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Biomass – Furfural based ion exchange resins. preparation of polymeric composition

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ABSTRACT

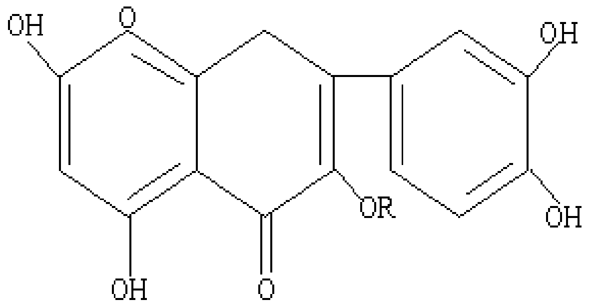
Novel organic cation - exchangers based on biomass and furfural suitable for processing into ion exchangers was prepared. The polymer has been processed chemically into different types of cation exchange resins. The role of various parameters such as catalyst concentration, the effects in the different particle sizes in exchange capacity, etc., for preparing the polymer is systematically studied and presented. Similarly, the conditions for preparing the various cation exchange resins (Sulphonated, Furfuraldehyde, and unmodified type from the polymer) are also described. The overall best particle size in exchange of ions is the 500μm size.

Keywords: Cation - exchange resins; Polymer, Exchange Capacity, Biomass.

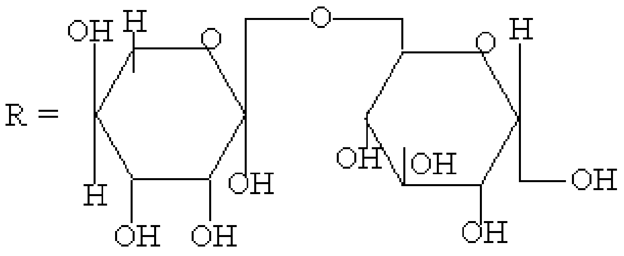
INTRODUCTION

A perusal of literature reveals that besides divinyl benzene co-polymers, a large number of materials (biomass) can be converted into ion exchange resins by chemical treatments [8]. Synthesis of polymer based on Biomass and furfural and preparation of cation exchange resins therefore were reported for the first time by the author,[2,3]. Given the increasing need to provide feedstock for the chemical industry by using renewable resources, the most convenient source to be considered is agricultural wastes or by-products. The pulps and peels of orange, grapefruits, lemons and table grapes contain flavonoids. The flavonoids present in these wastes are rutin (yellow crystal), hesperidin and naringin [4,9]. These flavonoids can be extracted from the peels and pulps with methanol. The structure of rutin is as shown below [9,10].

The actual chemistry involved in the production of phenolic resins using vegetable tannin from orange mesocarp as a source of phenol is based on the fact that since tannin has a phenolic nature, it thus will undergo the well known reactions of phenol with aldehyde [10]. Phenol reacts with formaldehyde (aldehyde) in the presence of catalyst to produce the phenol alcohols; these products (phenol alcohols) may condense with more phenol to yield compounds of the diphenylomethane type [9].



Quercetin-3-B-D-rutinoside ($C_{27}H_{30}O_{16}$) Rutin



Rutinose

Oil palm tree (*Elaeis guinansis*) is a member of small genus of only two species of palms, one species occurring in Africa and the other in Central and South America. The tropical oil palm is native to numerous countries in tropical Africa and is found in Southern Nigeria. A by-product of oil palm fruit refining is the oil palm fruit fibre which is used in some localities as source of fuel for heating in the absence of firewood [10].

The relative abundance of these agricultural wastes in Nigeria provides available source of tannin and furfural which stimulates our interest on the possible use of these materials for the production of resin.

MATERIALS AND METHODS

Collection of Materials

Orange mesocarps for this research were obtained from local sellers along the streets of Choba market in Port Harcourt. Palm fruit fibres were obtained from palm oil mills at Elele Town in Rivers State of Nigeria. All chemicals and solvents were of technical grade unless otherwise specified.

Furfural Extraction (Acid Hydrolysis)

15g of the washed and dried palm fruit fibres were refluxed with 750mls of a 4.5M Hydrochloric acid in a reflux condenser for one hour. Thereafter the content was filtered and the filtrate stored in a brown reagent bottle for further work. Each filtrate was used within 24hours of its production.
The equation for the hydrolysis is

Preparation of Cation Exchange Resins

The Biomass was chemically modified through sulphonation and condensation reaction. Particle sizes of 150, 300 and 500µm were used for the reaction.

Sulphonated Biomass Cation Exchange Resin (SB)

One part of orange mesocarp (150, 300 and 500µm*)* was sulphonated with fifteen parts (1:15 ratio) of $2MH_2S0_4$ by heating the mixture at 55^0C for 3 ½ hours. Thereafter the product was filtered and the residue was washed free of acid using water.

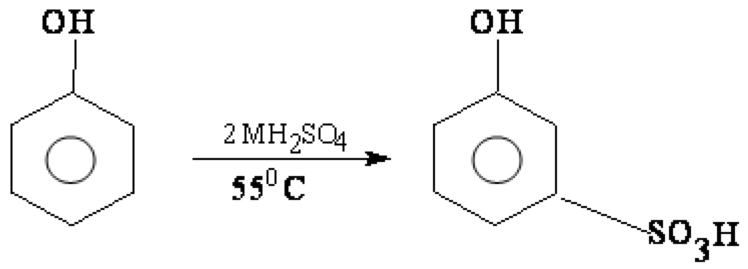


Fig. 2: Sulphonation of Phenol

Formaldelyde modified sulphonated Biomass Resin (FMB)

Five parts of the sulphonated product was treated with 2 parts of formaldehyde (37% w/v) and the mixture was heated at 60°C for 4 hours in acid condition. The product was filtered, and the residue was washed free of formaldehyde using water.

The equation of reaction

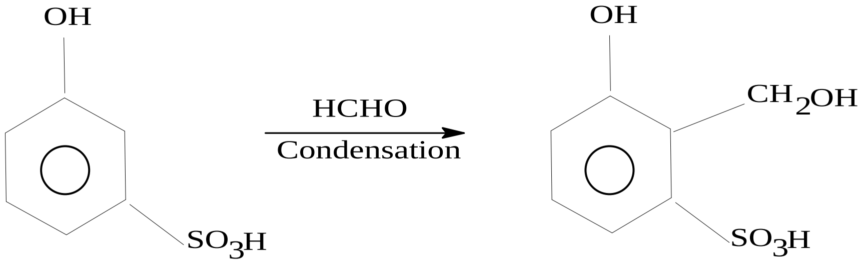


Fig. 3: Condensation reaction

The sulphonated product undergoes condensation with a further molecule of sulphonated phenol. The process continues until all the aromatic rings are substituted in the 2, 4 and 6 position. Finally a molecular network of resin (polymer) builds up, called formaldehyde modified sulphonated Biomass (FMB) as shown in Fig. 4.

Furfuraldehyde Modified sulphonated Biomass (Fur.MB)

The particles sizes of 150, 300 and 500µm were sulphonated as in the (FMB) products under similar reaction condition. Then these sulphonated products were treated thus: Five parts of these sulphonated products was treated with 10 parts of the extracted furfural- dehyde filtrate; and the mixture was heated at 60^{0}C for 4 hours. Thereafter the product was filtered, and the residue was washed free of furfural-dehyde using water. The product was dried at 60^{0}C in an oven.

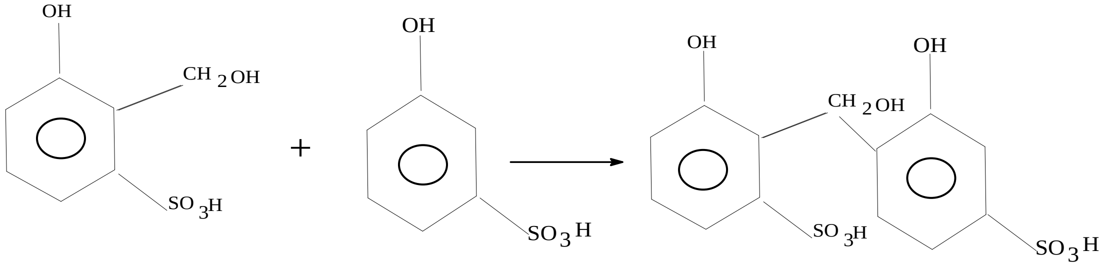


Fig. 4: Cation exchange Resin or Formaldehyde modified Sulphonated Biomass (FMB)

Determination of Cation Exchange Capacity of Resin

The ion exchange capacity of the cation exchange resin produced in this work was determined by the titration method of Dara [4].

DISCUSSION

The ion exchange capacity of the resin was determined by taking the exchanger in H^+ form by titrating with 0.1M NaOH and $Ca(OH)_2$ solutions. Metal ion capacity was determined by taking M^{2+} with the exchanger and titrating with a solution of Calcium hydroxide. The results are shown in Fig 7 with least value in Fur.MB for the mere fact that it resisted easy release of H^+ for Ca^{2+} ions.

It is therefore desirable that the exchanger should not be allowed frequent contact with solutions containing Ca^{2+} ion. Sodium ion has the highest exchange capacity of 0.45meq/g for formaldehyde modified biomass, however the exchange capacity for other ions are encouraging. Sodium ion has the highest exchange capacity of 1.36meq/g for F.M.B. However the exchange capacity for calcium was encouraging in 300µm particle size. Sodium ion has the highest exchange capacity of 1.03 meq/g in both aldehyde modified Biomass in the 500µm particle size. Therefore 300µm particle size F.M.B with sodium ion capacity of 1.36meq/g is the overall best exchanger. Hence it is recommended for any exchanger reaction. Harvey, [6] has reported condensation of α- pinene and formaldehyde in the ratio of 1:1.7 in the presence of water and acid catalyst. The product obtained was a liquid.

Isagulan, [8] have also reported condensation of α- pinene and formaldehyde in the presence of a strongly acidic cation exchanger resin. Since the product obtained was a liquid, an attempt was made in this investigation to cross link the same by treating separately with Phenol and Formaldehyde. It was observed that cross linked products could be obtained, and for comparison of exchange capacity and Rates of exchange, this observation prompted the use of furfural in the place of formaldehyde to obtain cross linked products for further testing.

It is clear from the capacity chart in figure 6 and 7 that Phenol formaldehyde and Phenol furfural polymers can be sulphonated successfully into a cation exchange resin. Literature reports that an increase in temperature has resulted in an increase in capacity. However sulphonation at a range of 55°C - 60°C for 3 ½ hours is ideal but an increase in hours to 6 hours will be more ideal. It is interesting to note that with this mild reaction time and temperature, at least, an average exchange capacity was realized.

Factors that positively or negatively affected the exchange capacity of an ion exchanger in cause of the research are:

Number of sulphonation and sulphonation time i.e. an increase number either in sulphonation and time increases capacity.

Ratio of sieves i.e. Furfural and Formaldehyde, the experimental observation reveals that equal ratio gives maximum yield and promotes capacity which is in line with literature.

Number of condensation with Formaldehyde and Furfural increases capacity, as even revealed by the capacity chart. Increase in temperature and catalyst e.g. is found to increase exchange capacity.

CONCLUSION

Furfuraldehyde modified sulphonated Biomass in 500µm particle size for Na^+ ion test is observed to be the overall best ion exchange material. This is because of the fact that it has an initial volume exchange rate time of 9 seconds; although formaldehyde modified sulphonated Biomass of 500µm particle size had 2.5 seconds initial time, but having a final volume exchange rate of 24 minutes, whereas Fur. MB had a final volume exchange rate time of 60 seconds.

Therefore the best particle size for rate of exchange determination between this two products is Fur.MB of 500µm particle size in Na^+ and Ca^{2+} ion tests as shown in the graphs, therefore it is recommend for use by oil companies, NNPC for treating effluents; other industries and domestic users as a local content.

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