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Resource recovery and reduction of tidal waste through clean processes to obtain cellulose

Ana Moral (amoram@upo.es)
Pablo de Olavide University
Valeria Greyer
Pablo de Olavide University
Roberto Aguado
University of Girona
Antonio Tijero
Complutense University of Madrid

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Abstract

The transition towards a sustainable cellulose industry needs more environmentally friendly technologies that include the use of less polluting processes and alternative raw materials. This work shows the potential of tidal waste from the Andalusian Mediterranean coastline as cellulosic material to obtain cellulosic pulp. With this purpose, predominant species in onshore residues (mainly *Posidonia oceanica*) were prepared, characterized, and subjected to a soda-anthraquinone pulping process. A central composite design was defined in order to relate the process conditions to the composition and characteristics of the cellulose pulp. It was concluded that polynomial models encompassing linear, quadratic, and binary effect parameters reproduce the experimental results satisfactorily. Results allowed to choose high anthraquinone concentration, soda concentration and temperature (1%, 30% and 150 ºC, respectively), low liquid/solid ratio (4) and short time (30 min) as a compromise solution, by which the brightness, ethanol-benzene extractives content, kappa index, lignin content and viscosity were near their optimal. Low values of liquid/solid ratio reduce water consumption, which is of utmost importance in cellulose industries likewise short time treatments to saves energy.

Introduction

Technological change has a relevant role to play in the transition towards a sustainable industry. Cellulose industry is a recognized source of pollution and therefore, more environmentally friendly technologies are sought. This includes the use of less polluting processes (Gülsoy et al. 2022). The most traditional process for wood pulping implies sodium hydroxide, which is interesting for its cellulosic pulp yield and its environmental friendliness in comparison with sulphite or kraft processes (Salem et al. 2021). Also, it can be applied to leafy and conifer wood, as well as to nonwood raw materials such as agricultural residues. In 1977 Holton proposed the adition of a small amount of anthraquinone in the cooking liquor which accelerated alkaline delignification, stabilized carbohydrates and increased cellulose pulp yield with respect to soda adition alone. This could be due to anthraquinone acting as a redox catalyst for the reactions that will take place in the digester, to then pass into its reduced form, anthrahydroquinone, which will attack the transient and reactive structures of lignin (Jahan et al. 2021). In addition, the soda-anthraquinone pulping process has the following advantages: a) it could be adapted to small industrial productions (Sharma et al. 2015); b) it has high throughput with a short cooking time (Saad et al. 1988); c) the cooking liquors can be recovered and reused (Zhang and Chen 2017).

The overuse of wood raw materials in the cellulose industry has increased the need to find new sources (Gabriel et al. 2020). Alternative raw materials that are commonly studied are non-woody and/or annual plants such as *Hesperaloe funifera*, with 76.50% of cellulose (Sánchez et al. 2010) or *Chamaecytisus proliferus*, with a 79.73% of cellulose (Jiménez et al. 2007). Other examples are agricultural residues including palm oil residues, with 66.00% of cellulose (Alriols et al. 2009), or sesame residues, with 66.40% of cellulose (Saeed et al. 2017). The use of agricultural residues also can solve the environmental problems associated with the accumulation of residual materials in woods and cropping fields (e.g. fires, the appearance of pests on the plant cover, etc.) (Vadrevu and Lasko 2018).

Although cellulose from marine species have similar structure and properties to those of terrestrial species (Percival 1979), there are few studies from marine plants or algae, and even less about the beach wrack as a cellulose source. Seaweed and seagrass constitute an irreplaceable element of the coastal environment because marine plants and algae are involved in the correct oxygenation of seawaters, and they act in the prevention of erosion (Himes-Cornell et al. 2018). However, important quantities of marine plants and algae fragments are rejected by the sea especially following storms or high tides in many coastal regions. These onshore residues are accumulated in the beaches resulting in several problems related to hygiene and public health when these beach wrack can provide adequate conditions for bacterial growth (de Araújo and Costa 2006; den Hartog 1994). Moreover, the smell of putrefaction and its consequences on the economy and local tourism makes it necessary to regularly remove and dispose this residue (Pal et al. 2020; Trégarot et al. 2021). The coast of Andalusia houses marine phanerogams such as *Cymodocea nodosa, Posidonia oceanica*, which 61.80% of cellulose (Khiari et al. 2010), *Zostera marina*, which 57.00% of cellulose (Davies et al. 2007), *Zostera noltii*, and an extensive variety of green, red, and brown algae which originates the waste on the coasts.

In this work, the predominant species in Andalusian tidal waste (*P. oceanica*) was selected and characterized in terms of its contents in α-cellulose, ash, ethanol-benzene extractable compounds, holocellulose, lignin, hot water-soluble compounds and 1% NaOH soluble material. Moreover, we used an experimental factorial design to examine the influence of operational variables (anthraquinone concentration, soda concentration, liquid/solid ratio, temperature, and time) on cellulose pulp content in ethanol-benzene extractables, holocellulose and lignin, and key properties like the dependant response (brightness, beating degree, Kappa number, viscosity, and yield).

Materials And Methods

Collection and identification

All collection processes involved in this work have been carried out according to the Spanish Catalogue of Threatened Species (Ministry of Environment, Rural and Marine 2011) and the state regulations of article 57 of the Law on Natural Heritage and Biodiversity (Head of State 2007). Onshore residues were collected on San Roque (Cádiz, Andalusia, Mediterranean Sea) in October 2021. Visual inspection showed the presence of phanerogams (many leaves and small number of rhizomes) and traces of algae. After collection, the waste was rinsed with fresh water, dry at room temperature and the species of marine plants and algae were identified. The predominant species was selected, separated from the rest of the waste, and exhaustively washed with cold freshwater in order to remove sand and other impurities and dried at 40 ºC for 3 days. Next, sampling and sample preparation followed the standard method TAPPI T257 cm-02 (TAPPI T257 2012).

Chemical characterization of the species

After sample conditioning, the species selected was characterized chemically according to TAPPI Standards shown next: α-cellulose content following the T203 (TAPPI T203 2009), ash content the T211

(TAPPI T211 2022), ethanol–benzene extractable content the T204 (TAPPI T204 2017), lignin content the T222 (TAPPI T222 2015), hot water-soluble compounds content the T207 (TAPPI T207 2008) and 1% NaOH soluble compounds content the T212 (TAPPI T212 2018). Holocellulose content was determined according to the method of Wise et al. (1946) (Hubbel and Ragauskas 2010).

Cellulose extraction

The lignocellulosic material collected and selected was cooked in a 15 L cylindrical batch reactor wrapped in a heating wire jacket. The reactor was connected via a rotary axis to the control unit, which included a motor actuating the reactor stirring (by turnover), and temperature and pressure measurement and control instruments. The species selected were placed in the reactor and amounts of soda, anthraquinone and water required were added in order to obtain the desired liquid/solid ratio. Then, the system was heated until reaching the cooking temperature, which was maintained for a specific time. After cooking, the reactor contents were filtered and the resulting solid was washed with water, fibres being separated from uncooked material by screening through a sieve of 1 mm mesh, to determine the cellulose pulp yield (by weight). The intervals of operation of the five operational variables used during soda-anthraquinone cooking were: anthraquinone concentration (0, 0.5 and 1% o.d.), soda concentration (10, 20 and 30% o.d.), liquid/solid ratio (4, 7 and 10), temperature (100, 135 and 150 ºC) and time (30, 60 and 90 min).

Characterization of cellulose pulps

In order to determine holocellulose and lignin content, the cellulose pulps were subjected to reflux in a Soxhlet extractor for 7–8 h to eliminate resins, waxes, sterols, fats, and fatty acids that might interfere in the measurements, and ethanol benzene extractables content was determined (TAPPI T204 2017). Holocellulose content was obtained from extractive-free biomass according to the method of Wise et al. (Hubbel and Ragauskas 2010) and lignin content with the TAPPI method T222 (TAPPI T222 2015). Brightness was determined according to T452 (TAPPI T452 2018), beating degree (using a Shopper-Riegler apparatus) according to UNE5267 (UNE5267 2001); Kappa index and viscosity according to T236 (TAPPI T236 2013) and T254 (TAPPI T254 2010), respectively. Yield was calculated gravimetrically, by weighting the solid fraction, measuring its moisture content, and comparing it to the initial biomass weight on a dry basis.

Experimental design

The proposed model used a series of experiments based around a central test plus several additional tests to estimate the terms of a second-order polynomial equation. This design meets the general requirement that every parameter in the mathematical model can be estimated in a small number of tests (Montgomery 2004). The total number of tests required for the five independent variables studied (anthraquinone concentration, soda concentration, liquid/solid ratio, temperature, and time) was 27. The independent variables were normalized to values from − 1 to + 1 using Eq. (1) in order to facilitate direct comparison of the coefficients of the resulting polynomial equation and an understanding of the effects

of the individual independent variables on the dependent variables of cellulosic pulp ones considered (brightness, beating degree, ethanol-benzene extractables content, holocellulose content, kappa index, lignin content, viscosity and yield).

$$X_n = 2\frac{X - X_{me}}{X_{max} - X_{min}}$$

1

where X_n was the normalized value of anthraquinone concentration, soda concentration, liquid/solid ratio, temperature, and time; X was the absolute experimental value of the variable concerned; X_{me} was the mean of the extreme values of X; and X_{max} and X_{min} were their maximum and minimum values, respectively. Experimental data were fitted to the second-order polynomial equation showed in Eq. (2):

$$\mathrm{Y} = \mathrm{a}_0 \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{b}_\mathrm{i} \mathrm{X}_\mathrm{ni} + \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{c}_\mathrm{i} \mathrm{X}^2{}_\mathrm{ni} + \sum_{\mathrm{i}=1,\mathrm{j}=1}^{\mathrm{n}} \mathrm{d}_{\mathrm{i},\mathrm{j}} \mathrm{X}_\mathrm{ni} \mathrm{X}_\mathrm{nj} \mathrm{i} \leq \mathrm{j}$$

2

where Y was the response or dependent variable [viz. brightness, beating degree, ethanol-benzene extractables content, holocellulose content, kappa index, lignin content, viscosity, and yield]; X_n was the normalized value of the independent variable concerned; and a_0, b_i, c_i and d_{ij} were unknown characteristic constants estimated from the experimental data. Table 1 shows the absolute and normalized values obtained for the independent variables in the 27 tests required to construct the model.

Table 1
Absolute and normalized values of the operational variables

Test	A (%)	S (%)	R	T (ºC)	T (min)	X_A	X_S	X_R	X_T	X_t
1	0.5	20	7	135	60	0	0	0	0	0
2	1	10	4	100	30	1	-1	-1	-1	-1
3	0	10	10	100	30	-1	-1	1	-1	-1
4	1	30	10	100	30	1	1	1	-1	-1
5	0.5	20	7	100	60	0	0	0	1	0
6	1	20	7	135	60	1	0	0	0	0
7	0.5	20	7	135	30	0	0	0	0	-1
8	0.5	10	7	135	60	0	-1	0	0	0
9	1	10	10	150	30	1	-1	1	1	-1
10	1	30	4	150	30	1	1	-1	1	-1
11	0.5	30	7	135	60	0	1	0	0	0
12	0.5	20	7	135	90	0	0	0	0	1
13	0	30	10	150	30	-1	1	1	1	-1
14	0.5	20	10	135	60	0	0	1	0	0
15	0.5	20	7	100	60	0	0	0	-1	0
16	0	10	10	150	90	-1	-1	1	1	1
17	0	20	7	135	60	-1	0	0	0	0
18	0	30	10	100	90	-1	1	1	-1	1
19	0	30	4	150	90	-1	1	-1	1	1
20	1	30	4	100	90	1	1	-1	-1	1
21	1	30	10	150	90	1	1	1	1	1
22	1	10	10	100	90	1	-1	1	-1	1
23	1	10	4	150	90	1	-1	-1	1	1

A, S, R, T and t = Absolute values of anthraquinone concentration, soda concentration, liquid/solid ratio, temperature and time

X_A, X_S, X_R, X_T and X_t = Normalized values of anthraquinone concentration, soda concentration, liquid/solid ratio, temperature, and time

Test	A (%)	S (%)	R	T (ºC)	T (min)	X_A	X_S	X_R	X_T	X_t
24	0	30	4	100	30	-1	1	-1	-1	-1
25	0	10	4	100	90	-1	-1	-1	-1	1
26	0.5	20	4	135	60	0	0	-1	0	0
27	0	10	4	150	30	-1	-1	-1	1	-1
A, S, R, T and t = Absolute values of anthraquinone concentration, soda concentration, liquid/solid ratio, temperature and time										
X_A, X_S, X_R, X_T and X_t = Normalized values of anthraquinone concentration, soda concentration, liquid/solid ratio, temperature, and time										

Results And Discussion

Identification and selection

More than half of the onshore waste collected corresponded to *Posidonia oceanica*. This agrees with the classification of marine phanerogams in Andalusia carried out by the project Life Blue Natura. It cites the majority meadows for *Posidonia oceanica* with 7097 ha (60.40%), followed by *Cymodocea nodosa* with 4179 ha (35.36%), by *Zostera noltii* with 474 ha (4.03%) and by *Zostera marina* with 0.09 ha (0.0008%) (Mendoza 2021). Marine phanerogams are composed by leaves, rhizomes, roots, flowers, and fruits. The parts of less weight and volume (roots, flowers, and fruits) with a part of the dead leaves are dragged by the waves to deeper areas while the parts of more weight and volume (leaves and rhizomes) are transported and accumulated on the coast generating residues (Moral et al. 2019). For species identification, a bibliographic search to know the differences between the species constituting these residues was carried out (Table 2).

Table 2
Characteristics of marine phanerogams residues in Andalusia

	C. nodosa	*P. oceanica*	*Z. marina*	*Z. noltii*
Leaves				
Form	Cintyform	Cintyform	Cintyform	Cintyform
Apex	Rounded	Rounded	Obtuse	Truncated
Bundles	3–4	5–8	3–8	4–5
Length	10–45 cm	20–140 cm	up to 90 cm	6–30 cm
Width	2–4 mm	7–11 mm	2–8 mm	0.50–1.50 mm
Grown	Spring-summer	September	Spring	Spring
Tidal	Autumn	Autumn	Autumn	Autumn
Rhizomes				
Direction	Plagiotropic (P) Orthotropic (O)	Plagiotropic (P) Orthotropic (O)	Plagiotropic (P) Erect axes	Plagiotropic (P)
Lenght	P: 25 mm O: 1.40 mm	P: up to 15 cm	P: 10–35 mm	P: 4–35 mm
Thickness	P: 2–3 mm O: 1–2 mm	P: up to 1cm O: up to 1cm	P: 2–5 mm	P: up to 2 mm
Grown	Spring-summer	Annual	Spring	Spring
Tidal	Not exported (traces)	Autumn	Not exported (traces)	Not exported (traces)
References				
	Barbera et al. 2005 Caye and Meinesz 1985 Da-Ros et al. 2021 Luque and Templado 2004 Olesen et al. 2022	Luque and Templado 2004 Kaal et al. 2016 Olesen et al. 2002 Piñeiro-Juncal, 2021 Tomas et al. 2005	Boutahar et al. 2020 Davies et al. 2007 García-Redonto et al. 2019 Niemhuis et al. 1980 Tanner et al. 2010	Ankel et al. 2021 Brun et al. 2006 Luque and Templado 2004 Vermaat et al. 1987

The leaves found in the tidal waste were cintyform and measured between 20 and 100 cm in length and 4 to 10 mm in width. Those that remained on the rhizomes were of 70–90 cm in length, 8–10 mm in with

and in bundles of 7–8. The loosest leaves were similar to those that remained on the rhizomes (70–100 cm in length, 8–10 mm in width). Narrower and shorter loose leaves (27–35 cm in length, 2–3 mm in with) were found in small quantities. At numerous apexes, the shape could not be distinguished due to fractures or being bitten by herbivores; this factor was mentioned by other authors in literature (Tomas et al. 2005). The apexes that could be classified were rounded.

The residues of phanerogam leaves were deposited on the coasts throughout the year due to natural detachment, storms, or other causes. However, there were periods of greater generation. The collection was done in October, autumn, when the phanerogams generate more waste. Plagiotropic and orthotropic rhizomes with a length between 5 and 13 cm and a thickness between 8 mm and 1 cm were also found.

P. oceanica was identified as the only phanerogam that exports a large quantity of rhizomes to this coast. Leaf bundles (7–8) and the size of the plants (leaves of 50–100 cm in length and 8–10 mm in with, rhizomes of 5–13 cm in length and 8 mm-1 cm in thickness) were within the intervals indicating high growth in accordance with the maximum growth in September and the collection in October. The narrower and shorter loose leaves (27–35 cm in length, 2–3 mm in width) corresponded to *C. nodosa*; both have rounded apex. Although the replacement of leaves is faster in *C. nodosa* that in *P. oceanica*, the remains of *C. nodosa* reach the coast in small quantities (Piñeiro-Juncal 2021). *C. nodosa* is common in places where there are meadows of *P. oceanica* where it is found in a discontinuous distribution (Olesen et al. 2002). Due to the small number of leaves of *C. nodosa*, a single predominant species, *P. oceanica*, was selected.

Chemical characterization of Posidonia oceanica

The results of chemical characterization, along with values from other authors and terrestrial raw materials (conventional, non-wood and agricultural residues), are shown in Table 3.

Table 3
Chemical characterization of *P. oceanica* and different lignocellulosic materials

Analysis (%)	α-C	ASH	E:B	HOL	KLS	HWS	%NS	Reference
***P. oceanica* - residues**								
Plant	35.80	9.90	10.10	59.00	21.30	9.60	19.90	This study
Leaves	32.50	6.40	6.50	55.80	28.20	7.40		Ahmed 2019
Leaves	31.40	10.50	19.20	57.10	24.70			Bettaieb et al. 2015
Balls	40.00	12.00	10.70	61.80	29.80	12.20	16.50	Khiari et al. 2010
Wood raw materials								
Eucalyptus camaldulensis		0.80	15.90	55.40	21.80	3.00	29.70	Neiva et al. 2015
Eucalyptus globulus	55.40	0.60	12.10	64.30	22.10	3.80		Gominho et al. 2012
Pinus halepensis		0.31	1.50	46.30	26.90	3.20		Haddad et al. 2009
Pinus pinea	24.52	0.65	7.00	62.81	39.29	6.41	10.58	Dönmez et al. 2012
Non-wood raw materials								
Chamaecytisus proliferus	45.37	2.31	2.64	79.73	16.80	2.79	16.67	Jiménez et al. 2007
Hesperaloe funifera	40.90	5.90	4.00	76.50	7.30	13.50	29.50	Sánchez et al. 2010
Leucaena leucocephala	39.41	2.23	8.19	68.34	18.40	6.81	23.41	Jiménez et al. 2007
Melissa officinalis	42.70	9.50		57.00	26.50	20.00	68.90	Ashori et al. 2011
Pawlonia fortunei	37.70	0.89	4.66	71.40	24.60	13.32	28.63	López et al. 2012
Prosopis juliflora	31.40	4.30		67.40	28.30			Naseeruddin et al. 2013
Agricultural residues								

α-C = α-cellulose content; ASH = ash content; E:B = ethanol-benzene extractables content; HOL = holocellulose content; KLS = lignin content; HWS = hot water-soluble compounds content; %NS = 1% NaOH-soluble compounds content

Analysis (%)	α-C	ASH	E:B	HOL	KLS	HWS	%NS	Reference
P. oceanica - residues								
Karkadeh stalks	45.80	3.20	3.40	45.80	19.32	8.60	19.50	Saeed et al. 2017
Millet stalks	40.99	5.96	4.60	61.89	18.20	10.20	21.30	Saeed et al. 2018
Palm oil tree – fruit	62,00	1.80	7.10	66.00	25.00	2.50	26.00	Alriols et al. 2009
Rice straw	41.20	0.20	0.56	60.70	21.90	7.30	57.70	Moral et al. 2012
Sesame stalks	42.30	3.80	5.90	64.40	20.80	10.70	20.30	Saeed et al. 2017
Sorghum stalks	35.40	5.31	5.20	54.81	10.27	13.20	16.20	Saeed et al. 2017
Sunflower stalks		12.20	4.50	40.20	16.20	22.00	44.90	Khristova et al. 1998

α-C = α-cellulose content; ASH = ash content; E:B = ethanol-benzene extractables content; HOL = holocellulose content; KLS = lignin content; HWS = hot water-soluble compounds content; %NS = 1% NaOH-soluble compounds content

Reportedly, a proportion of cellulose above 34% is an indicator of suitability for paper and cellulose industries (Agu et al. 2014). Photosynthetic aquatic species such as phanerogams also contain other fibrous materials that are potentially beneficial for paper production (Kuo and den Hartog 2001). Comparing the results of *P. oceanica* with the chemical characterization from other authors, the values were similar to those found in literature except for lignin content, which was lower. This was probably due to the high number of leaves, accounting for less lignin content than rhizomes, and the variation of the plant depending on the geographic area (Kaal et al. 2016).

Comparing the results obtained for *P. oceanica* with values of wood raw materials, α-cellulose content (35.80%), ethanol-benzene extractable content (10.10%), holocellulose content (59.00%), lignin content (21.30%) and NaOH-soluble compounds (19.90%) were into the corresponding ranges: (24.52–55.40%), (1.50–15.90%), (46.30–64.30%), (21.80-39.29%) and (10.58–29.70%). However, ashes content for *P. oceanica* (9.90%) and hot water-soluble content (9.60%) were higher.

Regarding non-wood raw materials, results for *P. oceanica* were found within their ranges of α-cellulose content (31.40-45.37%), holocellulose content (57.00-79.73%), lignin content (2.46–28.30%), hot water-soluble compounds content (2.79-20.00%,) and NaOH-soluble compounds content (16.67–68.90%). Ash and ethanol-benzene extractable content were found in higher proportion.

The content of α-cellulose, ashes, holocellulose, lignin, hot water-soluble compounds and NaOH-soluble compounds in *P. oceanica* waste was found to lie within the general ranges of agricultural residues, except for the content in ethanol-benzene extractables, which was higher.

The higher proportion of ashes in *P. oceanica* could be due to the abundant presence of minerals in marine phanerogams. Likewise, the contribution of the remaining sand and carbonated deposits, despite being largely washed away after waste collection, should not be neglected. The higher content in ethanol-benzene extractives was probably due to the presence of lipids, organic salts and polyphenols. Finally, the water-soluble fraction can be mostly attributed to starch.

Characterization of cellulose pulps

All tests were conducted in triplicate, the average results obtained for the dependent variables are shown in Table 4. The time needed to reach the working temperature (4–8 min) was excluded.

Table 4
Experimental values of the dependent variables in the soda-anthraquinone pulping of *P. oceanica* obtained with the experimental design

Test	BR (%)	BD (ºSR)	E:B (%)	HOL (%)	KI	KLS (%)	VI (mL/g)	YI (%)
1	53.93	34.00	5.85	76.80	7.10	4.06	910.00	45.50
2	41.17	27.00	6.21	61.39	13.20	4.54	1156.00	50.33
3	41.70	29.00	6.26	62.14	13.40	4.53	1071.00	50.38
4	42.37	49.00	6.07	77.56	13.10	3.55	892.00	40.26
5	54.03	30.00	5.56	77.24	6.00	3.98	903.00	44.65
6	53.39	37.00	5.70	76.63	6.50	4.02	933.00	45.20
7	49.64	36.00	6.02	76.20	8.80	4.10	951.00	45.89
8	49.82	23.00	6.06	76.07	8.80	4.50	982.00	49.75
9	42.83	20.00	5.99	89.90	12.00	4.49	790.00	49.69
10	55.20	42.00	4.42	69.81	4.20	3.49	1008.00	39.71
11	54.09	45.00	5.58	79.39	6.20	3.51	873.00	39.92
12	54.68	31.00	5.68	78.30	6.40	4.00	885.00	44.90
13	54.85	40.00	4.73	71.16	4.30	3.49	996.00	.39.83
14	54.53	33.00	5.80	76.98	6.10	4.06	907.00	45.44
15	43.87	35.00	5.96	72.38	11.70	4.15	930.00	46.27
16	55.50	18.00	5.13	75.88	5.00	4.48	913.00	49.75
17	50.28	30.00	5.91	76.15	6.60	4.10	901.00	45.52
18	54.87	44.00	5.13	66.41	5.20	3.53	1043.00	40.09
19	55.33	38.00	4.25	97.05	3.70	3.48	606.00	39.71
20	54.05	45.00	5.10	63.14	4.90	3.51	1072.00	39.96
21	56.10	37.00	4.16	96.44	3.30	3.47	635.00	39.64
22	42.30	23.00	6.00	84.40	12.00	4.50	860.00	49.89
23	54.85	18.00	4.76	71.21	3.90	4.47	936.00	49.62
24	42.90	46.00	6.12	77.63	11.90	3.54	891.00	40.26
25	42.67	22.00	6.10	87.54	13.30	4.51	845.00	50.09

BR = brightness; BD = beating degree; E:B = ethanol-benzene extractables content; HOL = holocellulose content; KI = Kappa index; KLS = lignin content; VI = viscosity; YI = yield

Test	BR (%)	BD (ºSR)	E:B (%)	HOL (%)	KI	KLS (%)	VI (mL/g)	YI (%)
26	51.40	31.00	5.79	73.51	6.20	4.06	919.00	45.33
27	42.60	20.00	5.98	91.25	11.90	4.49	788.00	49.78

BR = brightness; BD = beating degree; E:B = ethanol-benzene extractables content; HOL = holocellulose content; KI = Kappa index; KLS = lignin content; VI = viscosity; YI = yield

As shown, the brightness and the beating degree indicated cellulose pulp with promising potential. The content in ethanol-benzene extractables found in *P.oceanica* residue (10.10%) decreased by half with the soda-anthraquinone process, probably due to the alkaline hydrolysis of organic salts and esters. The holocellulose content, as expected, increased after the process by eliminating the rest of the components. The lignin content changed from 21.30% in the residue to 3.47–4.54% in the pulp, improving hardness, bleachability and colour. Soda-anthraquinone process was quite efficiently delignified judging by the Kappa index of the pulp; this, together with its good viscosity (in the order of 1000 mL/g), facilitates bleaching without degradation of cellulose fibres. Yield was acceptable for cellulosic pulps.

The BMDP software package (Dixon 1988) was used to conduct a multiple linear regression analysis involving all terms in Eq. (2); those with Snedecor´s F-values smaller than unity were eliminated using the stepwise method (Draper and Smith 1998). The equations thus obtained for the different dependent variables, their *multiple-r*, r^2 and fitted-r^2 values, the highest *p*-values and the smallest Student´s *t* values for the terms in such equations (at a confidence level of 95%) were as follows (statistics showed in brackets):

$$BR = -3.68X_T^2 - 2.82X_AX_R + 3.13X_S + 3.63X_T + 3.17X_t + 52.42 \quad \textbf{(3)}$$

(multiple-R = 0.99; R^2 = 0.97; fitted-R^2 = 0.96; $p < 0.001$; $t > 2.12$)

$$BD = 10.33X_S - 3.17X_T - 1.83X_t + 32.70 \quad \textbf{(4)}$$

(multiple-R = 0.99; R^2 = 0.97; fitted-R^2 = 0.97; $p < 0.001$; $t > 2.79$)

$$E:B = -0.38X_T^2 + 0.18X_AX_R - 0.38X_S - 0.44X_T - 0.30X_t + 5.82 \quad \textbf{(5)}$$

(multiple-R = 0.95; R^2 = 0.91; fitted-R^2 = 0.89; $p < 0.001$; $t > 2.86$)

$$HOL = 1.66X_S^2 + 10.03X_AX_R + 4.85X_T + 2.41X_t + 76.02 \quad \textbf{(6)}$$

(multiple-R = 0.98; R^2 = 0.96; fitted-R^2 = 0.95; $p < 0.001$; $t > 2.07$)

$$KI = -0.70X_R^2 + 2.00X_T^2 + 1.69X_AX_R - 2.04X_S - 2.47X_T - 1.95X_t + 7.12 \quad \textbf{(7)}$$

(multiple-R = 0.99; R^2 = 0.98; fitted-R^2 = 0.97; $p < 0.001$; $t > 2.10$)

$$KLS = -0.05X_S^2 - 0.50X_S - 0.03X_T - 0.01X_t + 4.06 \quad \textbf{(8)}$$

(multiple-R = 0.99; R^2 = 0.99; fitted-R^2 = 0.99; $p < 0.001$; $t > 2.16$)

$$VI = -18.87X_TX_t - 118.00X_AX_R - 65.83X_T - 41.56X_t - 18.01X_S + 910.96 \quad \textbf{(9)}$$

(multiple-R = 0.97; R^2 = 0.95; fitted-R^2 = 0.93; $p < 0.001$; $t > 2.00$)

$$YI = -0.49X_S^2 - 4.99X_S - 0.29X_T - 0.14X_t + 45.41 \quad \textbf{(10)}$$

(multiple-R = 0.99; R^2 = 0.99; fitted-R^2 = 0.99; $p < 0.001$; $t > 2.30$)

where X_A, X_S, X_R, X_T and X_t are the normalized values of anthraquinone concentration, soda concentration, liquid/solid ratio, temperature, and time, respectively.

The values estimated using the previous equations reproduced the experimental values with standard errors of 1.06, 1.57, 0.21, 2.16, 0.59, 0.03, 29.96, and 0.22 for brightness, beating degree, ethanol-benzene extractables content, holocellulose content, kappa index, lignin content, viscosity, and yield, respectively. The experimental results fitted to the polynomials models satisfactorily, as reflected by the statistical parameters.

Response surface plots for six of the dependent variables are displayed in Fig. 1. The other two, beating degree and viscosity, were omitted due to being fitted to simpler models, *i.e.*, multiple linear regression. In any case, there were no local minima or maxima around the central point, which means that, for each of the responses and under the range of conditions tested, their individual optimization lies in the star points (or, in this case, axial points) of the central composite design.

Identifying the independent variables most (or least) strongly influencing the dependent variables with the previous equations was not as simple as with linear equations, owing to the presence of quadratic terms and interactions between two independent variables. In order to identify the values of the independent variables that would provide the best values for the dependent variables, non-linear programming as implemented by More and Toraldo (1989) was used. Table 5 shows the optimum values of the dependent variables and the values of the independent ones required to obtain them.

Table 5
Values of the operational variables in the soda pulping of *P. oceanica* required to obtain the optimum values of the dependent variables

	Optimal values	Operating conditions					Normalized values				
		A (%)	S (%)	R	T (ºC)	t (min)	X_A	X_S	X_R	X_T	X_t
BR (%)	55.85	1	30	10	150	90	1	1	1	1	1
BD (ºSR)	48.04	1	30	10	100	30	1	1	1	-1	-1
E:B (%)	4.49*	0	30	4	150	90	-1	1	-1	1	1
HOL (%)	94.99	0	30	4	150	90	-1	1	-1	1	1
KI	3.70*	0	30	4	150	90	1	1	1	1	1
KLS (%)	3.46*	1	30	10	150	90	1	1	1	1	1
VI (mL/g)	1135.53	1	10	4	100	30	1	-1	-1	-1	-1
YI (%)	50.34	1	10	4	100	30	1	-1	-1	-1	-1
* Optimum value (minimum)											
A, S, R, T and t = Absolute values of anthraquinone concentration, soda concentration, liquid/solid ratio, temperature and time											
X_A, X_S, X_R, X_T and X_t = Normalized values of anthraquinone concentration, soda concentration, liquid/solid ratio, temperature and time											
BR = brightness; BD = beating degree; E:B = ethanol-benzene extractables content; HOL = holocellulose content; KI = Kappa index; KLS = lignin content; VI = viscosity; YI = yield											

From the data in Table 5 it was confirmed that to obtain optimal brightness, Kappa index and lignin content values, the application of the operation variables at their highest levels were required. The optimal beating degree was obtained by operating at minima of anthraquinone concentration, soda concentration, liquid/solid ratio; and maxima of temperature and time. The optimal values for content in ethanol-benzene extractables and holocellulose were obtained under minimum conditions of anthraquinone concentration, liquid/solid ratio and maximum conditions of soda concentration, temperature, and time. To obtain the optimal viscosity it was necessary to operate with minimum conditions except for the anthraquinone concentration, which was maximum. The increased viscosity resulting from the use of higher values for the operational variables of the pulping process, because of the severity of the treatment, increases the number of short chains. However, prolonged heating damages fibres through the combined effects of a high soda concentration and temperature, decreasing viscosity (Seng 2001). Finally, maximizing the yield entails using a low value of operating conditions.

To achieve the optimal values, the following maximum values of independent variables were used: anthraquinone concentration in six dependent variables (BR, BD, KI, KLS, VI and YI), soda concentration in

six (BR, BD, EB, HOL, KI and KLS), liquid/solid ratio in four (BR, BD, KI and KLS), and temperature and time in five dependent variables (BR, EB, HOL, KI and KLS). The minimum values were present through these conditions: anthraquinone concentration in two dependent variables (EB and HOL), soda concentration in two (VI and YI), liquid/solid ratio in four (EB, HOL, VI and YI) and temperature and time in three dependent variables (BD, VI and YI).

To save energy, water, and immobilized capital in industry it was necessary to reach a compromise about the conditions for the optimization of the product and the reduction of the resources required.

The independent variables which had a greater number of minimum values in the dependent variables to achieve the optimum ones were chosen (liquid/solid ratio, temperature, and time). The compromise sets of conditions to be evaluated were:

1. A) Low values for liquid/solid ratio and temperature (4, 100ºC) and high values for anthraquinone concentration (1%), soda concentration (30%) and time (60 min),
2. B) Low values for temperature and time (100 ºC, 30 min) and high values for anthraquinone concentration (1%), soda concentration (30%) and liquid/solid ratio (10)
3. C) Low values for time and liquid/solid ratio (30 min, 4) and high values for anthraquinone concentration (1%), soda concentration (30%) and temperature (150ºC).

By simulating the alternatives indicated and applying Equations (3) to (10), the resulting values of the dependent variables were found (Table 6).

Table 6
Values of the dependent variables for the cellulose pulp and deviations from the optimum levels obtained under the conditions stated

	Optimal	A	Error (%)	B	Error (%)	C	Error (%)
BR (%)	55.85	54.22	0.17	42.24	0.13	55.14	0.06
BD (ºSR)	48.04	44.37	0.63	48.04	0.96	41.70	0.30
E:B (%)	4.49	5.01	0.09	5.99	0.08	4.73	0.31
HOL (%)	92.72	65.20	2.06	80.46	2.90	70.09	0.28
KI	3.66	5.20	0.30	12.49	0.6	4.17	0.03
KLS (%)	3.46	3.52	0.01	3.55	0.01	3.49	0.01
VI (mL/g)	1135.53	1054.06	17.94	863.42	28.57	1005.50	2.49
YI (%)	50.34	40.08	0.11	40.36	0.09	39.78	0.07

BR = brightness; BD = beating degree; E:B = ethanol-benzene extractables content; HOL = holocellulose content; KI = Kappa index; KLS = lignin content; VI = viscosity; YI = yield

From the results of Table 6, to obtain bleachable cellulosic pulp of *P. oceanica* the compromise set C had to be used: high anthraquinone concentration, soda concentration and temperature (1%, 30% and 150 ºC, respectively), besides low liquid/solid ratio (4) and time (30 min). With these conditions, the values of BR, EB, KI, KLS and VI were near their optimal. Low values of liquid/solid ratio reduce water consumption, which is of utmost importance in cellulose industries, and the decreasing time allows energy savings.

The operating conditions of set C were compared with those of soda-anthaquinone cellulose pulps from terrestrial raw materials founded in bibliography (Table 7) and its corresponding characterizacion values (Table 8).

Table 7
Operating conditions in soda-anthraquinone process for different lignocellulosic materials

	A (%)	S (%)	R	T (ºC)	t (min)	Reference
P. oceanica	1	30	4	150	30	This study
Woods raw materials						
E. globulus	0.1	21	8	153	65	López et al. 2015
P. halepensis	1.5	60	5	165	75	Haddad et al. 2009
Non-woods plants						
C. proliferus	0.1	12	4	170	30	López et al. 2004
H. funifera	1	10	8	155	30	Sánchez et al. 2010
L. leucocephala	0.1	29	8	169	90	Feria et al. 2012
P. fortunei	0.1	23	12	163	90	López et al. 2012
Agricultural residues						
Karkadeh stalks	0.1	25	5	160	60	Saeed et al. 2018
Millet stalks	0.1	25	5	160	60	Saeed et al. 2018
Sesame stalks	0.1	25	5	160	60	Saeed et al. 2018
Shorgum stalks	0.1	25	5	160	60	Saeed et al. 2018

A, S, R, T and t = Absolute values of anthraquinone concentration, soda concentration, liquid/solid ratio, temperature and time

As it was shown in Table 7, anthaquinone concentration used to prepare *P.oceanica* (1%) was in the range of used in wood raw materials (0.1–1.5%) and in non-wood raw materials (0.1-1%), however, was higher than anthraquinone concentrations used in agricultural residues. Soda concentration in set C (30%) was in the range of used in wood raw materials (21–60%), and higher than the rest of soda concentrations used. Liquid/solid ratio to cook *P.oceanica* was the lower along with the value of *C. proliferus.*

Temperature used for *P. oceanica* pulping was the lower. Time reaction for *P. oceanica* was the lower along with the time of *C. proliferus* and *H. funifera*.

Table 8
Characterization of soda-anthraquinone cellulose pulps of different lignocellulosic materials

	BR (%)	BD (ºSR)	E:B (%)	HOL (%)	KI	KLS (%)	VI (mL/g)	YI (%)
P. oceanica	55.14	41.70	4.73	65.26	4.17	3.49	1005.00	39.78
Wood raw materials								
E. globulus	22.40				60.40			69.10
P. halepensis		42.00		43.80	28.60	4.61	1470.00	
Non-wood raw materials								
C. proliferus	23.10		0.53	93.90	47.40	9.50	902.00	44.70
H. funifera		61.50			15.20		737.00	48.30
L. leucocephala	31.10	15.50	3.20	85.10	21.10	2.00	683.00	40.90
P. fortunei		19.00	2.55	93.60		9.60		51.00
Agricultural residues								
Karkadeh stalks	77.64	40.50			18.00		655.00	46.60
Millet stalks	66.30	55.50			12.43		665.00	42.40
Sesame stalks	67.25	38.00			18.17		635.00	43.30
Shorgum stalks	71.15	43.00			15.12		744.00	33.15

BR = brightness; BD = beating degree; E:B = ethanol-benzene extractables content; HOL = holocellulose content; KI = Kappa index KLS = lignin content; VI = viscosity; YI = yield

Comparing the results of cellulose pulp of *P.oceanica* with the characterizations of soda-anthraquinone pulps of lignocellulosic terrestrial materials, as can be observed in Table 8, results showed than the brightness (55.14%) was higher than the one obtained in cellulosic pulps of *E. globulus* (22.40%) and in cellulosic pulps of non-wood plants (23.10–31.10%). However, the results also showed that this brightness was lower than the observed in pulps of agricultural residues (66.30-77.64%). The beating degree (41.70 ºSR) was similar in value to the obtained in cellulosic pulp of *P.halepensis* (42.00 ºSR). These results are comprised with the ranges of cellulosic pulps of non-wood plants (19.00-61.50 ºSR) and those of agricultural residues (38.00-55.50 ºSR).

The content of ethanol-benzene extractables in the cellulosic pulp of *P. oceanica* was higher than that obtained from pulps of terrestrial non-woods plants. Also, the results of holocellulose obtained from cellulosic pulp of *P. oceanica* (65.26%) were higher than the shown in pulp of *P. halepensis* (43.80%); though, lower than values from pulps of non-wood materials (85.10–93.90%). Kappa index (4.17) in cellulosic pulp of *P. oceanica* was the lowest between of the stidied raw material, lignin content (3.49%) was lower than values on pulp of *P. halepensis* (4.61%) and was in the range of pulps of non-wood materials (2.00-9.60%). Only pulps of *P. halepensis* had higher viscosity than those of *P. oceanica*, probably because the soda concentration in the cooking process was higher.

Comparing cellulose pulp of *P.oceanica* to all pulps of terrestrial raw materials, brightness, beating degree, hollocelulose content, lignin content, viscosity and yield were in the respectives ranges (22.40-77.64%, 19.00-61.50 ºSR, 43.80–93.90%, 2.00-9.60%, 635–1470 mL/g and 33.15–69.10%). Also, cellulose pulp from *P. oceanica* had the highest content in ethanol-benzene extractables and the lowest kappa index.

Conclusions

Using a central composite factorial design in order to identify the optimum operating conditions (anthraquinone concentration, soda concentration, liquid/solid ratio, temperature and time) for *P.oceanica* soda-anthraquinone pulping provided equations which related the brightness, beating degree, ethanol-benzene extractives, holocellulose content, Kappa index, lignin content, viscosity and yield with the operational variables. These models predicted the responses with errors less than 2.50% for all except viscosity.

Pulp amenable to bleaching (i.e. with a low kappa index) was obtained using more drastic conditions of anthraquinone concentration, soda concentration and temperature, besides low liquid/solid ratio and time, reducing water consumption and decreasing time to save energy. In these conditions, the values of brightness, ethanol-benzene extractives, kappa index, lignin content and viscosity were near their optima.

Comparing the values used in compromise set C (anthraquinone concentration: 1%, soda concentration: 30%, liquid/solid ratio: 4, temperature: 150ºC, and time: 30 min) with the operating conditions reported for other lignocellulosic materials, cooking processes of *P. oceanica* required, in general term, similar dosages of anthraquinone and soda, but lower temperature, time, and liquid/solid ratio. When it comes to compare the results of the pulp characterization with the responses for terrestrial raw materials, all *P. oceanica* values were within their ranges, except for the content of ethanol-benzene extractables, which was the higher, and the Kappa index, which was the lower. Overall, it can be concluded that the valorization of onshore waste from *P. oceanica* towards cellulosic materials has promising potential, a potential that should be addressed more by future research in terms of specific cellulose-based products.

Declarations

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Ethical Approval

Not applicable

Competing interests

Authors declare that they have no known competing interests or personal relationships that could have appeared to infuence the work reported in this paper.

Authors' contributions

All authors made substantial contributions to the conception of the work, the acquisition and interpretation of data, and writing. All authors approve the manuscript. All authors agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

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Availability of data and materials

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Figures

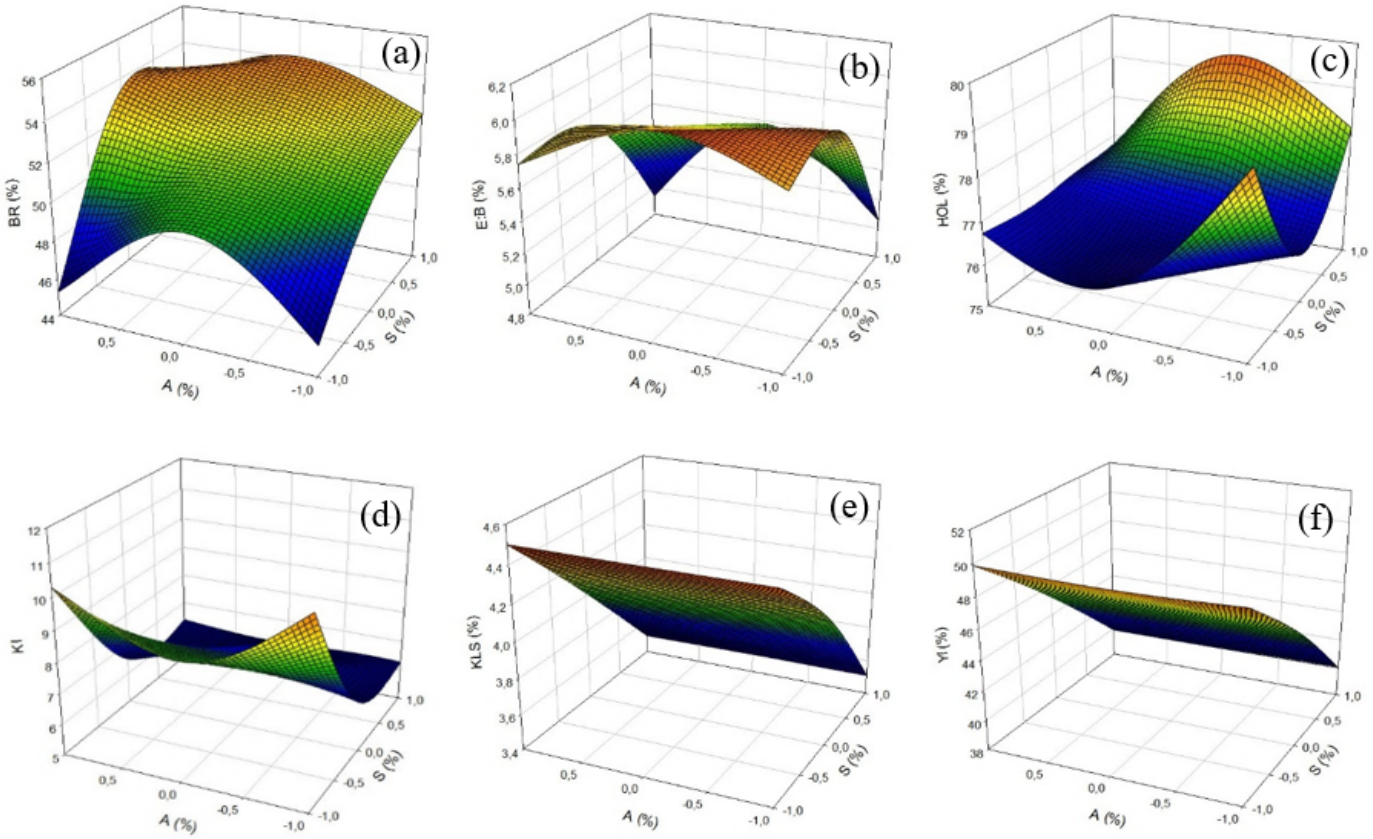

Figure 1

Response surface plots of brightness (a), ethanol-benzene extractables content (b) holocellulose content (c) kappa index (d) lignin content (e) and yield (f) of the pulp, as functions of anthraquinone concentration (A) and soda concentration (S)