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Production of uronic acids by hydrothermolysis of pectin as a model substance for plant biomass waste

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Abstract: The hydrolysis of high methyl ester citrus-apple pectin as a model substance for plant biomass waste rich in pectin fraction resulting in an uronic acids was performed in a batch reactor using subcritical water. The effects of the reaction temperature and time on the composition of the products contained in the separated liquid fractions were studied. The optimal experimental design methodology was used for modelling and optimizing the yield of uronic acids. In good agreement with experimental results (R2 = 0.986), the model predicts an optimal yield of uronic acids (approx. 77.3 g kg^{-1} ± 0.7 g kg^{-1}) at a temperature and a time of about 155°C and 36 min. Uronic acids were isolated from reaction mixture using the ion exchange method. Higher temperature and longer holding time resulted in a greater degree of thermal degradation of uronic acids and simultaneously higher yield of losses and gas fractions.

Keywords: hydrothermolysis; pectin; uronic acids; experimental design methodology; ion exchange technique

1 Introduction

Uronic acids (L-arabinuronic acid (a), D-xyluronic acid (b), D-galacturonic acid (c), D-glucuronic acid (d), D-mannuronic acid (e)) (Figure 1) are a group of monosaccharides, defined as aldohexoses, in which terminal hydroxyl groups have been oxidized to carboxylic acids [1].

Uronic acids exist in varying proportions and amounts in different types of plant biomass, mainly as constituents of polysaccharides, such as pectin. Uronic acids, particularly D-galacturonic and D-glucuronic acid, are highly valuable chemicals used in the pharmaceutical, cosmetic and food industries as, among other applications, antioxidants, detoxifying and inactivating agents of various substances in the human body [2], precursors of ascorbic acid [3], and chelating reagents with anti-cancer properties [4]. D-glucuronic acid is also used as a building block of hyaluronic acid [5] and a cosmetic ingredient in moisturizing and protective skin treatment cosmetic creams [2,5].

Uronic acids are considered to have enormous potential as platform chemicals that enable their future use in medicine and pharmacy as well as in polymeric materials technology [6].

Despite comprehensive investigations [7,8], there is no commercial-scale chemical production of uronic acids [1], while existing biochemical methods are multi-step processes with separation and purification issues known to be costly and time-consuming [1,5].

In recent years, there have been substantial efforts focused on the development of hydrothermal processes, a thermochemical approach involving hydrolysis under subcritical conditions of components contained in waste biomass into useful products [9-11].

Subcritical water is an environmentally harmless reaction medium (a reactant, a catalyst, and a solvent) whose properties are significantly different from those of water in normal conditions [12,13]. In water at high temperatures (150-230°C), the H-bonding starts weakening, allowing autoionization of water into acidic hydronium ions and basic hydroxide ions [14,15]. In the subcritical region (100-374°C) the ionization constant of water increases with temperature [14,16,17]. Therefore water in a subcritical state exhibits acid/base catalyst properties and its use in the processing of biomass can reduce or even eliminate the need for cumbersome conventional catalysts - mineral acids and alkalis.

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Another property of water, which changes with temperature and pressure, it is dielectric constant, which decreases as the temperature of water rises [17]. In the application of hydrothermal conditions for the processing of waste biomass, decreasing polarity of water dissolves ingredients contained in the biomass more easily and quickly as well as increasing the conversion reaction rate and obtained efficiency. Also, the low density, viscosity and surface tension of water and the advantageous solute diffusion coefficients and self-diffusion coefficients contribute to the solubilization of the raw material and to the fact that the transport processes proceed without significant constraints [11,12,17].

The effectiveness of the processes in subcritical water is ensured without the use of any additional substances and the preliminary, often energy-intensive, preparation (e.g., drying, grinding, briquetting) of the raw material for conversion. Owing to the catalytic properties of subcritical water the reactions taking place in its presence proceed faster and are easier to control by adjusting the reaction system temperature and pressure. Other benefits stemming from the use of processes running in hydrothermal conditions are the absence of equipment corrosion problems and the simplified operating procedure [14]. Hydrothermal processes possess the advantages embodied in green chemistry and green chemical engineering concepts. They are energy-effective and environmentally friendly with high potential for practical applications [9-11].

A recent proposition for the production of uronic acids is hydrothermolysis of waste plant biomass rich in pectin constituents - a polysaccharide of D-galacturonic acid as well as other minor monosaccharides (rhamnose, arabinose, galactose) [18] and D-glucuronic acid [19-21], such as sugar beet pulp, sunflower heads, apple pomace and citrus peel. This article focuses on the effects of the most relevant criteria of the process (reaction temperature and holding time), as the first step toward a mechanistic interpretation and an assessment of the feasibility of its technical development. The purpose of this study was to determine the optimal experimental conditions for the production of uronic acids from citrus-apple pectin by subcritical water hydrolysis. The optimal experimental design (OED) methodology was used to determine a statistically significant reaction model as well as to optimize the conditions for the production of uronic acids from renewable, agricultural resources.

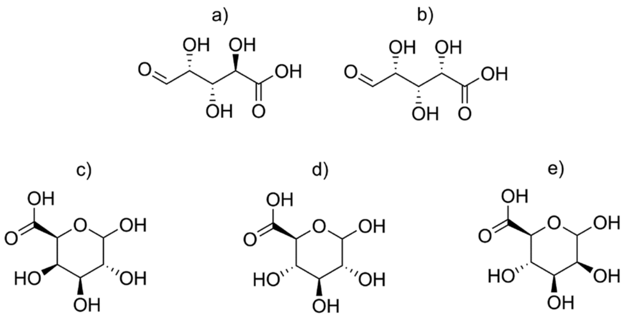

Figure 1: Structure of uronic acids.

2 Experimental

2.1 Materials and reagents

High methyl ester citrus-apple pectin (HMP) with the degree of esterification more than 50% (Naturex-Pektowin S.A. Company, Jasło, Poland) was used for the tests. Uronic acids (galacturonic acid monohydrate and glucuronic acid), furfurals (2-furfural (2-FA) and 5-hydroxymethylfurfural (5-HMF)) and water were provided by Aldrich. Acetic acid and monosaccharides (arabinose, galactose, glucose, mannose, rhamnose, and xylose) were purchased from Fluka. Formic acid, the compounds required for the preparation of Luff-Schoorl reagent (sodium carbonate, citric acid, copper sulfate) and used in chromatographic determination were supplied by POCh (Poland). In this study, the reagents used were analytically pure or HPLC pure, depending on the requirements of the applied analytical method.

2.2 The reactor and the course of hydrothermolysis of high methyl ester citrus-apple pectin

The hydrothermolysis of HMP oven-dried to constant mass at a temperature of 45°C was performed in a high-temperature and high-pressure 4576A-type batch reactor (Parr Instrument Company, USA). A schematic diagram of the experimental set-up, as well as a detailed description of the reactor equipment, is published elsewhere [22].

The investigation of hydrothermolysis of 5 g of HMP in 195 g of water was carried out in 2 experimental series. A description of the experimental conditions is given in Table 1. The preliminary stage (experimental series 1) involved the examination of the effect of the studied reaction parameters: reaction temperature and holding time on the hydrothermolysis of HMP. The parameters established in first step reaction, in which uronic acids were obtained with the highest yield, were applied in experimental series 2. There the optimal experimental design (OED) methodology (Doehlert array) was adopted [22] to determine studied process parameters for uronic acids optimal yield. The precise description of this experimental procedure was published elsewhere [22].

2.3 Separation of high methyl ester citrus-apple pectin hydrothermolysis products

A suspension containing water-soluble products (WS) and a water-insoluble solid post-reaction residue (WI) was obtained as a result of the hydrothermolysis of HMP. A detailed description of the separation of HMP hydrothermolysis products is published elsewhere [23-25].

The yields (Y_i) of all studied treatment products - the WS and WI fractions, and individual substances contained in both the WS fractions and WI fractions - were calculated using the following equation (Eq. 1):

$$Y_i\,(\mathrm{g\,kg^{-1}}) = m_i/m_{HMP} \quad (1)$$

where m_i is the mass (g) of reaction product i, and m_{MP} is the mass (kg) of HMP subjected to hydrothermolysis.

The gaseous products generated during HMP hydrothermal treatment were not collected, but the gas fractions (Y_g) yield was calculated using the following equation (Eq. 2):

$$Y_g\,(\%) = 100 - Y_{DM} - Y_{WI} \quad (2)$$

where Y_{DM} is the yield of dry matter contained in the WS fractions and Y_{WI} is the yield of solid post-reaction residue.

Table 1: Experimental conditions of high methyl ester citrus-apple pectin hydrothermolysis.

Experimental series 1		Experimental series 2	
T (°C)	*t* (min)	*T* (°C)	*t* (min)
120	0; 10; 20; 30; 40; 60	140	40
130	0; 10; 20; 30; 40; 60	145	20; 60
140	0; 10; 20; 30; 40; 60	150[a]	40[a]
150	0; 10; 20; 30; 40; 60	155	20; 60
160	0; 10; 20; 30; 40; 60	160	40
170	0; 10; 20; 30; 40; 60		
180	0; 10		
200	0; 10		
40 runs		9 runs	

[a] Experiments repeated 3 times.

2.4 Isolation of uronic acids

Uronic acids were isolated from the WS fractions using the ion exchange method. The isolation of uronic acids was carried out using a stationary method, and strongly basic, anion exchange resin Amberlite®IRA402 (OH^- form, total exchange capacity 0.95 meq mL^{-1}) with polystyrene divinylbenzene copolymer matrix and quaternary ammonium functional groups. To the anion exchange procedure, there was used 20 mL of the anion exchange resin with moisture content in the range of 49-60% by weight and 150 mL of the WS fraction. After 48 h the resin was separated from the WS fraction by filtration and washed with water. The resulting eluate was diluted with water to a volume of 250 mL and subjected to determination for the content of uronic acids. The regeneration procedure of the anion exchanger was carried out also by batch method, using 100 mL of 2 M HCl. After 48 h the resin was separated from the excess of HCl by filtration and washed with water until the pH of the post-regeneration solution was neutral. The regenerant solution and post-regeneration solution consisted final solution containing isolated uronic acids. This final solution was diluted to a volume of 250 mL and subjected to determination of uronic acids. The isolation experiment was repeated twice.

2.5 Analytical techniques and measurement methodology

HMP dried to constant mass was investigated except for moisture content determinations. All the analytical determinations were performed in triplicate, and the mean values were calculated.

The content of dry matter in HMP was determined using NFTA procedures [26], while the content of ash was determined using NREL-LAB protocols [27]. Lignocellulosic content in HMP was assayed using the detergent method [26,28,29].

The chemical composition of HMP and the WS fractions were determined by high-pressure liquid chromatography (HPLC). A detailed description of the analyses and analytical methods is published elsewhere [25,30].

All analytical chromatographic determinations were performed in duplicate, and their mean values are presented.

The reducing sugars content in the WS fractions was determined by the Luff-Schoorl's method [31].

2.6 Modeling and optimization method

The OED methodology was employed to determine process parameters ensuring the optimal yield of uronic acids. A thorough description of this methodology is published elsewhere [32,33]. We selected the Doehlert array from among the possible experimental matrices based on a quadratic model [33,34]. We used The NEMROD software for calculation (by the least-square regression method) the coefficients of the model, evaluating the significance of the regression, and for validity tests.

3 Results and discussion

3.1 Composition of pectin

The HMP dry matter content amounted to (mean values and standard deviations, respectively) 959.1 g kg^{-1} ± 1.1 g kg^{-1}, ash to 8.7 g kg^{-1} ± 1.5 g kg^{-1}, hemicellulose represented 5.6 g kg^{-1} ± 2.1 g kg^{-1}, sulphuric acid insoluble lignin 13.6 g kg^{-1} ± 1.6 g kg^{-1}, the sum of neutral monosaccharides 97.6 g kg^{-1} ± 2.4 g kg^{-1} (including arabinose 21.7 g kg^{-1}, xylose 20.8 g kg^{-1}, glucose 25.1 g kg^{-1}, rhamnose+galactose+mannose 30.0 g kg^{-1}) and uronic acids 827.6 g kg^{-1} ± 1.9 g kg^{-1}. The degree of methoxylation in HMP amounted to 74.0% mol. (111.3 g kg^{-1} ± 2.1 g kg^{-1}) and the degree of acetylation to 2.5% mol. (6.9 g kg^{-1} ± 2.0 g kg^{-1}).

The initial pH value of a 2.5% (w/w) HMP water suspension was pH = 6.32.

3.2 Effect of reaction temperature and holding time on the yield of uronic acids

Figure 2 shows the effect of reaction temperature and holding time on the yield of uronic acids contained in the WS fractions. Under hydrothermal conditions, the water dissociates and results in a higher concentration of hydronium ion [35], which promotes hydrolysis of pectin to uronic acids. Initially, both temperature increase and holding time extension favored hydrolytic depolymerization of HMP. The highest yield of uronic acids of 79.7 g kg^{-1} was obtained in temperature of 150°C and time of 40 min. In addition, the WS fraction contained 35.8 g kg^{-1} of nonsolubilized and unreacted HMP, 5.7 g kg^{-1} of acetic acid, 296.5 g kg^{-1} of monosaccharides, 9.6 g kg^{-1} of lactic acid and 63.7 g kg^{-1} of formic acid, 18.6 g kg^{-1} of furfurals and 400.6 g kg^{-1} of unidentifed products not subject to any indication for the content of reducing sugars, nor for the content of nonreducing sugars (estimated as reducing sugars after their inversion) – probably oligosaccharides [35]. The presence of lactic acid, formic acid, and furfurals in the WS fraction indicates the co-occurrence of unwanted side reactions along with the depolymerization of HMP - chain fragmentation and degradation of low molecular weight primary reaction products [36].

Further increase in HMP hydrothermolysis temperature, especially above 160°C resulted in a decrease in the yield of uronic acids, which were readily decomposed under hydrothermal conditions [37-42]. The degradation of uronic acids was accompanied by secondary transformations of components present in the reaction mixture, leading, among others, to the progressive increase of furfurals content (Figure 3).

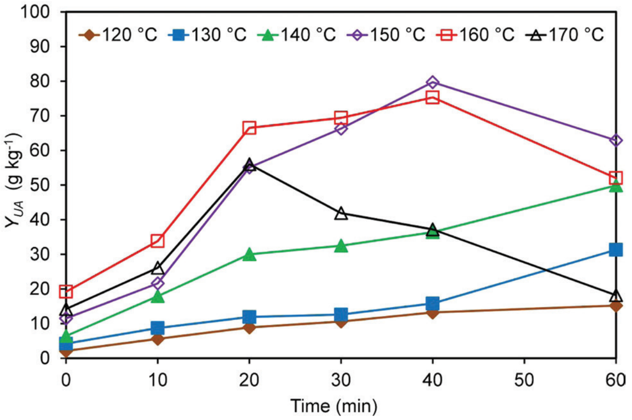

Figure 2: Effect of reaction temperature and holding time on the yield of uronic acids.

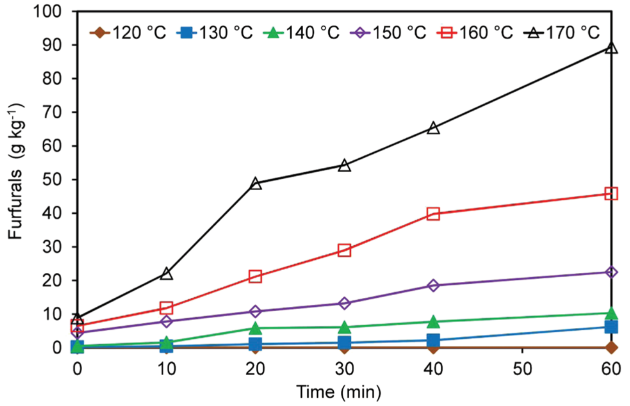

Figure 3: Effect of reaction temperature and holding time on the yield of furfurals.

On the other hand, both in the temperature of 180°C, as well as 200°C, the dominating transformation of the components of the reaction mixture, became their progressive gasification - the yield of gaseous product fractions rose with the increase in temperature and longer holding time, reaching 47.4% at 200°C and a holding time of 10 min (Table 2).

3.3 Modeling of the hydrothermolysis of high methyl ester citrus-apple pectin

Hydrothermal treatment temperature and holding time were the parameters affecting the rate of hydrolysis of HMP and the production of uronic acids. In the second stage of this work, based on the results obtained in experimental series 1, the experimental region was explored using Doehlert matrices with hydrothermolysis temperature and holding time as significant variables. The conditions of the experiments carried out in series 2 and the obtained yields of uronic acids are listed in Table 3.

Table 2: Effect of reaction temperature and holding time on the yield of uronic acids and furfurals and gaseous product fractions obtained at 180°C and 200°C.

Temperature/ holding time (°C/min)	Uronic acids (g kg^{-1})	Furfurals (g kg^{-1})	Gaseous product fraction (%)
180/0	8.2	3.8	9.8
180/10	7.3	12.8	33.2
200/0	6.4	7.7	22.4
200/10	3.6	18.2	47.4

Table 3: Doehlert experimental design with significant (u_i) variables and values of corresponding experimental and calculated responses (Y_{UA} in WS fractions) for hydrothermolysis of high methyl ester citrus-apple pectin.

Experimental series 2				
Experiment	u_1 T (°C)	u_2 t (min)	Y_{UA}-exp.[a] (g kg^{-1})	Y_{UA}-cal.[b] (g kg^{-1})
1	170.0	40	37.2	34.8
2	140.0	40	29.4	31.8
3	162.5	60	43.8	46.2
4	147.5	20	53.5	51.1
5	162.5	20	64.8	67.2
6	147.5	60	61.6	59.2
7	155.0	40	78.3	77.0
7'[a]	155.0	40	75.8	77.0
7''[a]	155.0	40	76.9	77.0

[a] Experiments repeated at the centre of the experimental region to calculate the standard deviation on the response: 1.25.

[b] Experimental values.

[c] Calculated values.

Initially, both the increase of temperature (Exps. 4 and 5, Exps. 2 and 7-7") and holding time (Exps. 4 and 6), as well as the simultaneous increase of these variables favored hydrolytic depolymerization of HMP (Exps. 2 and 6, Exps. 4 and 7-7"). However, the increase in hydrothermolysis temperature above 155°C or the extension in holding time to 60 min (Exps. 3 and 5) did not favor the increase in the yield of uronic acids (Exps. 1, 3 and 5).

Attempts to fit the experimentally determined uronic acids yield to a quadratic model led to satisfactory results. Predicted values are consistent with experimental ones, within experimental errors. The following quadratic model was calculated by multi-linear least square regression from the results obtained from experimental series 2 (Eq. 3):

$$Y_{UA} = 77 + 1.52x_1 - 3.72x_2 - 43.7x_1^2 - 13.53x_2^2 - 16.8x_1x_2 \qquad (3)$$

The standard error for coefficients b_0, b_1, b_2 was 0.72, for b_{11}, b_{22} *1.14*, and b_{12} 1.15.

Two- and three-dimensional representations of Y_{UA} in the WS fractions as a function of hydrothermolysis temperature and holding time, calculated using the above models are shown in Figure 4. The contour plots in Figure 3a represent the curves of constant value of the estimated responses Y_{UA} using the quadratic models.

In the investigated experimental region, the optimal range of HMP hydrothermolysis leading to uronic acids was predicted at a reaction temperature of 151 to 160°C and holding time from 49 to 24 min, respectively. The maximum value of uronic acids was 77.3 g kg^{-1} (±0.7) predicted at 155°C and 36 min.

The pH of WS fraction obtained in optimal conditions was 2.76, and content of dry mass was 822.1 g kg^{-1}, including reducing sugars of 459.8 g kg^{-1}. Among the identified low molecular weight reaction products in the WS fraction, the uronic acids content was 77.5 g kg^{-1} (±0.26) (including galacturonic acid 45.9 g kg^{-1}, glucuronic acid 31.6 g kg^{-1}), glucose 135.8 g kg^{-1}, xylose 91.7 g kg^{-1}, rhamnose 47.7 g kg^{-1}, acetic acid 5.7 g kg^{-1}, lactic acid 10.7 g kg^{-1}, formic acid 65.7 g kg^{-1}, 2-FA 7.8 g kg^{-1} and 5-HMF 13.2 g kg^{-1}.

As shown, the hydrothermal treatment of HMP in the optimal region proceeded with a low yield of uronic acids in comparison with literature data [7,43], obtained as a result of applying traditional - chemical and enzymatic hydrolysis methods. For instance, Wikiera et al. [8] performed both acidic and combined acidic/enzymatic hydrolysis of pectin isolated from apple pomace using trifluoroacetic acid (TFA) and commercial multicatalytic preparation Energex and Viscozyme derived from

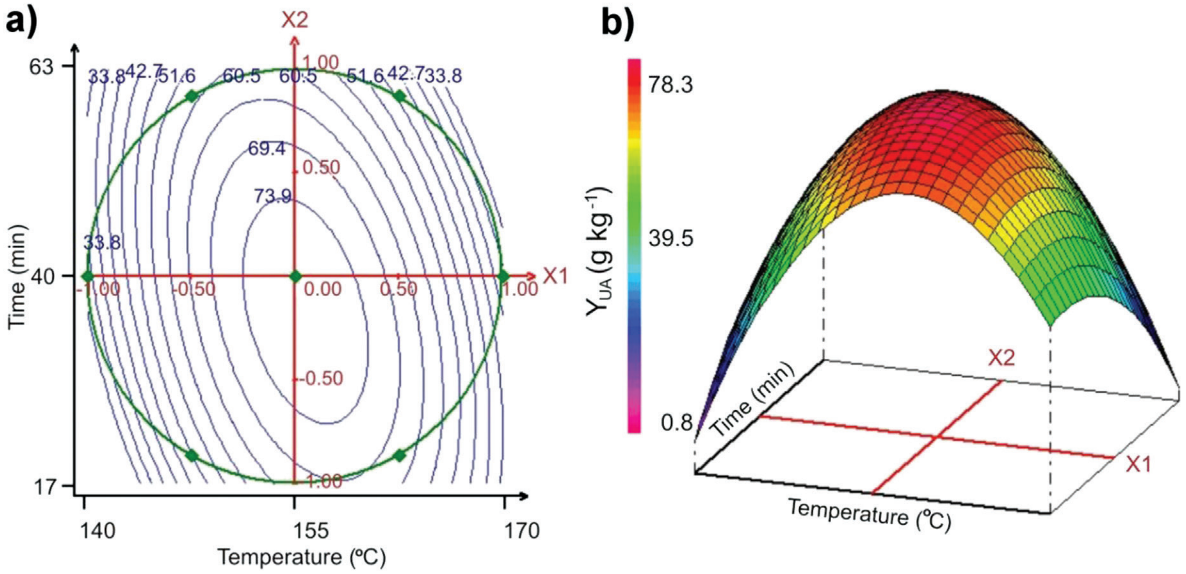

Figure 4: Two- (a) and three-dimensional (b) representations of the yield of uronic acids Y_{UA}, as a function of reaction temperature and holding time during the hydrothermolysis of high methyl ester citrus-apple pectin.

Aspergillus aculeatus. The highest yield of galacturonic acid - 613 g kg^{1} was obtained after 2.5 h of hydrolysis with 2 M TFA at 120°C. In turn Leh et al. [43] hydrolysed citrus pulp rich in pectin by direct addition of “pectinolytic fermented solids”, produced by solid-state fermentation of mixture of ground sugarcane bagasse and orange peels, using a strain of *Aspergillus aryzae* isolated from rotting passion fruit peels and obtained 247 mmol L^{-1} of D-galacturonic acid in the hydrolysate.

The unsatisfactory yield of uronic acids obtained in hydrothermal conditions is caused by high susceptibility of acids to degradation. The specific mechanism of hydrothermal decomposition of uronic acids is challenging to study. Depending on the used reaction conditions, they can be degraded into a massive number of compounds, which may be obtained via different reaction pathways [37-42].

In the literature [38,41,42] there was described mechanism of galacturonic acid degradation under hydrothermal conditions which are probably based on its decarboxylation. Bornik and Kroh [41] and Wegener et al. [42] under slightly acidic to alkaline conditions, identified two processes leading to two detected intermediate products: decarboxylation to L-arabinose and eliminative decarboxylation to unsaturated 4-deoxy-L-arabinose. These compounds were further converted to carbocyclic products such as reductic acid by ring opening followed by dehydration and cyclization. Wang et al. [38] proposed also the formation of ketone as one of the reactions (ketonic decarboxylation [44] leading to galacturonic acid degradation.

In turn, based on the results obtained by Wang et al. [40], the degradation of glucuronic acid in subcritical water led to the formation of the primary stable product - glucuronolactone. The proposed mechanism of glucuronic acid conversion involved intramolecular hemiacetalization and intramolecular esterification. The resulting lactone was further decomposed to other degradation products.

3.4 Isolation of uronic acids

Uronic acids were isolated using the ion exchange method from the WS fractions obtained under optimal conditions of the 2 series of experiments. After ion exchange, the content of uronic acids in the WS fraction was trace and amounted to 2.6 g kg^{1} (3.3% of the initial value). After regeneration of the anionite with 2 M HCl, the content of uronic acids in the eluate was 52.4 g kg^{1} (70.2% concerning the amount deposited in the bed).

4 Conclusions

This article evaluated waste plant biomass rich in pectin fraction, as a potential source for the production of uronic acids. Hydrolysis of high methyl ester citrus-apple pectin as a model substance was performed using subcritical water technology. The yield of uronic acids significantly affected by applied temperature and holding time.

It can be concluded that the application of subcritical water treatment might valorize plant waste biomass rich in pectin fraction, leading to obtaining uronic acids with relatively low yield. Uronic acids, after isolation, e.g. through an ion exchange process, may be used for various industrial purposes.

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