

# Synthesis and Studies of Egyptian Bagasse Pith Phenol Formaldehyde Cationic Exchangers

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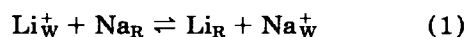
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## SYNOPSIS

The article is concerned with a simple method for preparing cationic resins from polycondensation of Egyptian bagasse pith (as a source of cheap and renewable material) with phenol and paraformaldehyde as a cross-linking agent. Optimum principal reaction conditions of the preparation and properties are determined and compared with resin without bagasse pith content. The synthesized resins are stable in water, organic solvents, thermal treatment, and mineral acids (1M). The samples having a cation exchange capacity up to 3.92 meq g<sup>-1</sup> of dry resins are being introduced as new cationic exchangers. The synthesized resins are used in the study of the possible separation of univalent cations. The rational thermodynamic equilibrium constants (ln *K*) are calculated for Li<sup>+</sup>-Na<sup>+</sup> exchanges on the resins having a various amount of bagasse pith. The thermodynamic parameters are computed and suitable explanations are described. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Bagasse pith is generally used as a furnace fuel of sugar mills<sup>1</sup> and for production of furfural.<sup>2</sup> The synthesis of resins from wood, lignin, and other cellulosic materials have been studied,<sup>3-5</sup> especially for the synthesis of polycondensate bagasse pith phenolic resins.<sup>6,7</sup> Many ion exchangers owe their origin to petroleum products and there is a continual increase in their cost. Attempts have been made in earlier studies<sup>8-12</sup> to preparing cheaper cationic resins from natural products. The aim of the present work is to determine the optimum conditions of preparation and properties of sulfonated cationic exchangers from Egyptian plant by-products of bagasse pith, to study the selectivity coefficients of Li<sup>+</sup>-Na<sup>+</sup> exchanges, and to find the optimum conditions for using cationic resins for the separation of Li<sup>+</sup> from Na<sup>+</sup> ions. The selectivity coefficients (*K<sub>a</sub>*) of the general ion-exchange reaction of



where the subscripts W and R refer to the ions in water and exchanger, respectively, are given by

$$K_a = \frac{X_{\text{LiR}} C_{\text{NaW}}}{X_{\text{NaR}} C_{\text{LiW}}} \quad (2)$$

where *X<sub>LiR</sub>* and *X<sub>NaR</sub>* are the equivalent ionic fractions of the ions in the resin phase and *C<sub>LiW</sub>* and *C<sub>NaW</sub>* are the concentrations of the ions in solutions. The rational thermodynamic equilibrium constant (*K*) is represented by:

$$K = \frac{X_{\text{LiR}}}{X_{\text{NaR}}} \frac{L_{\text{LiR}}}{N_{\text{NaR}}} \frac{m_{\text{NaCl}}}{m_{\text{LiCl}}} \frac{\gamma_{\text{NaCl}}^2}{\gamma_{\text{LiCl}}^2} \quad (4)$$

which has been calculated from the plots of ln *K<sub>a</sub>* versus *X<sub>LiR</sub>*,<sup>13-15</sup>

$$\ln K = \int_0^1 \ln K_a \frac{\gamma_{\text{NaCl}}^2}{\gamma_{\text{LiCl}}^2} dX_{\text{LiR}}. \quad (5)$$

Thus, the standard molar Gibbs free energies Δ<sub>r</sub>*G<sub>m</sub>*<sup>o</sup> of the exchange of Li<sup>+</sup>-Na<sup>+</sup> are given by:

$$\Delta_r G_m^o = -RT \ln K. \quad (6)$$

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**Table I** Characterization of Raw Material of Bagasse Pith

Fraction	Content (wt %)
Hollocellulose	77.50
Resistant cellulose	33.60
1% Sodium hydroxide solubility	25.80
Pentosan	28.20
Lignin	19.10
Hot water solubility	10.50
Ash	5.30

The standard molar enthalpies  $\Delta_r H_m^\circ$  are calculated from the plots of  $\ln K$  versus  $1/T$ . The standard molar entropies  $\Delta_r S_m^\circ$  are calculated from the expression:

$$\Delta_r S_m^\circ = (\Delta_r H_m^\circ - \Delta_r G_m^\circ)/T. \quad (7)$$

## EXPERIMENTAL

### Materials

The raw material used was bagasse pith obtained from Egyptian plant by-products. The bagasse pith was air dried, crushed, and screened between 641–520 microns; the coarse grain particles were rejected. The mean values of the raw material are given in Table I. The solid dry content was 96.11%. Other chemical reagents were of chemically pure grade.

### Preparation of Cationic Exchangers

The reactions were carried out in a three-necked flask (500 mL) equipped with reflux condenser, thermometer, and mechanical stirrer in a thermostated bath. The following steps were carried out:

1. Polycondensation of bagasse pith with phenol (Compound I): 30 g of bagasse pith was stirred with 30 g phenol at 95°C in the presence of 150 mL concentrated HCl for 8 h. The product was dissolved in methanol and filtrated.
2. Cross-linking the polycondensate resin (Compound II): Various amounts of paraformaldehyde (15, 25, 35, 45, and 60 wt %) were added to the filtrate over a period of 20 min in the presence of HCl as a catalyst (5 mL HCl/20 g of compound I). The reactions were stirred for 2 h at 90°C. The obtained products were cross-linked bagasse pith phe-

nol formaldehyde resins that were not dissolved in methanol or any other solvents. The same procedures were repeated with 21 g paraformaldehyde (the most stable cross-linked percentage), 30 g phenol, and various amounts of bagasse pith (0, 15, 30, 45, and 60 g). The products were dried at 100°C for 6 h. The resins were crushed and washed with water, HCl, and NaOH (0.1M) several times and put in an oven at 110°C for 3 h. Irregular particles were obtained by breaking up bulk resins.

3. Sulfonation of cross-linked resins (Compound III): 10 g of the resulting cross-linked resins (compound II) were stirred with 30 mL  $H_2SO_4$  (98%) in the presence of silver sulfate as a catalyst (0.5 g) at 95°C for 6 h. The length of time required depended upon the amount of both paraformaldehyde and bagasse pith added. When the reactions were completed, the mixtures cooled, the excess acid removed by filtration; the mixtures were hydrated and free from acids.

### Physical and Chemical Treatments

#### Particle Size

Particle size of sulfonated cross-linked resins were determined by sieving samples between 420–250 microns.

#### Capacity Determination

Approximately 2.0-g samples of cationic resins were weighed into a dry 250-mL flask; exactly 200 mL of NaOH (0.1M) prepared in 5% NaCl was added. The flasks were left overnight under dynamic conditions. Then 5-ml aliquots of the supernated liquid were titrated with 0.1M HCl. The capacity was calculated as described in the literature.<sup>16,17</sup>

#### Weight Swelling Percentage ( $\alpha$ )

Swelling measurements were made by allowing the samples of cationic resins to equilibrate with demineralized water overnight under static conditions. The wet weight samples were measured as ( $M_w$ ), then the corresponding dry weights ( $M_d$ ) were obtained after drying the samples at 100°C (~ 8 h). The gravimetric percent of swelling ( $\alpha$ ) is<sup>10,18</sup>

$$\alpha = \frac{M_w - M_d}{M_d} \times 100. \quad (8)$$

**Table II Sulfonated Bagasse Pith Phenol Formaldehyde Resins Properties**

Bagasse Pith (wt %)	Capacity	Weight Swelling % (H <sup>+</sup> form)	Absolute Density (g ml <sup>-1</sup> )	
			Hydrated State	Dehydrated State
0.00	3.00	112	1.20	1.31
22.72	3.42	124	0.89	0.92
37.04	3.65	132	0.86	0.89
46.88	3.85	143	0.83	0.86
54.05	3.92	152	0.81	0.83

**Volume (V) and Density ( $\rho$ ) Determination**

The density of the resins were calculated in both hydrated and dehydrated states with the aid of the specific gravity bottle. The cationic exchangers were equilibrated with the solutions (water and toluene) and weighed in swollen form ( $'Q$ ). After thermal equilibrium was attained (at 25°C), the bottles were weighed. The volume of the exchangers ( $'V$ ) calculated from<sup>18</sup>

$$'V = V_b - (Q_b - 'Q)/\rho \quad (9)$$

where  $Q_b$  is the weight of the bottle content,  $V_b$  is the volume of the bottle, and  $\rho$  is the density of solution. The density ( $'\rho$ ) of cationic resins (Table II), can be calculated from<sup>15,19</sup>

$$' \rho = 'Q/'V. \quad (10)$$

**Chemical Stability**

The stability studies of the sulfonated cationic resins against several treatments, acids, bases, organic solvents, and boiling water are shown in Table III. Thus, 2.0 g of the resins were used with 100 ml of the reagent, and the capacity determined as meq g<sup>-1</sup> dry resin.

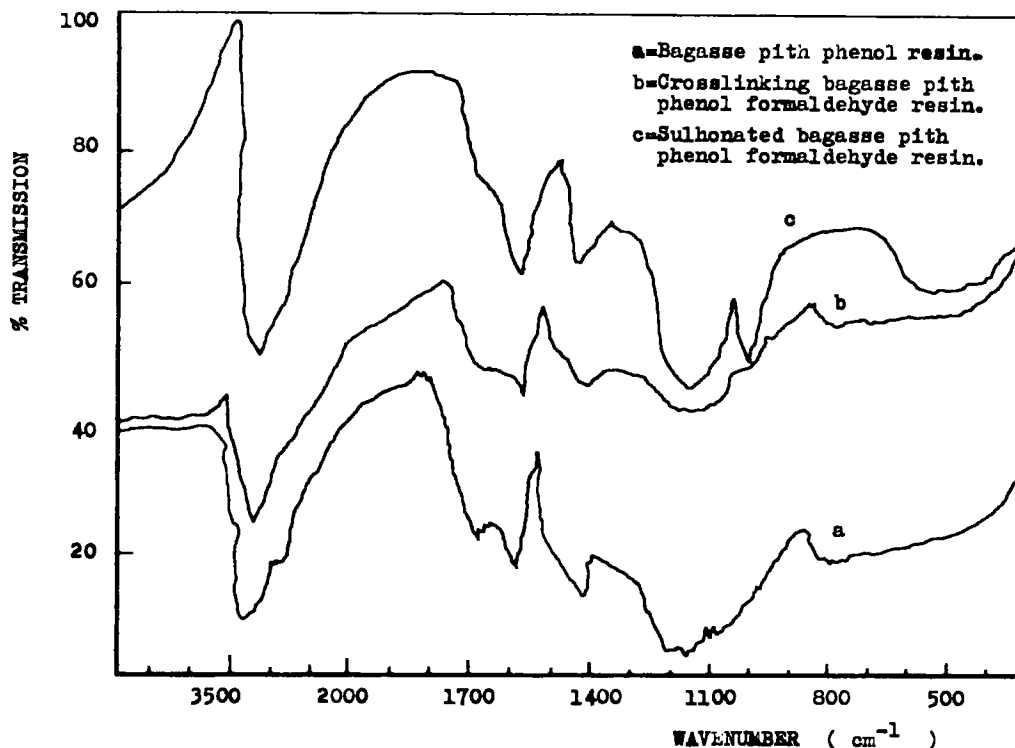
**Chemical Composition**

The infrared spectrum of the synthesized sulfonated cross-linked bagasse pith phenol formaldehyde resin is shown in Figure 1. The bands at  $\sim 800$  cm<sup>-1</sup> may be due to C—O—C in the furan ring or due to the CH<sub>3</sub> rocking vibration; thus this band disappeared after sulfonation. A new asymmetrical band at  $\sim 1000$  cm<sup>-1</sup> is shown also for the resin after sulfonation. Characteristic bands for —OH phenolic

**Table III Effect of Different Reagents on Capacity of Cationic Resins Containing Various Amounts of Bagasse Pith**

Reagents	Capacity, meq g <sup>-1</sup> Dry Cationic Resins				
	0% BP	22.72% BP	37.04% BP	46.88% BP	54.05% BP
Original capacity	3.0	3.42	3.65	3.85	3.92
NaOH (0.2 M) for 24 h at 30°C	2.90	3.30	3.50	3.67	3.71
HCl (1 M) for 24 h at 30°C	2.95	3.34	3.55	3.73	3.85
H <sub>2</sub> SO <sub>4</sub> (1 M) for 24 h at 30°C	2.96	3.35	3.54	3.72	3.83
HNO <sub>3</sub> (1 M) for 24 h at 30°C	2.92	3.31	3.52	3.70	3.74
Acetone, ethanol, benzene, dioxane, CHCl <sub>3</sub> , toluene for 24 h at 30°C	2.97	3.38	3.60	3.79	3.87
Boiling water for 8 h	2.96	3.36	3.57	3.75	3.78
Thermal treatment in drying oven at 120°C for 10 h	2.88	3.28	3.48	3.66	3.72

BP, bagasse pith.



**Figure 1** Infrared spectrum of Bagasse pith phenol formaldehyde cationic exchanger (with 35% bagasse pith content).

or CH aromatic appeared at  $1150\text{ cm}^{-1}$ . A stretching aromatic group band at around  $1550\text{ cm}^{-1}$  was observed clearly before and after sulfonation. A weak overtone and combination band of CH from the benzene rings are shown at  $1650\text{ cm}^{-1}$ . The broad band characteristic of strong hydrogen bonding is indicated at  $3500\text{ cm}^{-1}$ . Elemental analysis of the cationic exchanger with 35% bagasse pith gave: C = 63.1; H = 5.1; S = 3.7; and O = 17.1.

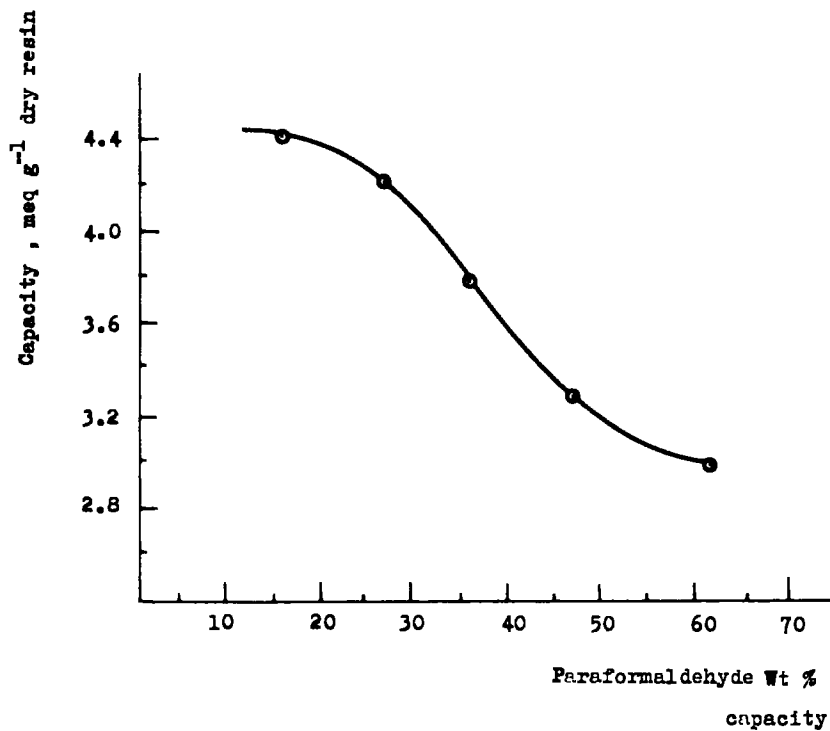
#### Equilibrium Procedure

Various resins (0, 22.72, 37.04, 46.88, and 54.05 bagasse pith) were used in the sodium form. The resins were conditioned<sup>13-15,20</sup> by double cycles of sodium and lithium exchanges on the resins and air dried to constant weight. All equilibrium studies were carried out using 1 milliequivalent of the dry resins. The stock electrolyte solutions (0.5M) were prepared using Analar chlorides of lithium and sodium. To prepare solutions for exchange studies, these were suitably diluted with distilled water to 0.1M strength with respect to the alkali cations. All exchange studies were carried out in a thermostatic bath (controlled within  $\pm 0.1^\circ\text{C}$ ) at four temperatures, 20, 30, 40, and  $50^\circ\text{C}$ . The reaction flasks were

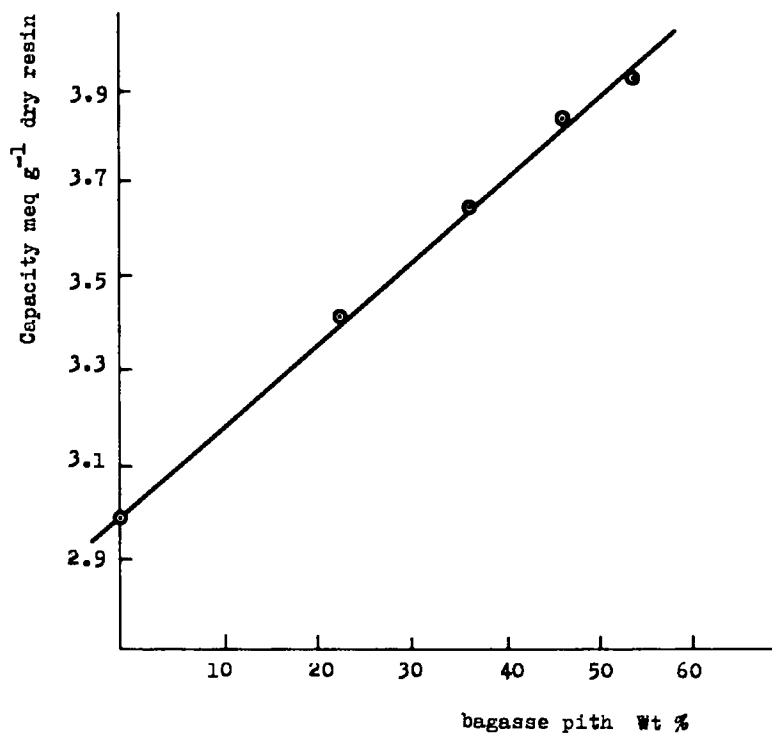
shaken intermittently during equilibrium under thermostatic conditions. A sufficient time interval ( $\sim 6\text{ h}$ ) allowed for the attainment of equilibrium. The solution phase was analyzed for the equilibrium exchange by Atomic absorption (Perkin-Elmer Model 2380).

#### RESULTS AND DISCUSSION

The present work deals with the synthesis of cationic resins from waste Egyptian bagasse pith by condensation first with phenol in the presence of HCl (Compound I), second by treating the resulting soluble polycondensate resins with various percent of paraformaldehyde as a cross-linking agent (Compound II) and then finally by sulfonation of compound II in the presence of catalyst (Compound III). The relation between the various amounts of paraformaldehyde in the resins and the capacity are shown in Figure 2. Higher values of the capacity are shown at 15 and 25% paraformaldehyde content; however, these percentages are less chemically stable than the resins that contain 35% paraformaldehyde. The capacity decreased with increased paraformaldehyde content in the matrix. The effect of the



**Figure 2** Effect of paraformaldehyde percentage on the capacity of the cationic resins.



**Figure 3** Variation of the bagasse pith percentages versus the capacity of the cationic resins.

change in the amount of bagasse pith in the resins on the capacity is shown in Figure 3 (for resins with 35 g paraformaldehyde + 30 g phenol). The higher the amount of bagasse pith in the matrix, the larger the capacity of the cationic resins. The average swelling percentage, absolute density, and the capacities of the cationic exchangers with various amount of bagasse pith in the resins are shown in Table II.

The weight swelling percentages were increased with increases in the amount of bagasse pith in the resins, and higher values are shown for resins containing 54.05% bagasse pith. The rigidity of the resin matrix was proved from the swelling measurements. Therefore these cationic resins with lower bagasse pith, that is, lower swelling, showed much higher rigid shape; and the rigidity decreased with increasing bagasse pith in the exchanger. The absolute densities for the different resins in the dehydrated state are much higher than the hydrated state (Table II). Generally the absolute density decreased with an increased amount of bagasse pith in the resin.

The effect of different reagents on the capacities of various cationic resins are shown in Table III. With treatment of the exchangers with soda (0.2M), the loss in capacity ranged from 3.3 to 5.36%. A higher decrease in the capacity was observed for resins containing 54.02% bagasse pith. Upon treatment of the resins with mineral acids, the decrease in the capacities were 1.3–4.59%. When treated with different organic solvents, the loss in capacity was 1–1.28%. The decrease in the capacity with boiled water was 1.3–3.57% according to the amount of bagasse pith in the resins. Heating the resins for 10 h at 120°C caused a loss in the capacity between 4–5.10%.

The variation of the selectivity coefficients ( $\ln K_a$ ) versus the equivalent fraction of lithium in the cationic resins  $X_{LiR}$  are represented (not shown). As the bagasse pith in the resin was increased, the  $K_a$  values were increased and a higher value of  $K_a$  was shown for 54.05% bagasse pith at 40°C. The same behavior was observed for all studied temper-

**Table IV Maximum Water Uptake for Cationic Resins With Various Bagasse Pith Percentages**

Resin Form	Maximum Water Uptake (g/equiv.)				
	0.00%	22.72%	37.04%	46.88%	54.05%
Li <sup>+</sup>	362	380	410	440	470
Na <sup>+</sup>	385	430	490	512	522

**Table V Thermodynamic Equilibrium Constant ( $\ln K$ ) for Li<sup>+</sup>/Na<sup>+</sup> Exchanges on Bagasse Pith Phenol Formaldehyde Cationic Resins**

Bagasse Pith (Mass Percent)	$\ln K$			
	20°C	30°C	40°C	50°C
00.00	0.27	0.42	0.55	0.64
22.72	0.40	0.53	0.69	0.79
37.04	0.48	0.64	0.78	0.88
46.88	0.54	0.69	0.82	0.97
54.05	0.62	0.80	0.97	1.11

atures. The rational thermodynamic equilibrium constants are evaluated from the graphical integration of eq. (5), between zero and one.<sup>21–23</sup> The maximum water content of the resins in the sodium and lithium forms were determined as reported previously<sup>24</sup> (Table IV). It has been found from the present studies that in general the rational thermodynamic equilibrium constant (Table V) shows an increase with both temperature and bagasse pith content in the resins. The increase in  $\ln K$  values correlates well with the increase in water content<sup>25–27</sup> of the two ionic forms. From the  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$  values (Table VI), it was observed that the entropies of exchange are increased with the uptake of the preferred ion by the exchanger matrix. The result is consistent with the entropy increases found in this study<sup>13,27</sup> and others.<sup>21,23,28</sup> It has been assumed that partial dehydration of Li<sup>+</sup> ions accompanies their interaction with the sulfonate groups in the exchanger matrix. The entropy values increase with increasing bagasse pith content in the exchanger, and this was attributed principally to the decrease in Li<sup>+</sup> ions hydration in the exchanger. The sizable entropy increase is due to transfer of bound water molecules from the resin phase to the dilute aqueous

**Table VI Standard Gibbs Free Energies, Enthalpies, and Entropies of Li<sup>+</sup>/Na<sup>+</sup> Exchanges on Various Bagasse Pith Phenol Formaldehyde Cationic Resins**

Bagasse Pith (Mass Percent)	$-\Delta_r G_m^\circ$ $J \cdot mol^{-1}$	$\Delta_r H_m^\circ$ $J \cdot mol^{-1}$	$\Delta_r S_m^\circ$ $J \cdot K^{-1} mol^{-1}$
00.00	1058	9704	35.51
22.72	1335	10229	38.17
37.04	1612	10491	39.94
46.88	1738	11278	42.96
54.05	2015	12851	49.06

electrolyte and the rejection of bound water.<sup>27,28</sup> The values of  $\Delta_r G_m^\circ$  for all reactions are negative and decrease with an increase in the bagasse pith content. The  $\Delta_r H_m^\circ$  values are positive, indicating that bonding of  $\text{Li}^+$  cation with sulfonate anion of the exchanger is generally endothermic.

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Received March 10, 1993

Accepted July 29, 1993