Studii şi Cercetări Ştiinţifice 2017, **18** (1), pp. 097 – 100
Chimie şi Inginerie Chimică, Biotehnologii, Industrie Alimentară

Scientific Study & Research
Chemistry & Chemical Engineering, Biotechnology, Food Industry *ISSN 1582-540X*

SHORT COMMUNICATION

A GREEN CHEMICAL APPROACH OF CORN STARCH MODIFICATION FOR INNOVATIVE SOLUTIONS IN ADSORPTION OF POLYCYCLIC AROMATIC HYDROCARBONS

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Received: December, 16, 2016
Accepted: March, 01, 2017

Abstract: The aim of research is to achieve chemical modifications of corn starch. Therefore, the present study focuses on its chemical modifications, in order to increase its aqueous solubility and to ameliorate its adsorption properties for one hydrophobic pollutant, belonging to Polycyclic Aromatic Hydrocarbons (PAHs), benzo[a]pyrene (BaP), as a model. Starch chemical modifications are realized by alkylation reactions using ether (propylene oxide) or ester (succinic anhydride) alkyl agents. Starches obtained are characterized by ^{1}H NMR technique in order to verify the alkylation procedure. Water solubility of the obtained product was determined and its capacity to adsorb the considered model pollutant was studied. According to the registered results, starch modification with succinic anhydride conducts to an aqueous solubility of 34.00 $g \cdot L^{-1}$, significantly increased in comparison with the solubility of native corn starch which is insoluble in water at room temperature. With this modified starch, promising results for BaP aqueous solubilisation were obtained.

Keywords: *benzo[a]pyrene, starch, synthesis, succinic anhydride, adsorption properties*

INTRODUCTION

Starch is one of the most known polymer naturaly manufactured by plants. It is widely employed in food industry, but a growing interest is paid for its use as a renewable raw material for different other applications [1 – 3] one of them being the persistent organic pollutants removal [4 – 8]. One promising way is represented by their adsorption on different materials. For non-food uses, starch is modified in order to obtain products with several improved properties [9, 10]. The modification of starch can be realized by physical, thermic and chemical reactions allowing the increase of its hydrophobicity and thermoplasticity. Hydrophobic acetylated and etherified starches derivatives have more applications than hydrophilic ones [11]. In particular, starch modifications with ether agents result in products with amphiphilic side chains. The length of alkenyl group determines the hydrophobic character of the modified starch.
The aims of the present work were to synthesize corn starch derivatives either by esterification with propylene oxide or by etherification with succinic anhydride in order to achieve two different purposes: increasing its water solubility and permitting the solubilisation of benzo[a]pyrene (BaP), a pollutant usually existing in contaminated soil and described as being almost insoluble in water (3 $\mu g \cdot L^{-1}$), allowing its retention in polysaccharide-based materials.

MATERIAL AND METHODS

Chemical modification of corn starch

Corn starch (10 g dry weight) was suspended in a solvent mixture of water : dimetylsulfoxid - DMSO (Panreac Quimica SA, Spain) (1 : 4) under stirring at 95 °C for 24 h. Milled sodium hydroxide (Acros Organics, Noisy-Le-Grand, France) was then added and the solution was mixed at ambiental temperature for 14 h. The reaction pH was 9 until the alkylation agent was added (mol agent alkylation : mol glucose 1:1). The agents used for alkylation were propylene oxide (99 % purity, Acros Organics, Noisy-Le-Grand, France) and succinic anhydride (99 % purity, Acros Organics, Noisy-Le-Grand, France). The addition of the alkylation agents led to pH decreasing until 6. After 48 h of chemical reaction, the resulted product was passed through a 12 - 14000 Da cellulose membrane (Medicell International) and lyophilized. Two reaction products were obtained: hydroxylpropylate corn starch (CO) and succinic anhydride corn starch (CA).

Chemical characterisation of the modified corn starch

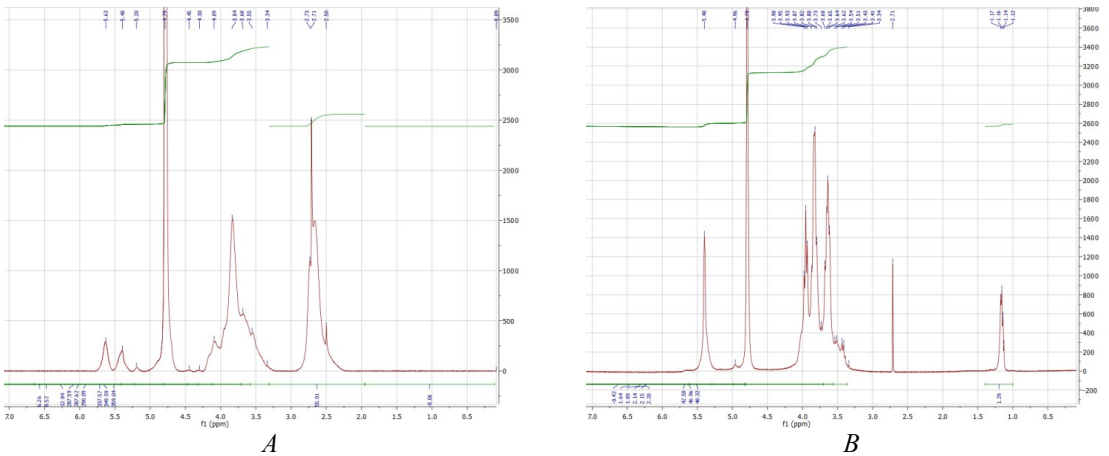
Sufficient amounts of modified starch samples were introduced in deionized water at ambiental temperature and at pH 6 in order to obtain saturated solutions. After 24 h, volumes of 10 mL of the liquid part were submitted to lyophilization. All the experiments were carried out in triplicate and their recorded solubilities were compared to that of the native corn starch (insoluble in water). ^{1}H NMR spectra were realized for each obtained starch with a spectrometer with 250 MHz Spectrospin NMR (Bruker, France) using deuterated DMSO (DMSO-d6).

Determination of BaP water solubility

Samples of 375 µL BaP were solubilised in dichloromethane (DCM) (0.26 mg·L^{-1}) and submitted to complete evaporation at 60 °C. After adding 3 mL of modified starch solution (5 mM), the mixture was protected from light for 4 days. BaP molecular fluorescence in polymer solutions was analyzed into a quartz cell on a Perkin Elmer LS50B spectrometer (excitation 295 nm, emission 406 nm, time integration 10 s) [12]. The experiment was conducted in triplicate.

RESULTS AND DISCUSSION

This paper was aimed to establish an appropriate way of modifying native corn starch so as to increase its water solubility. For this reason, several chemical reaction conditions were tested. Preliminary assays on the influence of temperature variation of corn starch solubilisation revealed that corn starch is solubilised at 95 °C. Chemical introduction of ester or ether groups into hydrophilic starch molecules causes large changes of its chemical and physical properties. The chemical reaction with succinic anhydride led to a CA product which presented a higher aqueous solubility (34.00 g·L^{-1}) in comparison with the hydroxylpropylate corn starch CO (19.16 g·L^{-1}) and the native one (0.3 g·L^{-1}). The chemical modifications of corn starch by ester or ether groups were studied by ^{1}H NMR technique (Figure 1).



A *B*

Figure 1. *^{1}H NMR spectra for succinic anhydride (A) and hydroxylpropylate (B) corn starch*

The signals from 1.15 - 2.55 ppm intervals are attributed to ester and ether groups, which confirmed the success of the alkyl substituents graftings. The proton signals from 3.00 - 4.00 ppm were attributed to the protons of anhydroglucose unit. The etherification and esterification rate may depend on the hydrophobicity of the modified starch.

An experimental value of 4.35 µg·L^{-1} was acquired for benzo[a]pyrene solubility in presence of the obtained modified starch product. Considering that the modified starch solubility in water was calculated as being of 34.00 g·L^{-1} [13], one can conclude that

this product is able to desorb of 164.37 $\mu g \cdot L^{-1}$ BaP (an amount 55 times more important that BaP aqueous solubility which reaches a value of only 3.00 $\mu g \cdot L^{-1}$).
This desorption of BaP could be linked to the introduction of an alkyl chain to the native corn starch. The new modified molecule has an enhanced hydrophobic character, permitting consequently efficiency to desorb and solubilize hydrophobic molecules like BaP.

CONCLUSIONS

A chemical approach of corn starch modification was developed with DMSO as solvent. In the studied experimental conditions (95 °C, 72 h), starch esterification by succinic anhydride was performant. This type of starch modification enhanced the apparent starch aqueous solubility. The results revealed theat the product can be successfully employed to develop environmental friendly methods for PAHs removal.

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