Advanced oxidation processes in treatment of agricultural biomass residues

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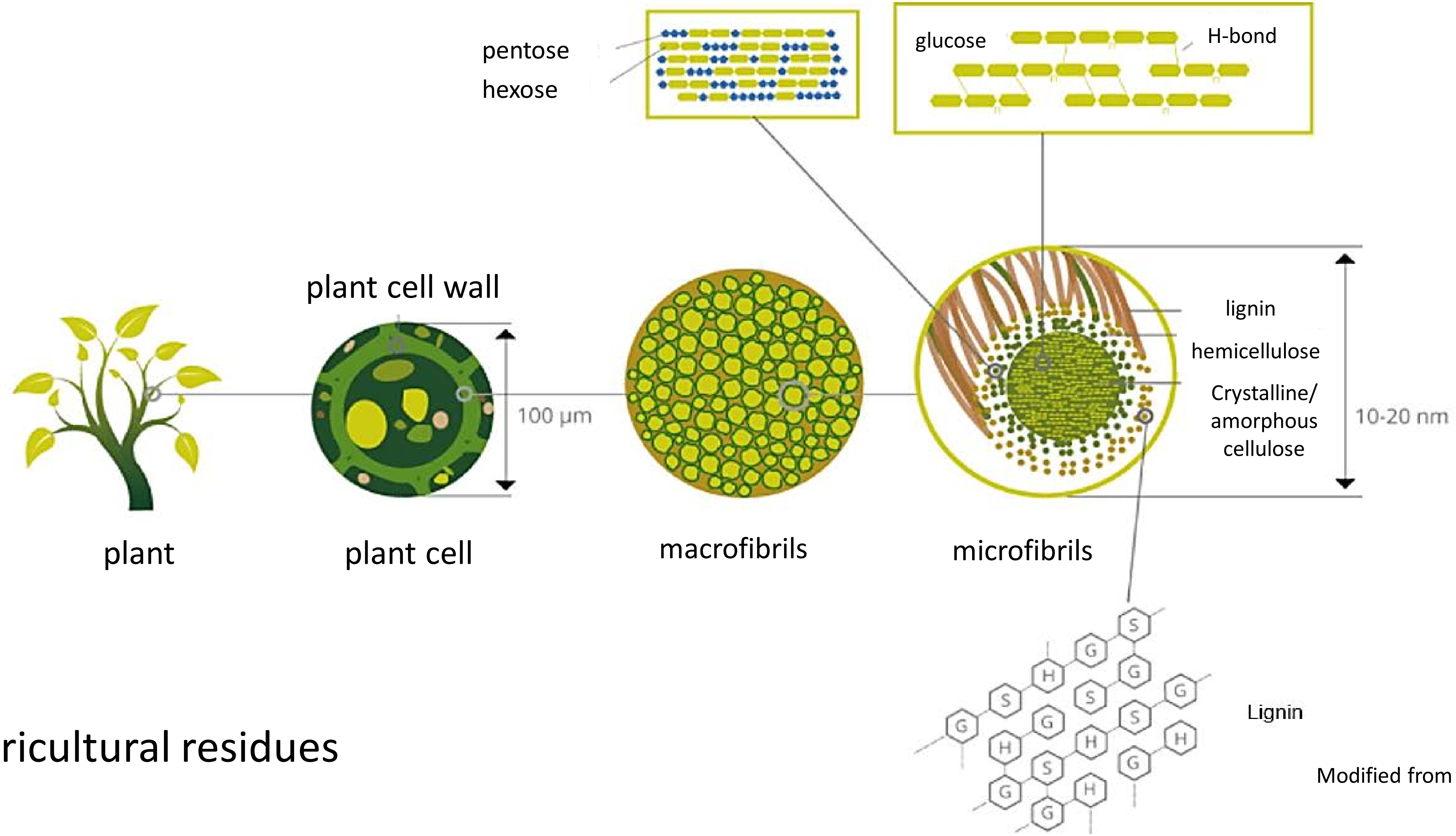
9th International conference on sustainable solid waste management CORFU 2022

Lignocellulose substrates



Agricultural residues

Modified from Pantić, TMF, 2020

Fenton reaction

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\cdot + H^+$

$2\ H_2O_2 \rightarrow OH + HOO\cdot + H_2O$

$H_2O_2 + \cdot OH \rightarrow HOO\cdot + H_2O$

$HOO\cdot \leftrightarrow \cdot O_2^- + H^+$

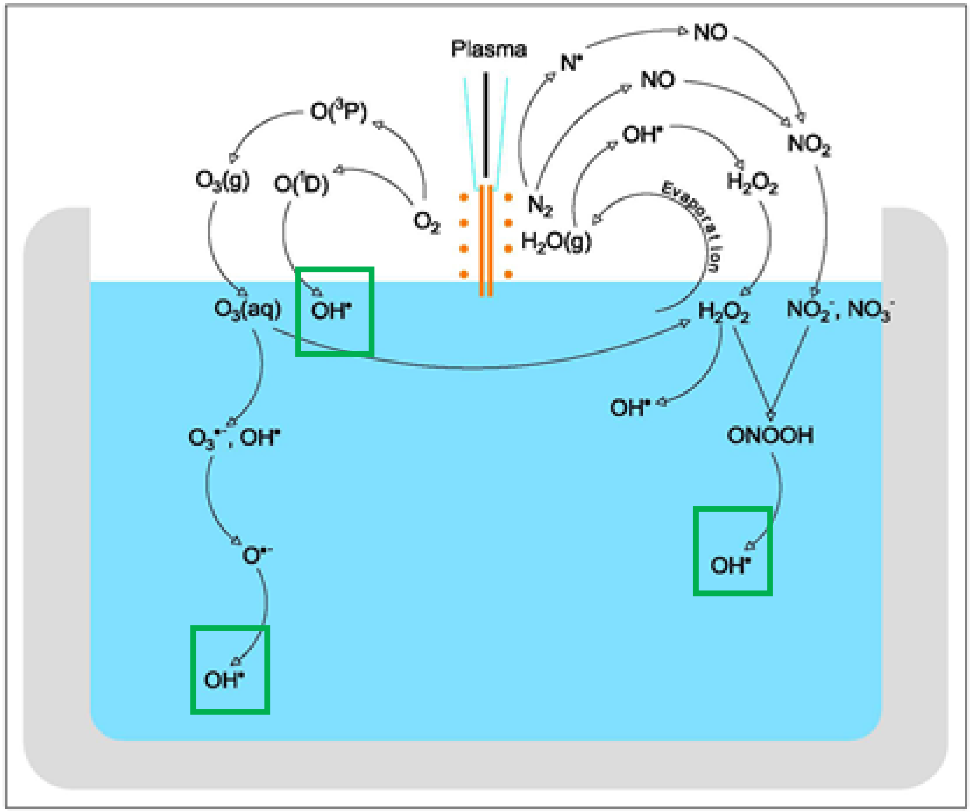
$Fe^{3+} + HOO\cdot \rightarrow Fe^{2+} + O_2 + H^+$

$Fe^{3+} + \cdot O_2^- \rightarrow Fe^{2+} + O_2$

$Fe^{2+} + \cdot OH + H^+ \rightarrow Fe^{3+} + H_2O$

$\cdot O_2^- + H_2O_2 \rightarrow \cdot OH + OH^- + O_2$

Non- thermal plasma or cold plasma

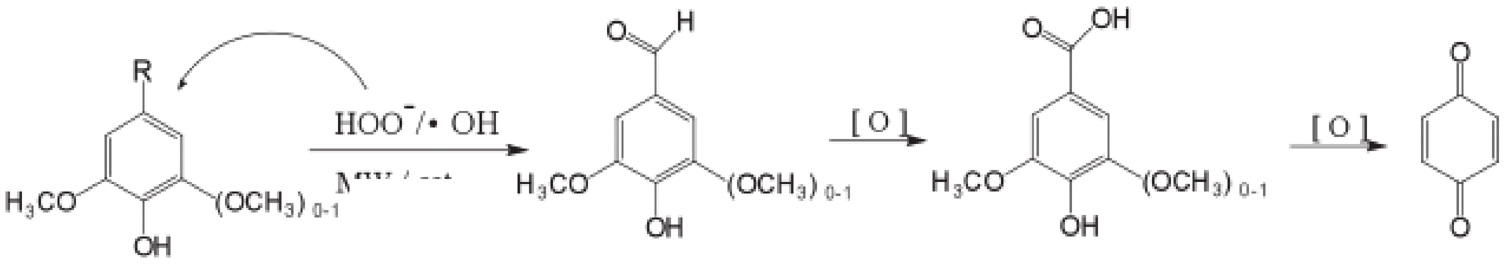


Mitrović et al. (2020). *Waste and Biomass Valorization*, 1-14.

Alkaline peroxide oxidation

$$H_2O_2 + OH^- \longrightarrow H_2O + HOO^-$$

$$HOO^- + H_2O_2 \longrightarrow H_2O + O_2 + \bullet OH$$



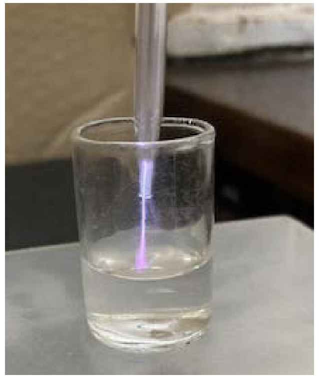
$$2\bullet OH \longrightarrow H_2O_2$$

$$H_2O_2 + \bullet OH \longrightarrow H_2O + O_2$$

Gu te al. (2012). *Ciencia y tecnologia*, *14*(1), 31-41.

Can non-thermal plasma treatment contribute to the better utilization of the biomass ?

Experimental



- Biomass – agricultural residues - grounded corn stalks
- Crude fiber analysis
- Plasma source: non-thermal plasma needle
  - Treatment time 10 minutes
  - feed gas was Ar, the gas flow = 0,5 slm,
  - distance between plasma needle and substrate was 2 cm

→Spectrophotometric assay / ABSL – acetyl bromide soluble lignin (*Fukushima i Hatfield, Journal of Agricultural and Food Chemistry, 49(7), 3133–3139, 2001*)

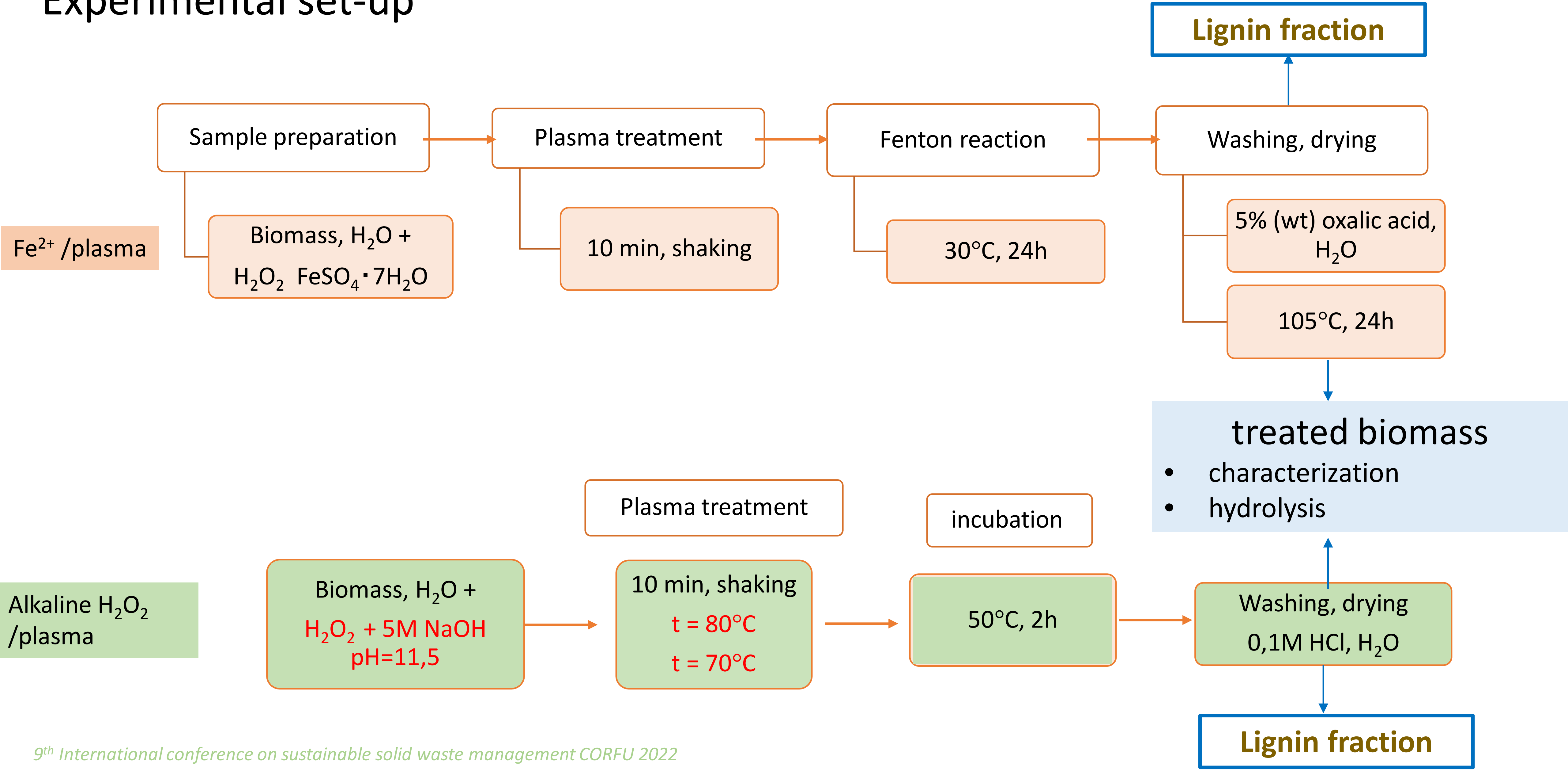
$$\%\, ABSL = (0{,}11452 \cdot A + 0{,}0008) \cdot 10 \cdot \frac{R}{m} \cdot 100(\%)$$

→Bioassesibility - (*Nikolić et al., Chemical Industry and Chemical Engineering Quarterly, 17(3), 367–374, 2011*)

$$\%\, C_{r_I} = 100 - \left(\frac{ISV}{412} \cdot 100\right) \qquad ISV = \frac{(V_b - V_s) \cdot 2{,}04 \cdot 2{,}54}{m}$$

- ATR-FTIR spectrometry

Experimental set-up



- Sample preparation

Fenton				
Sample	Biomass, mg	H_2O, ml	H_2O_2 (30 wt%), ml	$FeSO_4 \cdot 7H_2O$, mg
C	50	10.000	-	-
H-1	50	9.975	0.025	-
H-2	50	9.950	0.050	-
H-3	50	9.900	0.100	-
F-1	50	9.975	0.025	1.85
F-2	50	9.950	0.050	4.35
F-3	50	9.900	0.100	9.23

Alkaline H_2O_2 , pH=11,5		
70°C	50	10.000
70°C + P	50	10.000
80°C	50	10.000
80°C + P	50	10.000

treated biomass

Alkaline H_2O_2/plasma   Fenton/plasma

Experimental

To evaluate potential of remaining carbohydrate fraction for hydrolysis/fermentation

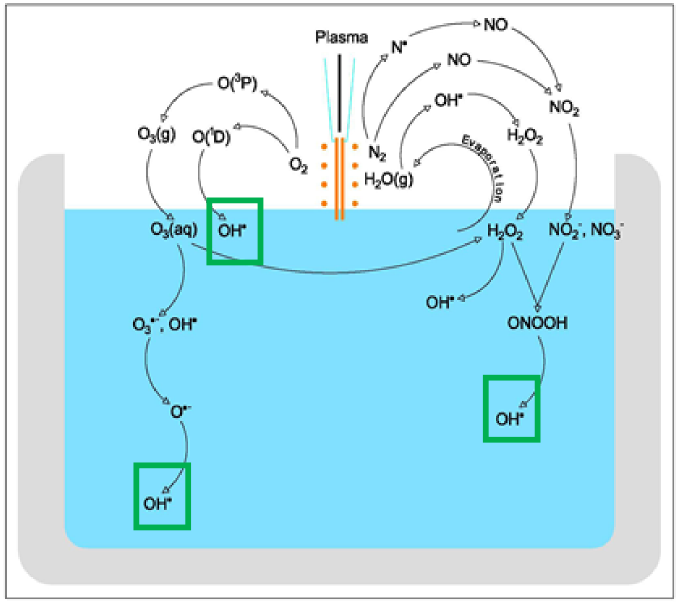
- **Enzyme hydrolysis**
  - Citrite buffer pH=4.8, 2.5 µl Cellic Ctec®, 50 mg biomass/ml, incubation 48h, 50°C, 170 rpm

- HPLC – for analysis of carbohydrate composition in hydrolysate

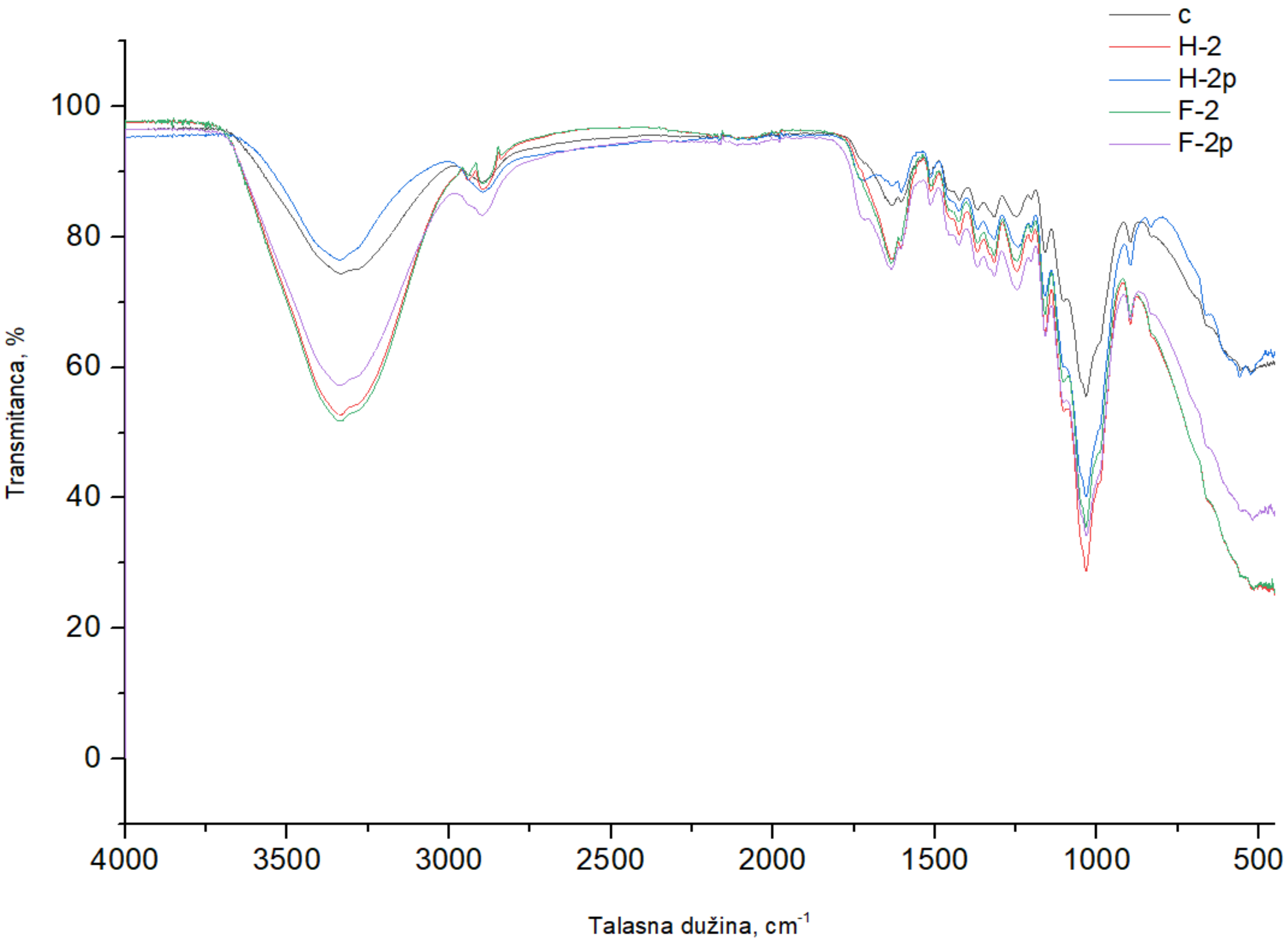
Chemical composition	
ABDL, %	28,37±5,29
Celuloza, %	36,02±2,98
Hemiceluloza, %	26,95±0,79

Effects of plasma treatment *per se* :

- Generation of H_2O_2
  - 10 min treatment , 10 ml of H_2O, 50 mg of biomass → **c(H_2O_2)=0,008-0,01 mg/ml**
- Acidification of media
  - 10 min treatment of 10 ml of media with 50 mg of biomass → **pH ~4,0**
  - 10 min treatment of 10 ml of H_2O – **pH~ 3,0** - this way obtained water is called „**plasma –activated water**“



Fe^{2+} /plasma



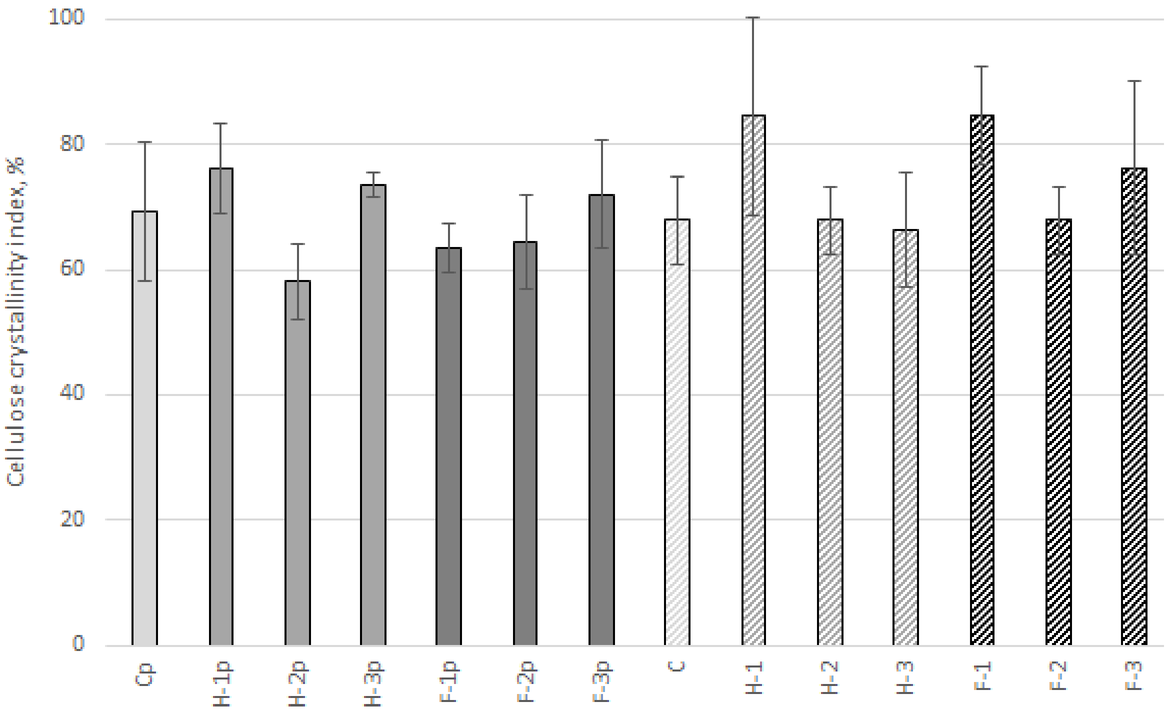
HBI – hydrogen bond intensity

Biomass with a higher crystallinity and a more ordered structure of cellulose – often through H-bonding

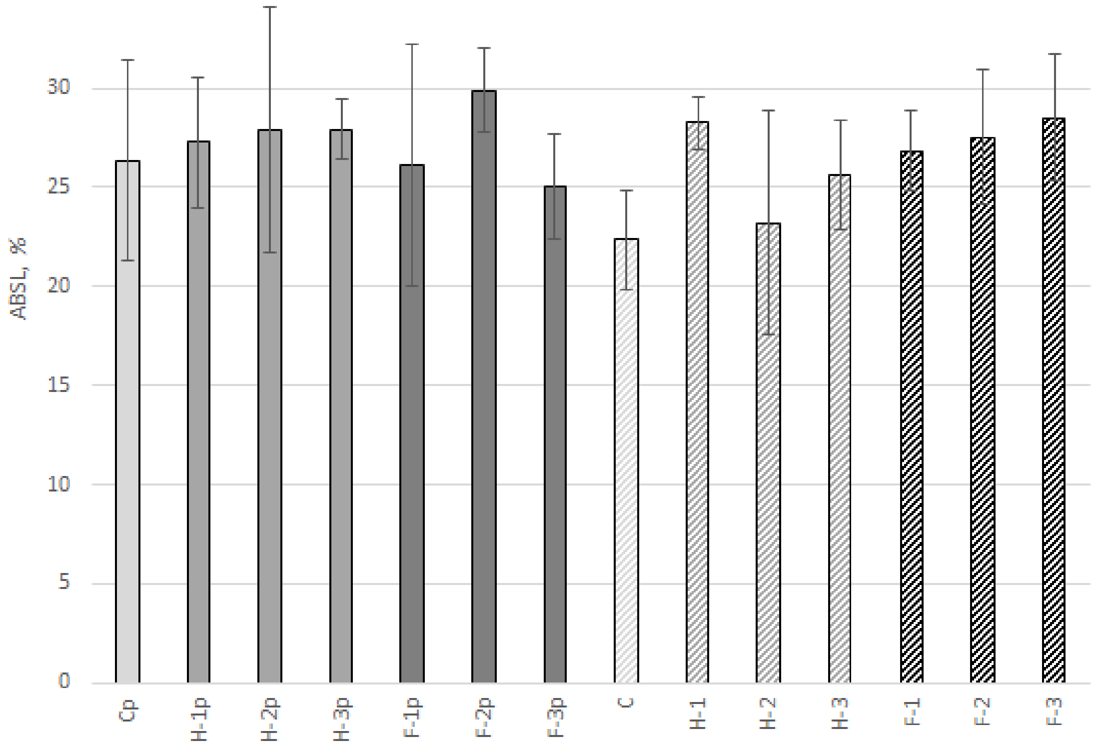
Sample	HBI (Hydrogen Bond Intensity, $_{4000-2995}/A_{993}$)
c	0,65
H-2	0,55
F-2p	0,59

Fe^{2+} /plasma

Bioassibility assay – iodine solution

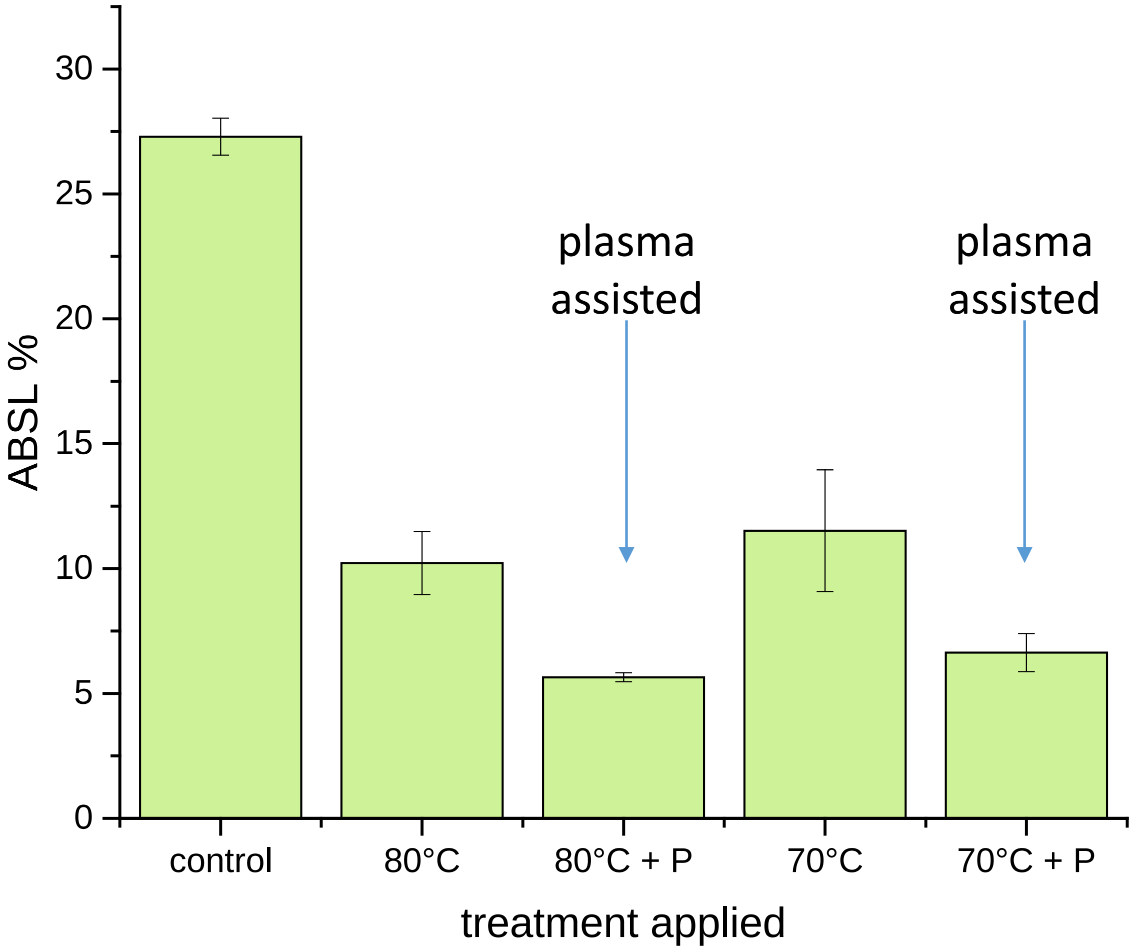


Acetyl bromide soluble lignin

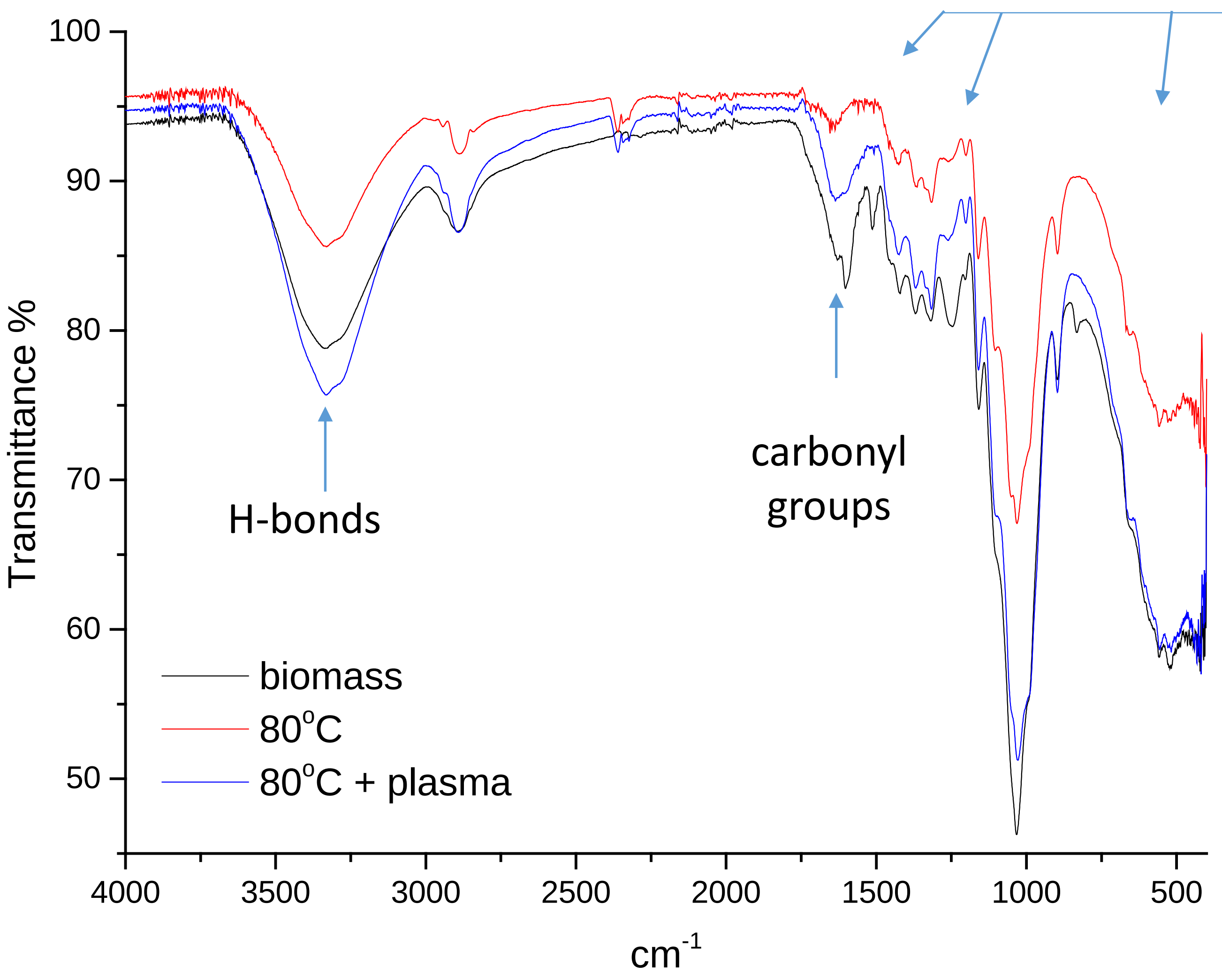


Under applied conditions, very limited degradation of lignin was obtained

Alkaline H_2O_2 /plasma



Alkaline H_2O_2 /plasma



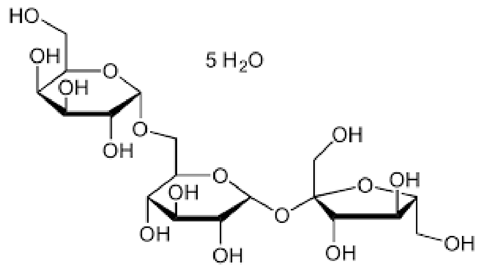
Changes in the part od structure related to lignin

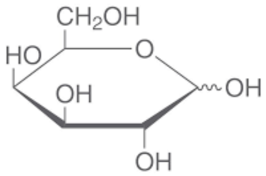
	biomass	70°C	70°C + P	80°C	80°C + P
TCI	0,74	0,61	0,63	0,60	0,62
HBI	0,47	0,48	0,50	0,51	0,55

HBI – hydrogen bond intensity
TCI – total crystallinity index

Enzymatic hydrolysis

Alkaline H_2O_2	Glucose concentration (mg/ml)
70°C	**23,8**
70°C + plasma treatment	**22,3** ↓
80°C	**25,2**
80°C + plasma treatment	**24,6** ↓





Plasma assisted treatment does not result in higher glucose concentration.

Although, lignin concentration is lower in plasma treated samples.

- Higher cristallinity of carbohydrate fraction and lower assesibility to enzymes?
- Part of carbohydrate fraction hydrolysed during the plasma treated and removed with lignin fraction?

Conclusions

- Different treatments conditions were applied
- Plasma assisted alkaline H_2O_2 improved delignification of biomass.
- Obtained carbohydrate fraction was succesfully hydrolysed by commercial cellulase with glucose as the main constituent and galactose and raffinose also present in the hydrolysate.

For further improvement: lower T, different treatment conditions, XRD, SEM, analysis of lignin fraction

Acknolwedgment

This work and participation at the CORFU 2022 was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No. 451-03-68/2022-14/200135)

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Thank you for your attention!

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