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Optimization of isolation of cellulose from orange peel using sodium hydroxide and chelating agents

Ioan Bicu*, Fanica Mustata

Petru Poni Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda, Nr 41A, Iasi 700487, Romania

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ABSTRACT

Response surface methodology was used to optimize cellulose recovery from orange peel using sodium hydroxide (NaOH) as isolation reagent, and to minimize its ash content using ethylenediaminetetraacetic acid (EDTA) as chelating agent. The independent variables were NaOH charge, EDTA charge and cooking time. Other two constant parameters were cooking temperature (98 °C) and liquid-to-solid ratio (7.5). The dependent variables were cellulose yield and ash content. A second-order polynomial model was used for plotting response surfaces and for determining optimum cooking conditions. The analysis of coefficient values for independent variables in the regression equation showed that NaOH and EDTA charges were major factors influencing the cellulose yield and ash content, respectively. Optimum conditions were defined by: NaOH charge 38.2%, EDTA charge 9.56%, and cooking time 317 min. The predicted cellulose yield was 24.06% and ash content 0.69%. A good agreement between the experimental values and the predicted was observed.

1. Introduction

Although the peel represents on an average a quarter of the orange fruit weight, owing to the significant juice production in the world considerable quantities of orange peels (OP) were generated as a byproduct, or rather as a waste. As a consequence, the necessity for finding some appropriate ways to turn these peels into useful products has appeared, too. Several research studies reported in literature revealed that this byproduct is a valuable raw material for the production of various useful products, such as pectin (Ma, Cervera, & Mejia Sanchez, 1993; Kim, Kim, Lee, Kim, & Kim, 2008), carothenoids and flavonoids (Marin, Soler-Rivas, Benavente-Garcia, Castillo, & Perez-Alvarez, 2007; Wang, Chuang, & Hsu, 2008;), oils and perfumes (Braddock, Temelli, & Cadwallader, 1986), sugars (Grohmann, Cameron, & Buslig,1995), ethanol (Grohmann, Baldwin, & Buslig, 1994; Wilkins, Widmer, & Grohmann, 2007), citric acid (Rivas, Torrado, Torre, Converti, & Domínguez,2008), succinic acid (Li, Siles, & Thompson, 2010), and enzymes (Mamma, Kourtoglou, & Christakopoulos, 2008; Rangarajan, Rajasekharan, Ravichandran, Sriganesh, & Vaitheeswaran, 2010).

OP can also be used as feedstock for cellulose production, but until now too little attention has been paid to this recovery path. The few data available in literature showed that, almost entirely, isolation of cellulose from citrus peels was carried out under alkaline conditions, and that the related researches were only simple attempts to increase the cellulose content of citrus peels by treating them with lime (Braddock & Crandall, 1981; Li et al., 2008) or sodium hydroxide (Ejikeme, 2008; Yasar, Togrul, & Arslan, 2007). Of course, such chemical treatments always ended in cellulose materials with low yields and/or poor properties. In light of these considerations, one can assume that the conditions for alkaline isolation of cellulose from OP are still not fully established. An extra argument in this respect is the fact that the authors have not come across in the literature any report describing how to optimize OP alkaline cooking parameters in order to improve cellulose yield and/or cellulose properties.

With another opportunity the authors have mentioned that cellulose extracted from OP in presence of sulfite reagents was one with a high ash content, mainly calcium carbonate (Bicu & Mustata, 2011), just as high as the ash content of the starting raw material (Arotupin, 2007; Marin, Soler-Rivas, Benavente-Garcia, Castillo, & Perez-Alvarez, 2007; Ververis et al., 2007). Furthermore, some recent preliminary attempts showed that this observation remained valid even when cellulose recovery was performed in presence of alkaline reagents. But always, the high ash content of cellulose materials has proved to be particularly harmful for both chemical and pulp and paper end-use applications (Klemm, Phillip, Heinze, Heinze & Wagenknecht, 1998; Ververis et al., 2007). As such, the present research on the recovery of cellulose under alkaline conditions was extended with a complementary study aiming the decrease of cellulose ash content. For this purpose the chelating agents, e.g. ethylenediaminetetraacetic acid (EDTA), were used.

* Corresponding author. Tel.: +40 232 217454; fax: +40 232 211299.
E-mail address: ibicu@icmpp.ro (I. Bicu).

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Hence, the objectives of the present work are: (a) to determine a proper laboratory method for isolating cellulose from OP by using sodium hydroxide as cooking agent; (b) to find the best cooking parameters in order to optimize cellulose yield and minimize non-cellulose materials content, especially ash content; and (c) to characterize these cellulose materials in order to evaluate the influence of the main factors on cellulose yield and cellulose ash content. It should also be noted here that in order to find the best cooking parameters, the second objective, the response surface methodology (RSM) proved to be the most opportune approach.

In the recent times RSM, as an experimental methodology, has found inter alia numerous applications in the biochemical research. Many works referring to the application of RSM in the biochemical and biotechnological processes have been published in the recent specialty literature. Masmoudy et al. (2008) and Qiu et al. (2010) used RSM to optimize pectin recovery from citrus by-products or banana peels. Other times RSM has been applied in the recovery of glucose, xylose, arabinose and acetic acid from rice straw or reed stems (Rodriguez, Moral, Sanchez, Requejo, & Jimenez, 2009; Shatalov & Pereira, 2012), or of polysaccharides from different parts of plants (Sun, Liu, & Kennedy, 2010), or of cellulose pulp from oil-palm empty fruit bunches (Ferrer, Rosal, Valls, Roncero, & Rodriguez, 2011), perennial plant leaves (Rodriguez, Sanchez, Ferrer, & Requejo, 2011; Rodriguez, Moral, Sanchez, Requejo, & Jimenez, 2009) and reed chips (Shatalov & Pereira, 2013). Optimization of process parameters using RSM in the producing of nanocrystals from microcrystalline cellulose has been reported by Bondeson, Mathew, and Oksman (2006). In the present study RSM has been used for the first time to investigate the effects of the main processing parameters on the alkaline pulping of OP, and on this basis to find the optimum conditions for the recovery of cellulose pulp and diminishing of its ash content.

2. Materials and methods

2.1. Raw material and preparation of samples

Navel oranges (*Citrus sinensis*), purchased from the open market, were peeled (flavedo + albedo). The peels were segmented in the humid state to a particle size of about 2 cm × 2 cm, air-dried to an approximate 10% moisture content, coarsely milled in a laboratory milling machine, and sieved to a size ranging from 1.0 to 3.0 mm.

The chemicals used in the present research were of reagent grade. Sodium hydroxide, ethylenediaminetetraacetic acid, hexane, sodium hypochlorite were bought from Sigma–Aldrich (Steinheim, Germany). Methanol, ethanol, hydrogen peroxide, trichloromethane, and toluene, were purchased from Chemical Company SA (Iasi, Romania).

2.2. Analytical methods

Orange peel was analyzed for holocellulose, cellulose, lignin, ash, liposoluble fraction, alcohol soluble fraction, protein, and cellulose pulp for cellulose, hemicellulose, ash, bulk density, crystallinity, whiteness, intrinsic viscosity, and water retention capability. The analyses were carried out in duplicate and the average was reported. All results were calculated on an oven-dry matter basis.

Protein content was calculated by multiplying the nitrogen content by the factor 6.25 (Rivas et al., 2008). Liposoluble constituent content was determined gravimetrically by extraction with the trichloromethane–hexane azeotrope at 60 °C for 10 h, and was calculated by dividing the weight of dry residue obtained after the recovery of solvent by the weight of OP taken for analysis. Alcohol soluble constituent content was determined gravimetrically by extracting trichloromethane–hexane-extracted OP with the water–ethanol–toluene azeotrope at 65 °C for 32 h, and was expressed as percent of the weight of OP taken for analysis. Some chemical components were determined on the same trichloromethane–hexane-extracted OP by using the standard analytical procedures: ASTM D1102-84 for ash content, ASTM D1106-84 for Klason lignin content, ASTM D1104-56 for holocellulose content, and ASTM D1103-60 for cellulose content. Pulp viscosity was performed according to SCAN-CM 15:88 standard, in cupri-ethylenediamine (CED) solution. Water retention value (WRV) of cellulose was measured by immersing the cellulose material in distilled water (0.5% consistency) at 20 °C for 12 h, filtering at a centrifugal force of 1000 × *g* for 10 min, weighing the obtained wet mass, drying it at 103 °C for 6 h, weighing again, and using Eq. (1):

$$\text{WRV } (\%) = \frac{100\,(W_1 - W_0)}{W_0} \tag{1}$$

where W_0 and W_1 are the weights of dry and wet cellulose, respectively. Loose bulk densities of cellulose powders were determined according to the standard ASTM D7481-09.

The CIE whiteness of the bleached cellulose was estimated using CIE $L^*a^*b^*$ system. Measurements were made using a Pocket Spec Color QA spectrophotometer provided with a CIE D65 illuminant and a 10° standard observer. CIE whiteness was calculated according to Eq. (2) (Ganz & Pauli, 1995).

$$W_{\text{CIE}} = 2.41 \cdot L* - 4.45 \cdot b* [1 - 0.009(L* - 96)] - 141.4 \tag{2}$$

Cellulose crystallinity was studied by means of X-ray diffractometry. Wide angle X-ray diffraction (WAXD) was performed with a Bruker AD8 Advance diffractometer. WAXD patterns were obtained using CuKα radiation (λ = 1.541 Å) and a diffraction angle 2θ ranging from 4° to 40°. The crystallinity index (CrI) was calculated using Eq. (3) (Cao & Tan, 2005).

$$\text{CrI } (\%) = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100 \tag{3}$$

in which I_{002} is the maximum intensity of the crystalline plane (0 0 2) reflection (2θ = 22.5°) and I_{am} the maximum intensity of amorphous phase (2θ = 18°).

2.3. Soda pulping

In this work, an alkaline pulping process was used to separate cellulose in OP from the other constituents, hemicellulose, lignin, insoluble pectins, etc. This was accomplished by dissolving the noncellulosic materials in alkaline cooking liquors based on sodium hydroxide and EDTA. The pulping experiments were carried out in a 0.25 L laboratory rotary glass vessel equipped with an air cooled condenser and a thermometer. The reaction vessel was immersed in a hot oil bath held at 105 °C. All the above pieces and the rotating system were taken out from a laboratory rotary evaporator. The inclination of mechanical device was set at 45 degrees and the rotational speed at 40 rpm. Double extracted OP was charged into the digester together with the cooking liquor including distilled water, sodium hydroxide, and EDTA and was allowed to stand for 30 min to impregnate. Always 20.0 g of oven dry (o.d.) double extracted OP and 150 g of cooking solution (liquid-to-solid ratio 7.5:1) were added. Every time, after charging and impregnation operations were finished, the reactor was heated under agitation for 5 min to reach the setting temperature (98 °C). In order to optimize the cooking conditions, the cooking experiment parameters, namely sodium hydroxide and EDTA charges, and cooking time, were designed as shown in Table 2. After cooking, the fibrous product was separated from residual black liquor by filtration on a fiberglass fabric, disintegrated, and washed repeatedly

(three times) with warm and cold distilled water. The wet pulp was dehydrated to 10–12% consistency and, optionally, bleached.

2.4. Bleaching of pulp

In this study wet pulp was bleached in a three bleaching sequence, as follows: hypochlorite in alkaline medium (H1), hypochlorite in slightly acid medium (pH = 6.5) (H2), and hydrogen peroxide (HP). The addition of chemicals (% on dry weight pulp) was as follows: H1, 2.30 as active chlorine, H2, 1.2 as active chlorine and HP, 0.5 as H_2O_2. It seems that, in the last stage bleaching took place in presence of active oxygen formed from the reaction between hydrogen peroxide and hypochlorite. Bleaching process was conducted at 25 °C and at a pulp consistency of 3.5%. The treatment durations were as follows: 240 min for H1 stage, 120 min for H2 stage and 60 min for HP stage. Before and after each treatment stage, pulps were washed with distilled water until a neutral pH was reached. After bleaching, cellulose was washed three times with ethyl alcohol and dried under ambient conditions.

2.5. Experimental design and optimization

Generally, a cooking process is defined by four main parameters, namely chemical charge, cooking temperature, cooking time, and liquid-to-solid ratio. In this research, some process parameters as cooking temperature and the liquid-to-solid ratio were kept constant (98 °C and 7.5:1, respectively), the first for reasons to work at atmospheric pressure and the second for reasons to work at minimum value able to ensure a good homogenization of the reaction mass. This is why, in this study a central composite rotatable design (CCRD) with three variables at five levels and response surface methodology (RSM) were employed to investigate the influence of the other three parameters (sodium hydroxide charge, EDTA charge, and cooking time) on the isolation of cellulose from OP with alkaline reagents. RSM is the statistical-mathematical method useful for designing experiments, building numerical models, evaluating the effects of variables and searching for the optimum conditions of variables to predict the optimized responses (Montgomery, 1991).

Therefore, sodium hydroxide charge (X_h), EDTA charge (X_e), and cooking time (X_t) were chosen as independent variables. The percent yield of cellulose pulp and its ash content were chosen as dependent variables. Under these conditions a full factorial CCRD for three variables and five levels (−1.682, −1, 0, +1, +1.682), with 20 experimental runs (8 factorial points, 6 star points, and 6 central points), was fitted to perform the second order polynomial model (Cochran & Cox, 1992). The actual levels for each independent variable were selected in accordance with the results of some preliminary experiments.

The preliminary experiments were carried out under relatively extreme conditions of sodium hydroxide charge, ranging from 10 to 40%, of EDTA charge, ranging from 5 to 10%, and of cooking times, varying from 240 to 360 min, and are presented in Table 2. The experiments aimed the achievement of the maximum delignification, depectinization, and demineralization effects with minimum alkali consumptions. That is why in the last column of Table 1 the data on alkali consumptions leading to the performances shown in the previous two columns are included, too.

As can be seen from Table 1, under some pulping conditions as alkali charges of 30–35%, EDTA charges of 8–10%, and cooking times of 300–360 min, the pulp yields are close to cellulose content value of the starting crude OP, 27.62% (Table 3), which this time can be accounted as an optimum (a maximum delignification and depectinization ending in a minimum pulp yield). Under the same pulping conditions ash content values fall in the range 0.8–1.3%. These values can also be accounted as a minimum. As regards the accompanying alkali consumptions, one can observe that these are high enough (72–80%) to ensure on the one hand an judicious use of alkalies, and on the other a slight alkali excess necessary to achieve some reasonable cooking times. The satisfactory values for both cellulose yield and ash content being achieved, the tested ranges of the studied process parameters were latter used in statistical experimental design on OP pulping.

In Table 2 are given the coded and actual levels of the variables used in the design matrix as well as the data regarding the experimental yield of cellulose pulp and its ash content. A second order polynomial equation was employed to model the relationship between the independent variables and the dependent variables (responses). This choice was justified by the fact that this model fits well enough the parabolic response surfaces having a variety of alternative functional forms. Also, in such a model the method of least squares can be applied to evaluate the coefficients associated with the independent variables. Minitab statistical software (Minitab Inc., USA) was used to perform the regression analysis of experimental data and Statistica '99 edition software (StatSoft Inc.) was used to plot response surfaces. Mention must be made that response surfaces for the models in the work were plotted as a function of two variables, the third being kept constant at an advantageous value, usually zero coded level. The quality of the fit of the model was estimated using the coefficients of determination R^2. The optimum values of selected variables were obtained by equating the partial derivatives of dependent variables with respect to independent variables to zero and solving the resulting systems of equations.

3. Results and discussion

3.1. Chemical characterization of crude OP

The main characteristics of crude OP are presented in Table 3. The data included in table show that crude OP contain relatively high amounts of cellulose and hemicellulose, 12.9% and 8.8%, respectively. These values are comparable to those reported for orange byproducts by Ververis et al. (2007), Mamma et al. (2008) and Rivas et al. (2008), namely cellulose contents ranging from 9.2 to 16.2% and hemicellulose contents ranging from 6.1 to 13.8%. In Table 3 one can remark the particularly low content of lignin in OP, of only 1.3%. All these properties make OP a valuable source of cellulose which unfortunately has not yet been fully exploited for the preparation of high purity cellulose products.

Another observation refers to the high ash content (2.9%) of trichloromethane–hexane-extracted OP. The presence of such large amounts of ashes in the cellulose materials has proved to be particularly troublesome for both chemical and pulp and paper end-use applications. To reduce to near zero this undesired ash content, in the present research disincrustation of OP was conducted in presence of chelating agents.

3.2. Cellulose isolation

Now it is evident that OP can be used to produce cellulose. Any method of separation of cellulose from such a raw material involves the treatment of partly depectinated OP with a suitable disincrustation agent. The depectination can be performed by extraction with inferior alcohols (methanol or ethanol), or simply with hot water. But, the depectination is a partial one because by these routes only the soluble fraction of pectin can be removed. The insoluble fraction, composed of protopectin, pectic acid and its calcium and magnesium salts, can be labilized only by means of disincrustation and chelating agents. At the same time, the disincrustation agent also dissolves the lignin and protein fraction in the composition

Table 1
Preliminary experimental data on sodium hydroxide-EDTA pulping of OP.[a]

NaOH[b] (%)	EDTA[c] (%)	Cooking time (min)	Pulping yield (%)	Ash content (%)	Alkali consumption [d] (%)
10	5.0	240	68.6	9.55	Over 100
20	5.0	300	46.8	6.93	97.1
25	7.5	240	27.8	3.26	88.9
25	7.5	360	23.6	2.32	83.3
35	5.0	240	24.2	3.07	73.7
35	10.0	240	24.7	1.32	72.3
40	10.0	300	22.7	0.83	80.8

[a] Cooking temperature – 98 °C; liquid-to-solid ratio – 7.5.
[b] Alkali charge, calculated on oven-dry (od) OP weight
[c] EDTA charge, calculated on od OP weight.
[d] Calculated as the difference between the alkali charge and the residual alkali in the black liquor.

Table 2
Central composite experimental design of alkaline cooking tests and experimental responses.

Run	Coded variables			Uncoded variables			Response	
	X_h	X_e	X_t	NaOH charge (wt.%)	EDTA charge (wt.%)	Cooking time (min)	Cellulose yield (%)	Ash content (%)
1	−1	−1	−1	18.15	5.22	168.5	47.5	7.56
2	1	−1	−1	33.45	5.22	168.5	24.2	3.72
3	−1	1	−1	18.15	8.78	168.5	53.2	6.50
4	1	1	−1	33.45	8.78	168.5	23.9	2.23
5	−1	−1	1	18.15	5.22	311.5	46.4	6.22
6	1	−1	1	33.45	5.22	311.5	22.8	2.68
7	−1	1	1	18.15	8.78	311.5	53.2	5.33
8	1	1	1	33.45	8.78	311.5	24.4	1.04
9	−1.682	0	0	12.90	7.0	240	66.8	8.53
10	1.682	0	0	38.70	7.0	240	24.0	1.84
11	0	−1.682	0	25.80	4.0	240	28.6	5.44
12	0	1.682	0	25.80	10.0	240	33.9	2.92
13	0	0	−1.682	25.80	7.0	120	33.2	5.46
14	0	0	1.682	25.80	7.0	360	23.4	2.83
15	0	0	0	25.80	7.0	240	28.0	3.06
16	0	0	0	25.80	7.0	240	29.2	3.18
17	0	0	0	25.80	7.0	240	29.4	3.24
18	0	0	0	25.80	7.0	240	29.3	3.02
19	0	0	0	25.80	7.0	240	28.2	3.29
20	0	0	0	25.80	7.0	240	29.3	3.22

of double extracted OP. Usually, sodium hydroxide (soda) is that which has gained a larger spreading as cooking chemical for the non-woods, often annual plant. The pulping process in which the digestion of cellulose-containing raw materials occurs in the presence of sodium hydroxide is also recognized as "soda pulping process". The role of sodium hydroxide in such a process is to solubilize lignin by destroying its chemical structure and finally to dissolve it. In the case of OP this role is a minor one, because its low lignin content. But, the major role of sodium hydroxide in the disincrustation of OP is to break the ester linkages formed in the cell-wall between the carboxyl groups belonging to the accompanying substances (predominantly protopectin) and the hydroxyl groups of hemicellulose and cellulose, to allow chelating agent to easily combine with calcium and magnesium ions in pectin structure, and finally to contribute to an easier removal of the newly formed complex structure, become in the meantime water soluble. Indeed, experimentally, it has been found that only the combination sodium hydroxide–EDTA strongly reduced the ash content of cellulose extracted from OP. Neither sodium hydroxide nor EDTA, taken alone, were able to provide such a performance. The chelating action characteristic of EDTA can be estimated by comparing the ash content of the experiments carried out at low and high EDTA addition levels. Indeed, in Table 2, the ash contents corresponding to the high EDTA additions (experiments 3, 4, 7, and 8) are constantly lower than that corresponding to the low EDTA additions (experiments 1, 2, 5, and 6).

As can be observed from the data included in Table 2, the presence of EDTA in the cooking liquors has also contributed to a slight increase in cellulose yield. The increase amounted to about 4% for EDTA additions ranging from 4 to 10% (experiments 11 and 12). In general, the greater the EDTA addition, the higher the increase in

Table 3
Composition of dried orange peel (w/w dry basis).

	Compounds	Value (%)	Method
1	Liposoluble fraction (crude fats, essential oils, resins, coloring matters)	4.22	Hexane–trichloromethane azeotrope
2	Alcohol soluble fraction (sugars, pectin, flavonoids)	49.1	Water-ethyl alcohol-toluene azeotrope
3	Alcohol insoluble fraction (holocellulose, lignin, insoluble pectin, protein, ash)	46.7	By difference
4	Holocellulose	21.7 (46.47)	Sodium chlorite
4	Cellulose[a]	12.9 (27.62)	Kurschner
5	Hemicellulose[a]	8.8 (18.85)	By difference
6	Lignin	1.3	72% sulfuric acid
7	Protein	6.1	From nitrogen content
8	Ash	2.9	ASTM D1102-84
9	Other compounds (insoluble pectin)	14.7	

[a] Hollocellulose, cellulose and hemicellulose content values determined by reference to the weight of double extracted OP are enclosed within parentheses.

cellulose yield. This is probably due to an antioxidant protective action exerted by EDTA (Huvaere et al., 2011) against the degradative action of sodium hydroxide on hemicellulose and cellulose in cellulose fibers.

3.3. Fitting the models

RSM was used to optimize cooking yield and to minimize ash content of cellulose product during the isolation of cellulose pulp from OP using soda–EDTA pulping process. The effect of sodium hydroxide charge (X_h), EDTA charge (X_e), and reaction time (cooking time) (X_t) on cellulose yield (Y_c) and ash content of cellulose product (Y_a) was investigated by using CCRD. Based on this design 20 experiments were carried out according to the conditions indicated in Table 2. Response values as cellulose yields and ash contents are also rendered in the last two columns in Table 2. The second-order polynomial response surface model was fitted to the response variable (Y) in the both cases. The coefficients of the model were evaluated by regression analysis and tested for significance. Estimated regression coefficients of the quadratic polynomial models for response variables as well as the corresponding R^2, adjusted R^2, Student's t values, and p-values are given next to Eqs. (4) and (5). Because the computed values of t did not always exceed the critical value of 2.120 (taken from tables), some terms were considered as insignificant. The final response functions (variables in coded values) to predict cellulose yield and ash content of cellulose product at a confidence level of 95% are as follows:

$$Y_c = 28.87 - 12.58x_h + 1.52x_e - 1.38x_t + 5.50x_h^2 + 1.08x_e^2 + 1.31x_t^2 - 1.44x_h x_e \ (t < 2.120;\ p < 0.05;\ R^2 = 0.987;\ \text{Adj.}R^2 = 0.975;\ \text{Predict.}R^2 = 0.904) \quad (4)$$

$$Y_a = 3.17 - 1.99x_h - 0.68x_e - 0.67x_t + 0.68x_h^2 + 0.32x_e^2 + 0.31x_t^2 - 0.15x_h x_e \ (t < 2.120;\ p < 0.05;\ R^2 = 0.995;\ \text{Adj.}R^2 = 0.992;\ \text{Predict.}R^2 = 0.971) \quad (5)$$

The goodness of fit of models was estimated by means of determination coefficient (R^2). As can be seen the two values for R^2 are quite high. The lowest value of the two (0.987) corresponds to the case of cellulose yield and the highest (0.995) to ash content of cellulose product. Always a higher value for R^2 indicates a better fit of the model to the experimental data. The R^2 values indicate that the fitted models accounted for about 99% of the total variations in the experimental data, which means a high significance. In addition, the values of the adjusted determination coefficients for Y_c and Y_a, of 0.975 and 0.992, respectively, are also high enough to uphold the high significance of the models.

3.4. Optimization of alkaline pulping conditions by RSM

The three-dimensional (3D) response surface plots were drawn to illustrate the effects of the independent variables on the dependent variable. The graphs were built based on the final models by imposing a constant value, usually the central point of the interval taken into consideration, to one independent variable. The effects of sodium hydroxide charge, EDTA charge, and cooking time on cellulose yield and ash content of cellulose product are shown by the coefficients of the polynomial equations Eqs. (4) and (5), respectively.

The response surfaces derived from Eq. (4) are shown in Figs. 1–3 where one variable was kept constant at zero level (coded) and the other two were varied within their experimental range. In general,

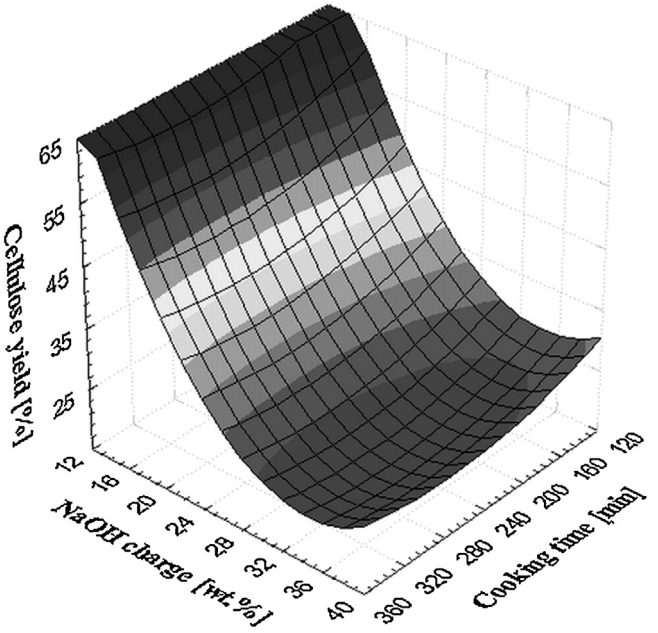

Fig. 1. Three-dimensional response surface plot of cellulose yield as a function of sodium hydroxide charge and cooking time, EDTA charge being kept constant at the coded value of zero (uncoded value – 7.0 wt.%).

exploration of these response surfaces denotes a complex interaction between the variables. Fig. 1 represents the effect of NaOH charge and of cooking time on cellulose yield at a constant EDTA charge level of zero (coded units). A quadratic effect of NaOH charge and a weak quadratic, or rather an almost linear effect of cooking time on cellulose yield can be observed. At low cooking times, e.g. at $x_3 = -1.682$, coded (120 min, uncoded), a strong decrease in cellulose yield, of about 25%, can be observed when NaOH addition increases from −1 to +1, in coded values (from 18 to 33.5% in uncoded values). The effect of EDTA charge and cooking time, at a constant NaOH charge level of zero (coded units), on cellulose yield is shown in Fig. 2. It can be seen that both EDTA addition

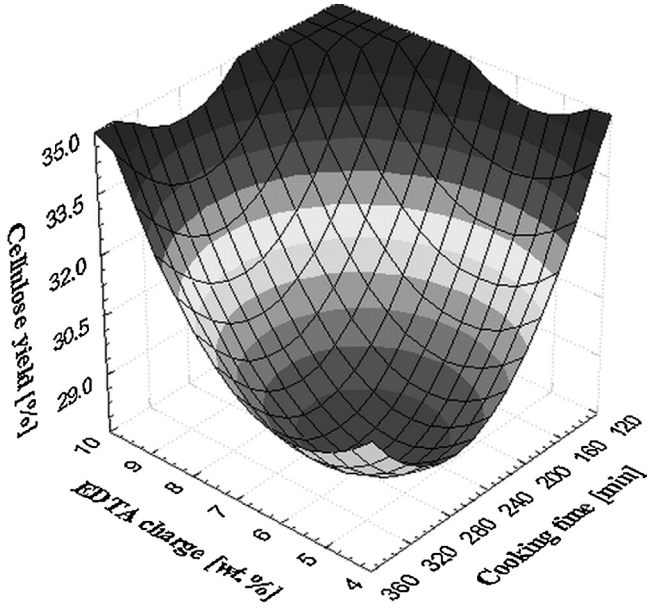

Fig. 2. Three-dimensional response surface plot of cellulose yield as a function of EDTA charge and cooking time, sodium hydroxide charge being kept constant at the coded value of zero (uncoded value – 25.80 wt.%).

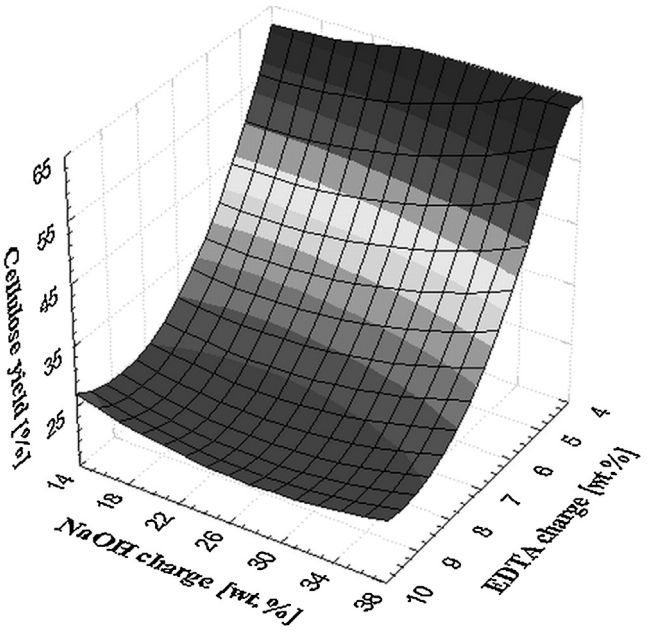

Fig. 3. Three-dimensional response surface plot of cellulose yield as a function of sodium hydroxide charge and EDTA charge, cooking time being kept constant at the coded value of zero (uncoded value – 240 min).

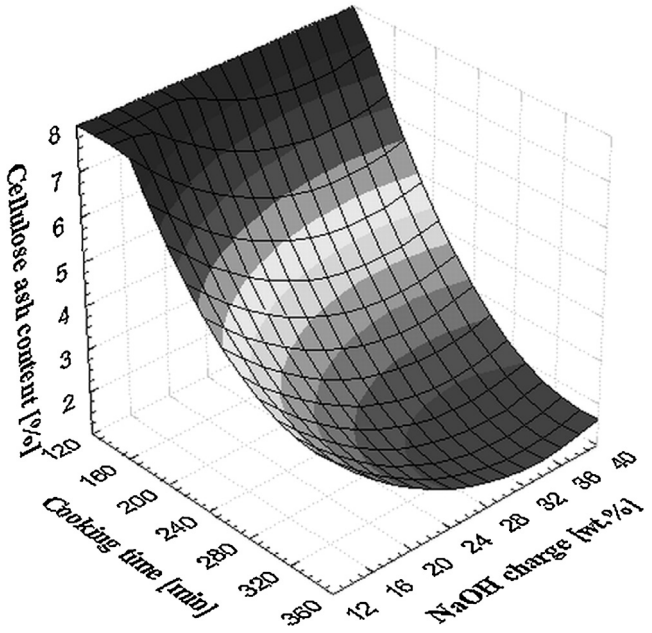

Fig. 4. Three-dimensional response surface plot of cellulose ash content as a function of sodium hydroxide charge and cooking time, EDTA charge being kept constant at the coded value of zero (uncoded value – 7.0 wt.%).

and cooking time exert quadratic effects on cellulose yield. Also, this figure makes once again evident the protective role played by EDTA on hemicellulose in OP pulping process in that cellulose yield increases, not decreases, with the chelating agent addition. The fact that these increases are relatively small but yet significant, of about 4–5%, denotes that the effect is one worthy of being taken into account. In Fig. 3 is shown the effect of NaOH charge and of EDTA charge, at a constant cooking time of zero (coded units), on cellulose yield. This time a quadratic effect of NaOH charge and a nearly linear effect of EDTA charge on response can be observed. On the whole, the increases of both charges and of the cooking time resulted in an expected continuous decrease in cellulose yield.

As regards the optimum conditions, these were calculated by equating the partial derivatives of dependent variable, cellulose yield, with respect to independent variables to zero and solving the resulting system of equations. The linear equation system corresponding to Eq. (4) is as follows:

$$-12.58 + 11.00x_h - 1.44x_e = 0 \quad (6)$$

$$1.52 - 1.44x_h + 2.16x_e = 0 \quad (7)$$

$$-1.38 + 2.62x_t = 0 \quad (8)$$

The optimum values of test variables, in fact the coordinates of the stationary point of response, in coded units, are: $x_h = 1.15$, $x_e = 0.06$, $x_t = 0.53$, or in uncoded units: $X_h = 26.8\%$ Na_2O (34.6% NaOH), $X_e = 7.1\%$ EDTA, $X_t = 278$ min. The corresponding value for the dependent variable (cellulose yield) is $Y_c = 21.31\%$. This time, as expected, the stationary point is a minimum. Taking into account the fact that cellulose content of double extracted OP is 27.62%, Table 3, it can be assumed that by soda–EDTA pulping carried out under optimum conditions all the accompanying substances and yet a small fraction, of about 20%, of cellulose itself were removed.

The response surfaces derived from Eq. (5) are shown in Figs. 4–6. Fig. 4 illustrates the effect of NaOH charge and of cooking time on ash content of cellulose product at a constant EDTA charge level of zero (coded units). A strong quadratic effect of NaOH charge and a mild quadratic effect of cooking time on ash content of cellulose product can be observed. Fig. 5 shows the response surface plot obtained as a function of EDTA charge and cooking time, at a constant NaOH charge level of zero (coded units). The examination of this response surface shows that the ash content of cellulose product strongly decreases with the increase of EDTA addition. This finding emphasizes the role of effective chelating agent exerted by EDTA on the calcium ions in the cooking mass. But, a particular mention must be made here that this action would not have been possible without the forerunner labilizing action exerted by NaOH on the calcium compounds in OP. This interdependence between the actions of the two above mentioned chemicals can be seen in Fig. 6, too. Indeed, Fig. 6 represents the influence of NaOH charge

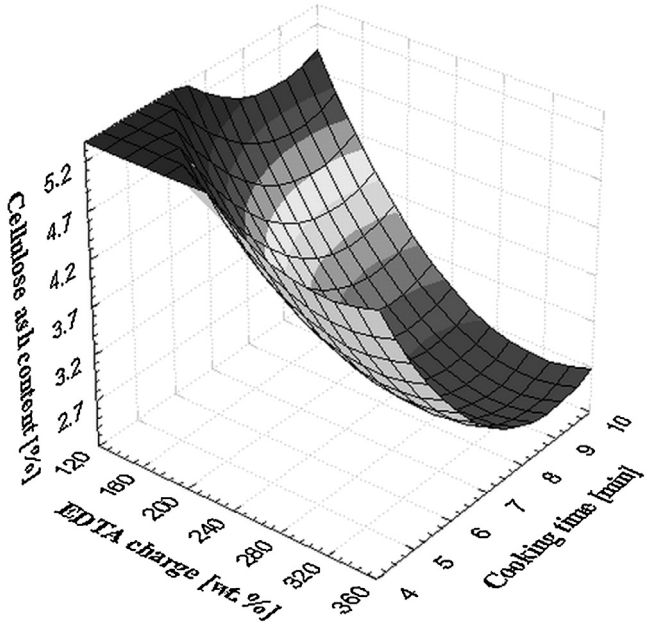

Fig. 5. Three-dimensional response surface plot of cellulose ash content as a function of EDTA charge and cooking time, sodium hydroxide charge being kept constant at the coded value of zero (uncoded value – 25.80 wt.%).

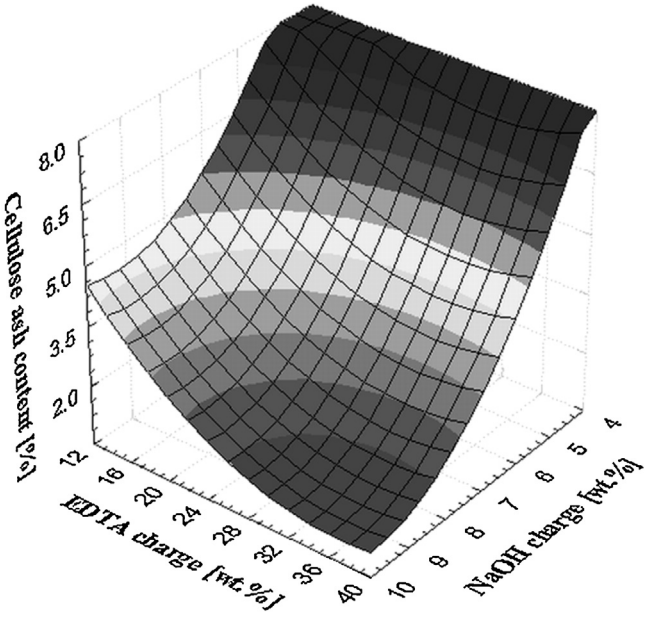

Fig. 6. Three-dimensional response surface plot of cellulose ash content as a function of sodium hydroxide charge and EDTA charge, cooking time being kept constant at the coded value of zero (uncoded value – 240 min).

and EDTA charge on ash content of cellulose product. It can be seen as a strong quadratic effect for both NaOH addition and EDTA charge. And ultimately, these strong quadratic effects may connote a significant interaction between the actions of the two disincrustation parameters.

Acting in a similar way to the case of Eq. (4), the resulting linear equation system corresponding to Eq. (5) is as follows:

$$-1.99 + 1.36x_h - 0.15x_e = 0 \quad (9)$$

$$-0.68 - 0.15x_h + 0.64x_e = 0 \quad (10)$$

$$-0.67 + 0.62x_t = 0 \quad (11)$$

By solving the system composed of Eqs. (9)–(11) the following optimum values for the coordinates of the stationary point of response, in coded units, are obtained: $x_h = 1.62$, $x_e = 1.44$, $x_t = 1.08$, or in uncoded units: $X_h = 29.6\%$ Na_2O (38.2% NaOH), $X_e = 9.56\%$ EDTA, $X_t = 317$ min. The corresponding value for the dependent variable (ash content of cellulose product) is $Y_a = 0.69\%$. As expected, again the stationary point is a minimum. The found value is not a very small one, but is close to that characteristic of the bleached commercial wood pulps, of around 0.5%. By introducing the above optimum conditions predicted for the minimum ash content of cellulose into Eq. (4), cellulose yield (Y_c) gets as high as 24.06%, value that is greater than that found as optimum in accordance with Eq. (4), 21.31%, and slightly smaller than the cellulose content of the starting double extracted OP, 27.62% (Table 3). It should also be noted that this increase in cellulose yield has occurred just when some pulping parameters which may be deemed to be harsher than that found as optimum were used. Of course, this finding could not be explained than by the protective role exerted by EDTA on holocellulose in OP pulping process, especially at high charge levels. That is why in the following only the last group of values of the independent variables will be considered to be the best for the production of cellulose materials with low ash contents, using double extracted OP as raw material.

Table 4
Properties of cellulose material made from OP by cooking with sodium hydroxide and EDTA.

Properties	Value
Cellulose yield[a] (%)	26.20
Cellulose content (%)	85.8
Hemicellulose content (%)	8.6
Ash content (%)	0.62
Bulk density (g/cm^3)	0.305
Intrinsic viscosity (ml g^{-1})	403
CrI (%)	68.7
WRV (%)	303
W_{CIE} (%)	86.5 (48.3)[b]

[a] Determined by relating the weight of crude cellulose to the weight of double extracted OP.
[b] W_{CIE} values of unbleached celluloses are in parentheses.

3.5. Verification of results

Validation of the predicted results was carried out by performing two additional digestion experiments involving the found optimum conditions and double extracted OP. In Table 5, the experimental conditions together with the predicted and the experimental cellulose yields and cellulose ash contents are given. The experiments ended in cellulose yields of 25.72 and 26.70%, and in cellulose ash contents of 0.47 and 0.76%. Because these results are in good agreement with the predicted ones, it may be concluded that the optimum conditions are confirmed experimentally, and that the experiments confirm the effectiveness of the two models, Eqs. (4) and (5). It should also be noted that, taking into account the percentage of alcohol insoluble fraction in crude OP of 46.7% (Table 3), the actual values for the above cellulose yields become 12.02 and 12.47%, respectively. By comparing these values with that for cellulose content of dried crude OP in Table 3, it can be seen that the three are quite close together. Therefore, these results can be a good starting point for discovering more about the use of soda process in the pulping of waste OP. The further work in the area of alkaline processing of OP will focus on the exploration of the possibilities for using closed vessel reactors with the intention to increase cooking temperature and, implicitly, to reduce cooking times and chemical consumptions.

3.6. Analysis of optimized cellulose sample

In order to evaluate the quality properties of cellulose material extracted from double extracted OP, cellulose, hemicellulose, ash content, degree of polymerization, and some interesting physical properties were determined. Table 4 summarizes the characteristics of cellulose produced from double extracted OP under the technological conditions found to be optimum by RSM. As can be seen from the table, this cellulose material shows a high content of alpha cellulose (85.8%), a low content of hemicellulose (8.6%), a very low content of ashes (0.62%), a moderate-to-high crystallinity (a CrI of 68.7), and a satisfactory degree of polymerization (312). It can

Table 5
Model validation.

Parameters and results	Optimum conditions	Optimum results
NaOH charge (wt.%)	38.2	–
EDTA charge (wt.%)	9.56	–
Cooking time (min)	317	–
Cellulose yield (%)		
Predicted	–	24.06
Experimental	–	25.72; 26.70
Cellulose ash content (%)		
Predicted	–	0.69
Experimental	–	0.47; 0.76

observe that these data are close to those reported in the specialty literature (Ejikeme, 2008; Virtanen et al., 2012) for cellulose materials, and even for some microcrystalline cellulose materials derived from orange mesocarp, spruce needles, pine needles, rice husk, or hemp stalks. For these reasons, cellulose material recovered from OP with sodium hydroxide and EDTA could be used, among others, as a starting material for the preparation of microcrystalline cellulose, or as raw material for the preparation of cellulose derivatives. As regards the ash content, in Table 4 is inserted the value of 0.62%. This value is much lower than that found when the same OP was processed by pulping with sulfite reagents, 5.70% (Bicu & Mustata, 2011). This finding again demonstrates the effectiveness of EDTA in decreasing the ash content of cellulose materials derived from OP.

4. Conclusions

An alkaline pulping process in which partly depectined OP was cooked in aqueous liquors containing NaOH and EDTA is provided. RSM proved to be a useful tool for finding optimum conditions for the recovery of cellulose from OP and diminution of its ash content. The physicochemical characterization data of these cellulose materials indicate good levels of purity and crystallinity, and moderate molecular weights, all these suggesting their potential use as precursors for generating microcrystalline cellulose.

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