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Starch Modification Using a Dry Reaction

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Abstract

New cation exchange resins are prepared through reaction of starch – as inexpensive and biodegradable backbone – and citric acid, as a cross linking and carboxyl groups bearing agent, at elevated temperature. Factors affecting the resin formation, such as reactants, concentration, reaction temperature; reaction time. The chemical structural characteristics were investigated by method of FTIR and ^{1}H NMR. These resins were used in the removal of some basic dyes from aqueous solutions.

Keywords: starch, dye, modification, cation exchanger.

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1. Introduction

Starch is the most abundant carbohydrate reserve in plants and is found in leaves, flowers, fruits, seeds, different types of stems and roots. Starch is used by plants as source of carbon and energy [1]. Starch is a natural polymer occurring in all plant organisms. It is the major component of most of plant-originated foodstuffs and feedstuffs and of numerous industrial raw materials. Being synthesized from glucose, which is formed from dioxide and water, starch is an indirect product of photosynthesis, hence it is called renewable raw material or gold from garbage [2] (Figure 1). The increasing number of publications on adsorption of toxic compounds by modified polysaccharides indicates a recent increase in interest in the synthesis of new low-cost adsorbents used in wastewater treatment [5].

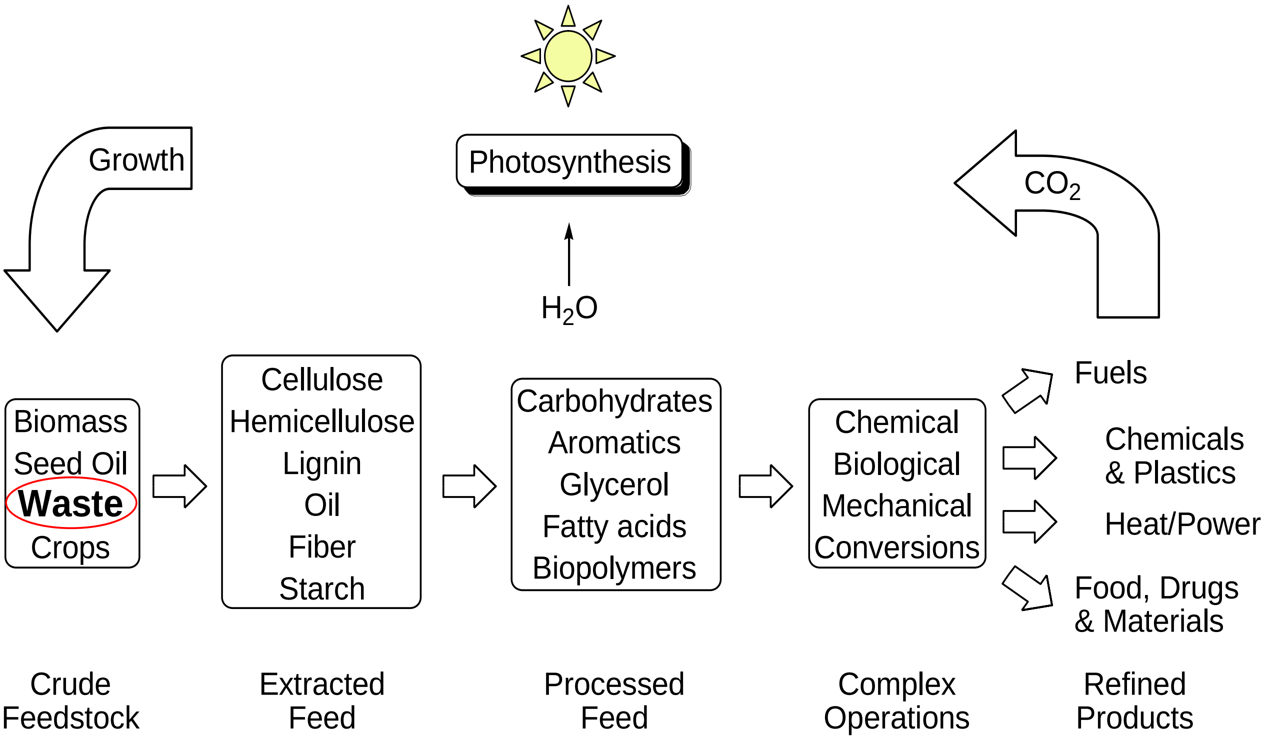

Figure 1: Processing of crude feed-stocks to refined chemical products [3-4].

Recent developments have focused on the synthesis of adsorbents containing polysaccharides, in particular modified biopolymers derived from chitin [6] , chitosan [7] , starch [5], cellulose [8- 9] and cyclodextrin [10] , which are not only eco-friendly and cost-effective but are also effective in remediation of common effluents present in the wastewater. Starch is applied in the food and many other industries, like: pharmaceutical, textile, chemical and building industries. Such a wide applicability of starch is feasible by imparting it new traits on the route of enzymatic, physical and chemical modifications. Properties of starch are modified so as to correspond toa specified practical application

[11] bellow some examples.

Acid-catalyzed dehydration of polysaccharides (Figure 2)

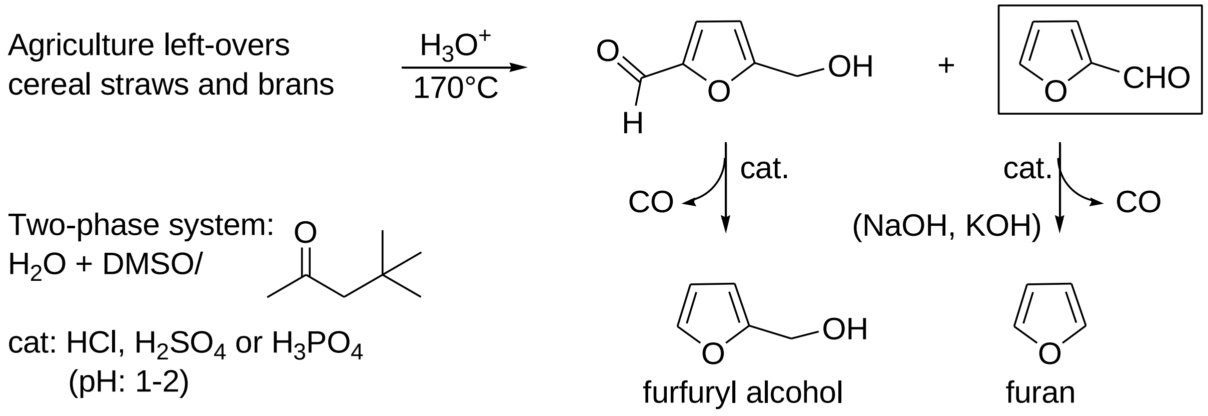

Figure 2: Transformation of agriculture leftover to furan and furfuryl [12-13]

Energy efficient production of H_2 and Syngas from biomass (Figure 3)

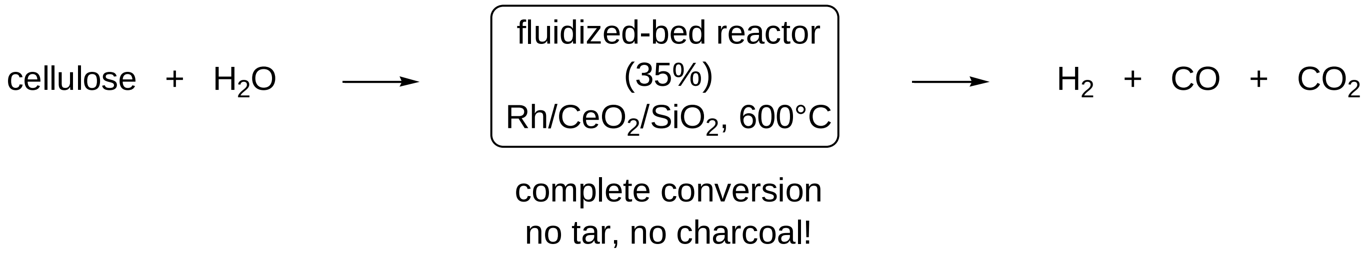

Figure 3: Method of production of H_2 from biomass [14-15]

2,5-Dimethylfuran: the liquid fuel of the future? (Figure 4)

The 2,5-dimethylfuran has a higher energy density (+40%) than ethanol (Figure 4)

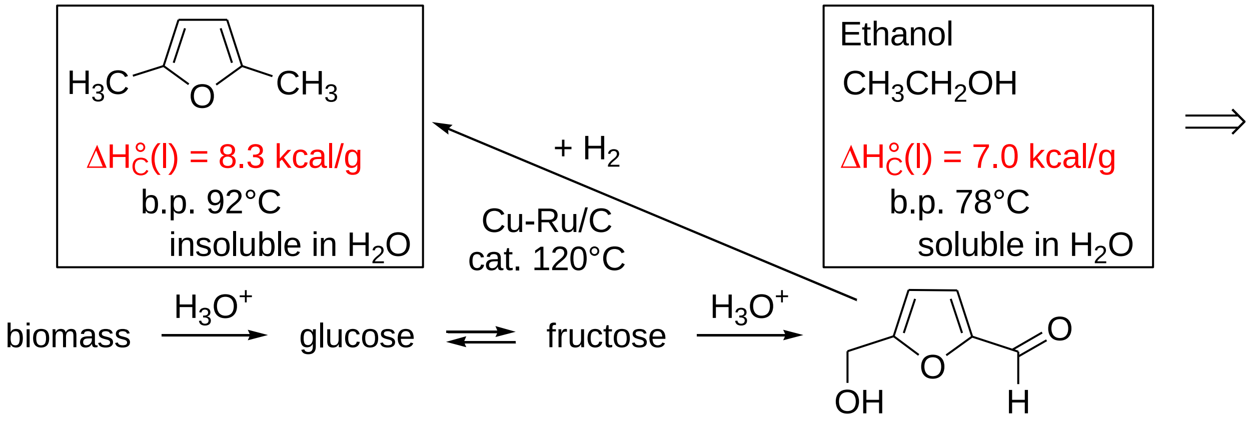

Figure 4: Method of production of H_2 from biomass [16-17]

Industrial uses of furan derivatives (Figure 5)

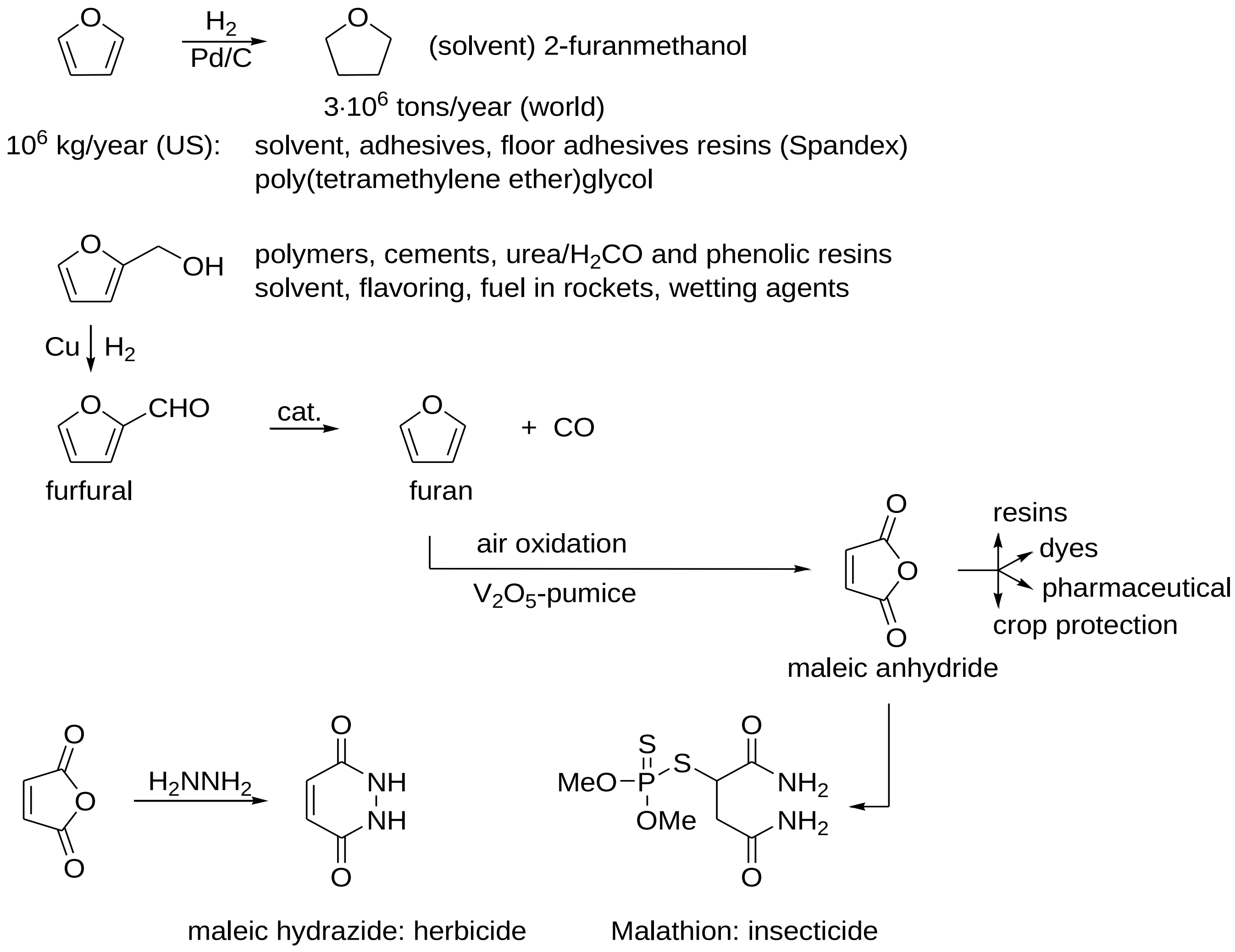

Figure 5: Industrial applications of furan derivatives [18-19]

From furan to nanomaterials and anti-cancer drugs

Survey literature show that among all the aromatic compounds, those containing furan rings (oxygen-based rings) demonstrated outstanding anticancer activity against all cell lines [20-21]. Y. Murti et al. showed that flavanones (Figure 6), a natural product with extensive biological activities such as antibacterial, antifungal, analgesic and antioxidant properties with low toxicity, also possess striking anticancer activities against HT29 (human colon adenocarcinoma), MCF7 (human breast adenocarcinoma) and A498 (human kidney adenocarcinoma). More notably, heterocycle flavanone derivative containing a furan ring, furfuraldehyde, exhibited pre-clinical evidence of a reasonably good anticancer compound despite the fact that the mechanism of action of this particular derivative is still uncertain. In similarity with coumarins, flavones might equally provide a sustainable building scaffold for potential new and improved pharmaceutical anticancer compounds [20,21].

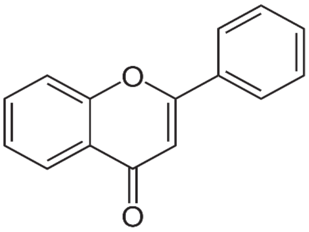

Figure 6: General Flavone molecule containing oxygen atoms

Figure 7 summarize that these naturally occurring heterocycles promise to play an important role in biochemical reactions in cells' metabolism. Their reactivity with cells and tissues makes the regulation of these molecules so tightly controlled that as a consequence any disturbance may be associated with pathological conditions [21].

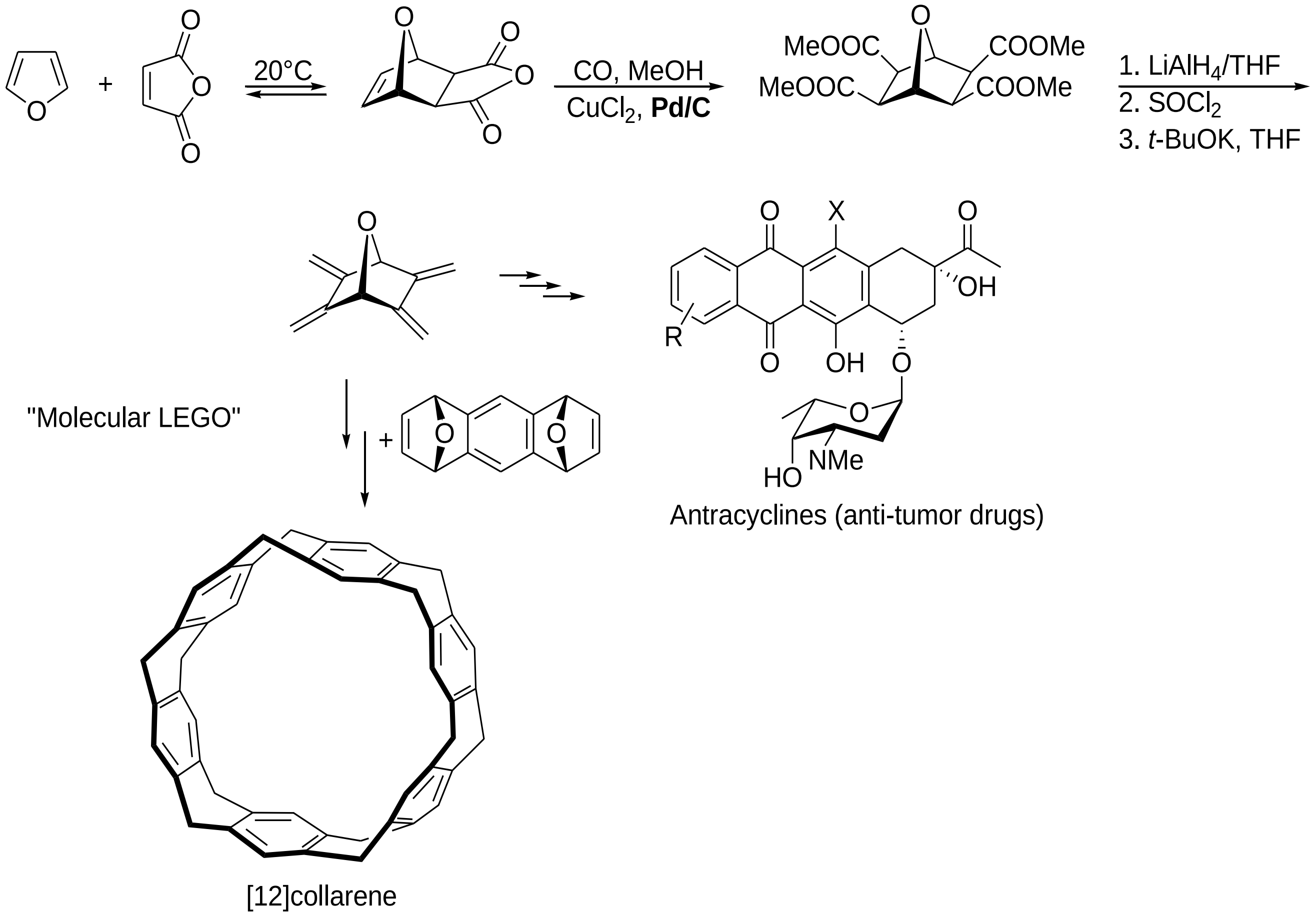

Figure 7: Application of furan derivatives in nanomaterials and anti-cancer [22-25]

Modification of starch

Modification of starch is carried out to enhance the positive attributes and to eliminate the shortcomings of the native starches. Various methods have been developed to produce a range of modified starches with a variety of characteristics and applications. Physically modified starches are simple and inexpensive because they can be produced without chemicals or even biological agents. In contrast, chemical modification is possible due to ubiquitous hydroxyl groups in starches that have been exploited for over a century, principally in the preparation of starch esters and ethers, but also in more subtle alterations, e.g., in order to tune the structure of starches for specific applications [26]. Starch ester is a kind of modified starches in which some hydroxyl groups have been replaced by ester groups. Esterification can impart hydrophobicity to starch products by the substitution of free available hydroxyl groups [27].

In recent years, commercial anion exchange resins have been shown to possess excellent adsorption capacities and demonstrate efficient regeneration properties for the removal dyes [28-29]. Exchanger resin is a novel material in the wastewater treatment process for its biocompatibility and biodegradability properties, and it does not cause any secondary pollution to environment.

Preparation and characterization of starch-based cation and anion exchanger resins [30-31], and their utilization in removing acid dyes [32] basic dyes [33] or hazardous anions [34] from aqueous solution. This work aims at preparing cation exchanger starches containing carboxyl groups via reaction of citric acid with starch.

2. Experimental

2.1Materials

2.1.1 Substrates

Maize starch (food grade) produced from maizery maghnia (Algeria).

Citric acid ($C_6H_8O_8.H2O$) (CA) is tricarboxylic acid. According to IUPAC nomenclature. Citric acid is 2-hydroxypropane -1.2.3tricarboxylic acid, it is also known as B̲-hydroxytricarballylic acid.

2.1.2Methods of characterization

IR-spectra were recorded on a Bruker Equinox 55FTIR Spectrometr, ^{1}H-NMR Spectra (Bruker AC-200 or WH-400FT, Bruker, Karlsruhe Germany.

2.2.3 Preparation of Cation Exchangers

A certain amount of starch substrate was added to a known amount of CA the components mixed well in petri-dish, followed by continuous and vigorous mixing using a mechanical mixer to ensure homogeneity of the mixture .At this end, the petri - dish contents were allowed to react in circulating air oven at certain temperatures for defined times .The product was dried first at 50° for 24h .After drying the obtained product (purified resin) was kept over $P_2O_5$for at least 48h before analysis.

3. Results and Discussion

Tentative mechanism

Under curing conditions and the mixture of citric acid and starch or its derivatives (St. OH) can undergo different reactions, the most important of which are:

1) **Formation of citric acid anhydride (Figure 8)**

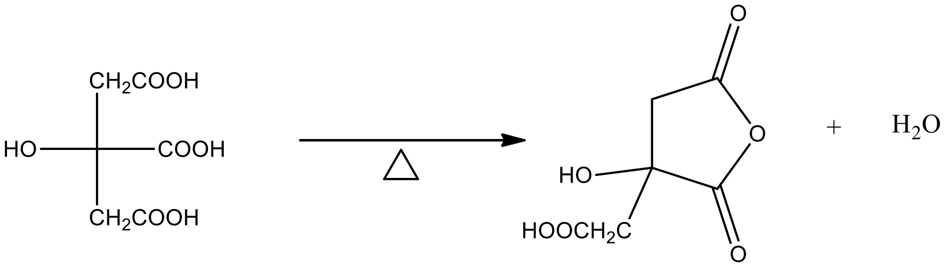

Figure 8: Formation of citric acid anhydride [35-36]

2) **Esterification of starch hydroxyl groups (Figure 9)**

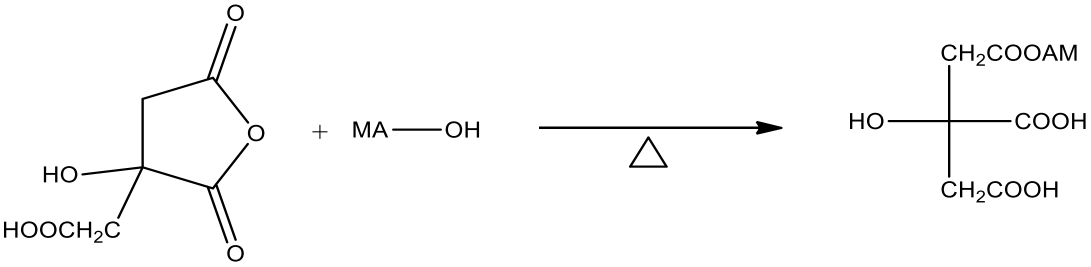

Figure 9: Esterification of starch hydroxyl groups [37]

3) **Ester – Crosslinking of starch** (Figure 10)

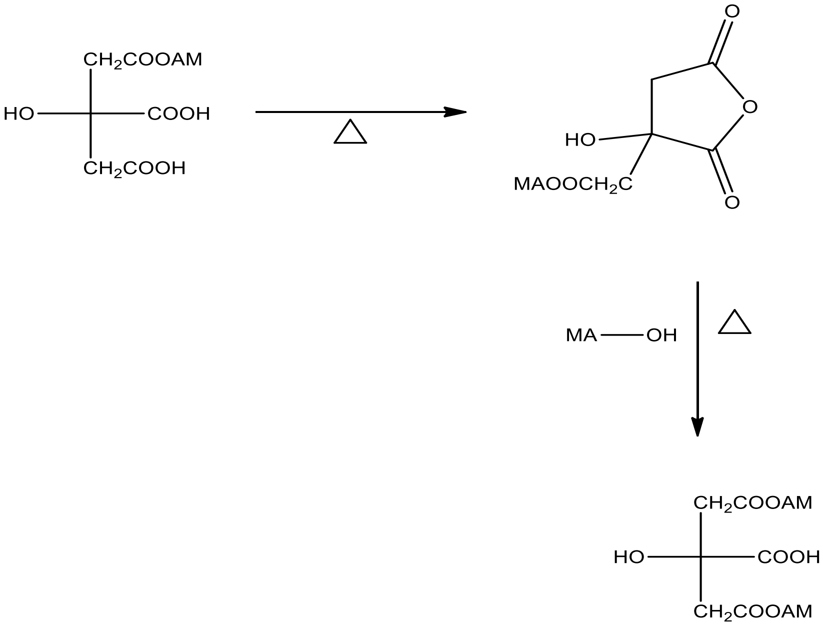

Figure 10: Ester crosslinking of starch [37]

4. Characterization

4.1. FT-IR Spectroscopy study

The IR-spectra of starch citrate (Fig. 11) showed characteristic peaks at 1756 cm^{-1} (due to C=O, carbonyl structure), and 3442 cm^{-1} (due to C-OH) and 2931 cm^{-1} due to (CH), At 2924 cm^{-1} corresponding to C-H stretching of methyl or methylene group of citric acid and 1591cm^{-1} carboxylate citrate starch [38,39]. At 1650 cm^{-1} and 1420 cm^{-1} correspond to δ (OH and δ (CH) bending [40].

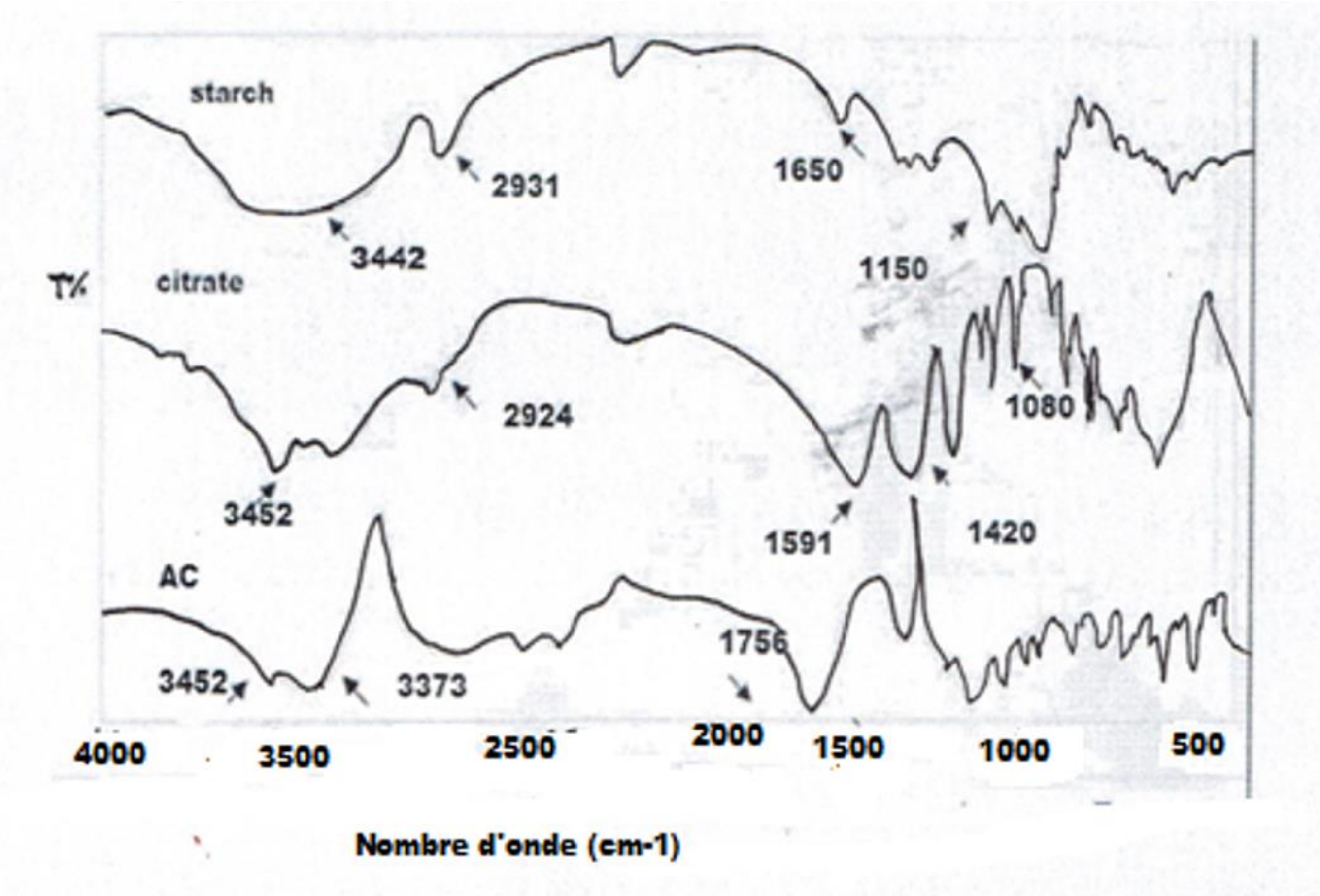

Figure 11: FT-IR spectra of starch, citrate, citric acid

4.2. Analysis of the NMR spectra

The chemical shifts are reported inparts per million downfied from 0.00 ppm . the ^{1}HNMR spectral signals between 3.2 and 5.2 ppm (Figure 12.c) corresponded to the protons of the constituent repeating α-D –glucopyranosyl units , while the starch citrate exhibited the characteristic peacks of citric acid proton in the region from 2 -2.5 ppm. The presence of a pair of downfield doublets at 2.33-2.55 ppm confirmed the presence of citric acid [41,42].

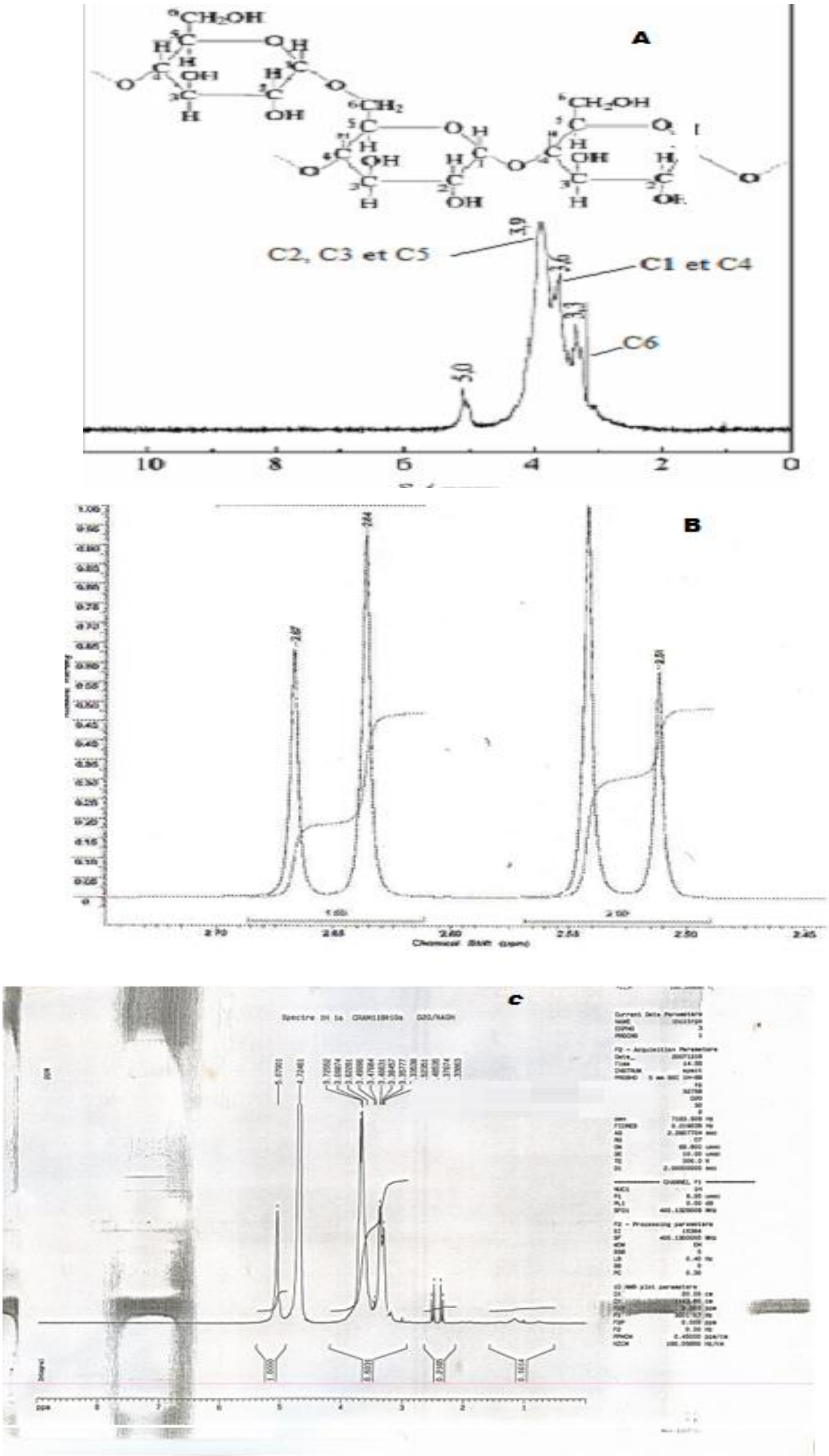

Figure 12: ^{1}H-NMR spectra of starch (a), citric acid (b), citrate starch(c).

Conclusion

Esterification of starch with citric acid has been investigated the formation of exchanger cation was verified by IR and ^{1}HNMR analysis. Maize starch base cation exchangers can be effectively used in the removal of some basic dyes.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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