrically by swelling a sample in water and determining the weight of the swollen sample (M_w) and the weight of the corresponding dry sample (M_d). The kinetics of swelling was also studied.

Stability. The stability of the composites was tested by boiling in water. For determining the thermal stability, a known weight of each sample was heated in an oven at $50 \pm 1^\circ\text{C}$ for 24 hr. The weight of the sample was taken immediately after cooling and also after exposing the same sample for 24 hr to air. The same procedure was repeated at 70°, 110°, and 150°C for both the H⁺ and Na⁺ forms of resins.

Identification and Estimation of Ionogenic Groups. The infrared spectra were recorded on Hilger & Watts, H 800.03 spectrophotometer by scanning over the range 900–4000 cm^{-1} . The samples were taken with KBr as a pellet. Potentiometric titrations of acid groups were performed by taking a known weight of sample in 0.5N NaCl, and adding 0.5N NaOH. After each addition, 24 hr were allowed for equilibrium, and the pH of the resulting solution was measured.

TABLE I
Thermal Stability of Na⁺ Forms of Sawdust-Based Ion Exchangers

Sample	% Sawdust	Weight loss (%) at temperature (°C) ^a							
		50		70		110		150	
		Before	After	Before	After	Before	After	Before	After
Pr	0	9.85	3.13	14.55	2.60	15.82	6.85	21.72	13.91
S-1	30	2.18	1.13	5.03	0.69	5.69	3.50	8.72	4.67
S-2A,B	50	1.78	0.80	0.45	0.42	5.14	1.27	11.21	3.37
S-3	60	1.79	0.88	4.06	0.57	4.72	3.21	17.03	10.56
S-4	75	10.84	6.02	8.77	6.31	12.02	10.84	13.46	9.30
S-5	100	10.33	5.84	9.12	6.71	10.02	7.44	12.66	9.50

^a "Before" and "After" refer to testing relative to air exposure of sample.

Titration was carried just beyond the neutralization point, and the titre value was used for scientific weight capacity. In determining apparent capacities, the method due to Kunin² was followed.

Regeneration of the Samples. The resins that were exhausted were regenerated to get the desired form back. To get the H⁺ form, 4N HCl was passed through the resin, and 0.15M NaCl to get Na⁺ form.

RESULTS AND DISCUSSION

The densities of two independent batches agree within 5%. The densities of the dry composite are in the range of 1.1–1.2 g/cc, whereas that of the pure resin (Pr) is 1 g/cc, indicating a closer packing in the former. The densities of wet samples are slightly higher (by 5%); 80–90% of the particles have a diameter >150 μ , 5–10% between 105 and <150 μ , and 5–10% <105 μ . The percentage swelling of pure samples extends over 100–300% in different experiments. However, the swelling of sawdust samples are in the region of 100–200% and are reproducible to within 10–20%. The percent swelling as a function of time for samples Pr, S-1, S-2A, and S-2B are shown in Fig. 1. The swelling equilibrium is attained within 3–5 hr, and accordingly, studies on capacity were done after swelling the samples for at least 5 hr. Not much difference was found in swelling between H⁺ and Na⁺ forms. The resins were stable in boiling water. As for the thermal stability, percentage losses incurred by Na⁺ form of the sawdust samples are shown in Table I. Figure 2 represents percent loss in weight vs temperature of H⁺ form. If weighed immediately after cooling, without exposure to air, up to 5% losses were registered for all samples, even when heated at 50–70°C. However, most of the loss was regained by exposure to air, indicating that the samples are porous and reversibly absorb air and water vapor. (Further experiments with phenol formaldehydes and composites have indicated that the resins are macroporous.⁴ The composites are stable at least up to 70–100°C. The substitution by sawdust has hardly any influence on the thermal stability,

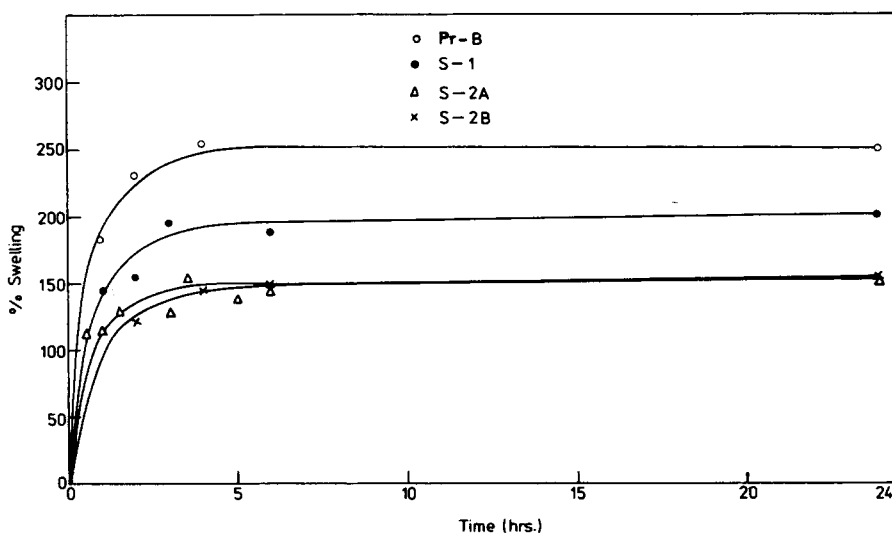


Fig. 1. Percent swelling vs time of sawdust based ionexchangers.

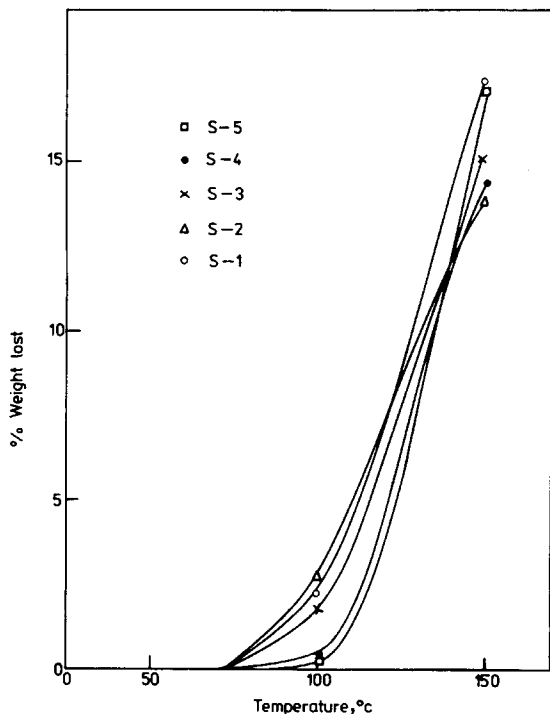


Fig. 2. Thermal stability of H⁺-form of sawdust based ionexchangers.

which is as good as that of pure resin. This is a trend in favor of substituting the cheaper materials for the costlier polymer.

All the samples except CC-1 have an infrared absorption in the region of 1030 cm^{-1} , corresponding to S=O stretching in sulfonic acid group. Thus, as expected, the resins carry the SO_3H group. The peak in the range of 1460 cm^{-1} indicates the presence of $-\text{CH}_2-$ linkages and aromatic C-C multiple bond stretching. The peaks in the range 3400–3200 cm^{-1} indicate the presence of $-\text{OH}$ grouping. Thus the resins are basically bifunctional, with SO_3H and the possibility of phenolic $-\text{OH}$ participating in the exchange at high pH.

The pH titration curves per gram of resin are shown in Figure 3. The end point is reasonably sharp, indicating strongly acidic SO_3H predominates. The pure resin has a capacity of 1.8–1.9 mEq/g, which is comparable to the capacities of the commercially available resins based on phenol formaldehyde, such as Wofatit P (1.9 mEq./g) and Zeokarb 215 (2.6 mEq/g). The pure resin and sample S-1 containing 30% of the resin have the same scientific weight capacity (1.8–1.9 mEq/g), indicating that the replacement of at least 30% of the resin has not reduced the capacity as compared to pure resin. The capacity falls from S-2 to S-5 as polymer content in the composite decreases.

Apparent Capacity. Coconut-charcoal-based resin did not show any significant capacity. This is in accordance with infrared data, which indicated absence of the SO_3H group. It seems that treatment with sulfuric acid in this case is not sufficient to produce the ionogenic groups. The apparent capacities for both the H⁺ and Na⁺ forms of the samples for the various ions (Na^+ , Mg^{2+} , or Ca^{2+}) at different concentrations (0.01–0.15M) are shown in Table II. The

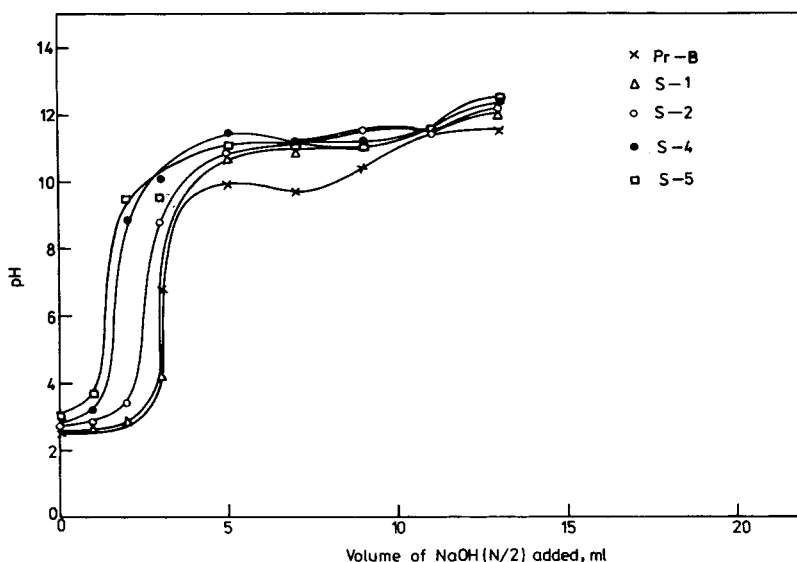


Fig. 3. Potentiometric titration of sawdust resins in N/2 NaCl.

capacity of the samples of the same composition prepared as independent batches are reproducible within 10% for a given ion at a particular concentration. Part of the deviations may be attributed to the heterogeneity of the samples. Variations in the degree of swelling may also make a contribution. In Figure 4 the capacity is plotted as a function of composition for the ions exchanged at a given concentration. In cases it was found that the capacity remains practically constant until the composition corresponds to 30%–50% of the sawdust and falls off therefrom to the value corresponding to pure sawdust.

Ion Selectivity. As can be seen from Figure 4 and Table II, for a given sample at a certain concentration, the order in the capacity is $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$, as expected. It is well known that at low concentrations, the higher the valence, and the lower the hydrated radius, the better the exchange. Although Mg^{2+} has a lower absolute ionic radius compared to Ca^{2+} , its hydrated radius is much more.² It is also seen that for univalent Na^+ , there is a clear-cut increase in capacity with increasing concentration, and the values at 0.15M Na^+ tend to match the values for the bivalent ions in the region 0.01–0.04M. Thus Na^+ at high concentration can easily be used for the regeneration of the resin.

TABLE II
Apparent Capacities of Sawdust-based Ion Exchangers

Sample	Apparent ion exchanger capacities, mEq/g								
	H ⁺ form					Na ⁺ form			
	Na ⁺ , 0.01M	Na ⁺ , 0.04M	Na ⁺ , 0.15M	Ca ²⁺ , 0.01M	Ca ²⁺ , 0.04M	Mg ²⁺ , 0.01M	Ca ²⁺ , 0.04M	Ca ²⁺ , 0.01M	Ca ²⁺ , 0.04M
Pr	0.7	1.3–1.4	1.6	1.7	1.7	1.4	1.5–1.6	1.7	1.8
S-1	0.8	1.2–1.3	1.6	1.7	1.7	1.4	1.5–1.6	1.6	1.7
S-2	0.9	0.9–1.0	1.4	0.9–1.0	1.4	1.4–1.5	1.3–1.4	0.8	0.9
S-3	0.7	0.7	1.1–1.2	0.8–0.9	0.8	0.9–1.0	0.9	0.8	0.8
S-4	0.6	0.6	0.7	0.7	0.8	0.7	0.7–0.8	0.7	0.7
S-5	–	0.4	0.4	0.4–0.5	0.4–0.5	0.5	0.3–0.4	0.6	0.6

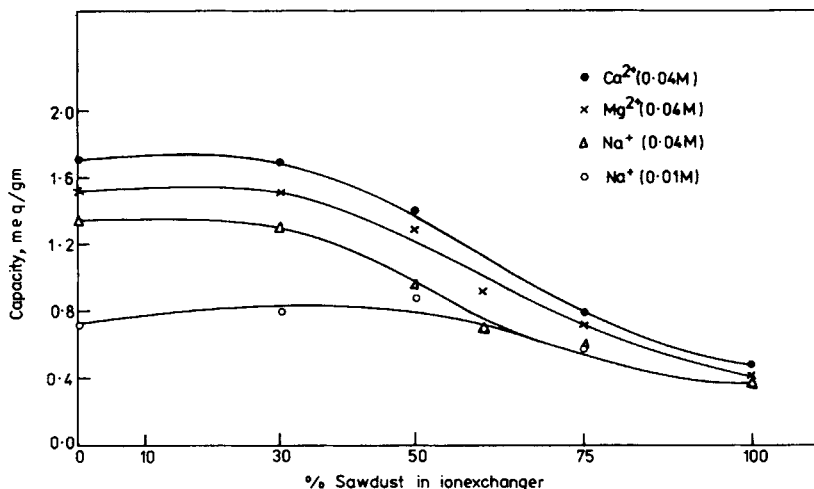


Fig. 4. Capacitance vs. composition for sawdust H⁺ resins.

CONCLUSIONS

Although the resins prepared may not in themselves be of industrial value, the following important trends in the preparation of composites have been established by the present work.

(1) Substitution of at least 30%–50% of the polymer content in the phenol formaldehyde cation exchanger by sulfonated sawdust does not lead to a reduction in their chemical and thermal stability or their apparent capacity for various ions. Thus the possibility exists for considerably reducing the cost of the resins per unit capacity of the resin. If the same could be achieved with other commercial resins of higher capacity, there would be a tremendous economic gain, wherever exchangers are used on a large scale.

(2) The data indicate that the resins can be successfully used for water purification where concentrations of Ca²⁺/Mg²⁺ are low and can be regenerated using concentrated brine solutions.

References

1. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
2. R. Kunin, *Ion Exchange Resins*, 3rd ed., Wiley, New York, 1958.
3. N. L. N. Sarma, M. Joseph, and P. Vasudevan, *Res. Ind.*, **21**, 173 (1976).
4. P. Vasudevan, M. Singh, S. Nanda, and N. L. N. Sarma, *J. Polym. Sci.*, **16**, 2545 (1978).
5. N. M. Khose and B. D. Dasare, 1.4, Abstracts of Papers, Ion-Exchange Symposium (1978), CSMCRI, Bhavnagar, India.

Received November 10, 1977

Revised March 15, 1978