Waste and Biomass Valorization
https://doi.org/10.1007/s12649-019-00795-7

ORIGINAL PAPER

Coagulation–Flocculation as an Alternative Way to Reduce the Toxicity of the Black Liquor from the Paper Industry: Thermal Valorization of the Solid Biomass Recovered

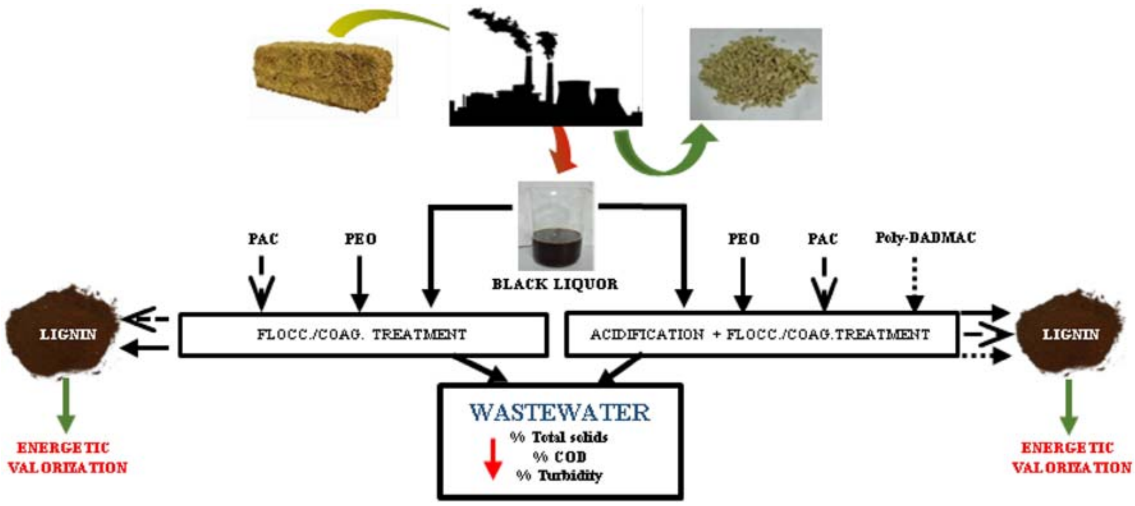
Juan Domínguez-Robles[1] · Mª del Valle Palenzuela[2] · Rafael Sánchez[1] · Javier Mauricio Loaiza[3] · Eduardo Espinosa[1] · Antonio Rosal[2] · Alejandro Rodríguez[1]

Received: 28 September 2018 / Accepted: 7 August 2019

Abstract

Pulp and paper mills generate a huge amount of wastewater and some of them, especially non-wood paper mills, do not possess recovery systems. In this research work, the effectiveness of coagulation–flocculation using poly (ethylene oxide), poly aluminium chloride and poly (dimethyl diallyl ammonium chloride) for the treatment of a black liquor obtained from a pulp mill (with wheat straw as the raw material) is reported. Furthermore, the calorific potential of the solid fraction generated after these treatments was investigated with the aim of enhancing this residue. Chemical oxygen demand (COD), turbidity and total solids (TS) were determined in the supernatants obtained from the different coagulation–flocculation processes. The treatment with poly (ethylene oxide) at pH 2.0 achieved the maximum reduction of TS (66%), COD (75%) and Turbidity (95%) in the black liquor and the precipitated solid fraction with the highest calorific value (19.9 MJ/kg).

Graphic Abstract



Keywords Pulp mill sludge · Acidification · Calorific potential · Biorefinery · Wastewater treatment

✉ Juan Domínguez-Robles
juadomrob@gmail.com

✉ Antonio Rosal
arosray@upo.es

Extended author information available on the last page of the article

Statement of Novelty

The optimal implementation of this type of technology is beneficial for the world. Black liquors generated in pulp processes of the paper industry have a vast environmental impact and the treatment to reduce this impact involves high economic costs. Furthermore, the recovery of the lignin in the black liquors, for its subsequent valorization, is in line with the circular economy concept and the creation of new employment opportunities.

This study delves into the optimal operating conditions necessary to improve the efficacy of the coagulation–flocculation processes applied to the treatment of contaminant black liquors. Moreover, an analysis of the calorific potential of the by-product recovered after the treatment of these liquors, for its possible energetic valorization, is presented.

Introduction

Sustainable development requires the optimal exploitation of both natural resources and the enormous quantities of residues generated by any human activity. In this regard, scientific interest is currently focused on getting the maximum use possible (and there is also an increasingly growing business interest in this) of the large amount of lignocellulosic biomass—as in the processes of the petroleum industry—used as a raw material or created as a residue in a multitude of industrial processes [1]. Following the exploitation of compounds in that biomass, a wide range of chemical substances can be synthesized and multiple materials produced, in addition to obtaining energy [2, 3].

Nowadays, many of the main biorefinery processes of lignocellulosic materials are aimed at the wide production of cellulose through pulping processes. As reference data, the production of pulp in 2013, at global level, was 170 million tons of pulp suitable for paper-making [4] and 6.4 million tons of dissolving pulp [5]. These tons are fundamentally produced through the exploitation of forest lignocellulosic materials (mainly, conifers and broadleaf species); although, recently, the use of alternative raw materials has risen, such as cereal straw (wheat, barley, rice), olive-tree pruning, or rapid-growth crops such as *Leucaena leucocephala* and *Chamaecytisus proliferus* [6–9].

Both wood and non-wood pulping processes generate large volumes of black liquors as by-products and/or liquid waste in the paper industry. Black liquors contain a high content of total dissolved solids (TDS, organic and inorganic materials), which is usually over 15% (w/w). TDS are mainly composed of lignin derivatives, low-molecular-weight compounds and the reagents employed in the pulping process [10]. This results in a high chemical oxygen demand (COD), turbidity and a large number of organic compounds, as well as an intense black/dark colour [11]. This characteristic colour is mainly due to the lignin and the degradation products formed during the pulping process. If these liquors are directly discharged into water, even in very small amounts, they can affect the aquatic life and food chain; and, therefore, decontaminating them before their spillage is necessary [12]. Nevertheless, the chemical composition of these residues makes the treatment of these liquors more complex, which can sometimes complicate the economic and environmental viability in the plants operating on a small scale and without systems for the recovery of reagents [13].

A vast amount of research has been done on the depuration of paper-industry black liquors through multitude of treatments with significant differences with regard to the effectiveness, the energy consumption and the economic cost. There are several processes including membrane-separation technology, anaerobic biological technology, ion-exchange, activated carbon, electrodialysis or combined technologies (membrane, aerobic biological, coagulation, flocculation), among others, that have been used for the treatment of the effluent from paper [14–21]. Coagulation and flocculation processes are one of the best options to reduce COD, TSS and even the colour of pulping wastewater, thanks to the addition of polymers (cationic/anionic) that interact, electrostatically, with the fraction of lignin in the black liquors, prompting the formation of chemical complexes and with it, their precipitation. Poly (ethylene oxide) (PEO) has been found to be an effective flocculant for pre-hydrolysis liquor (PHL) [22, 23]. Also, the use of an acidification process in conjunction with flocculants like PEO may reduce the quantity of flocculants required to cause the precipitation, and even improve the lignin removal [23, 24]. Other studies have proven the high effectiveness of flocculants, such as poly aluminium chloride (PAC), ferric chloride, ferrous sulphate or poly (dimethyl diallyl ammonium chloride) (poly-DADMAC), when applied to pulping wastewater [23–26].

The lignin recovered could be used as (1) an energy source [27, 28] (2) parent material of phenolic resins, adhesives or polyolefin [29, 30] (3) raw material for the production of carbon fibres [31] and (4) binding material for lithium batteries [32].

Research studies are currently aimed at the optimal recovery and later use of the fraction rich in lignin in order to raise the usage of the lignocellulosic biomass. Everything expounded is in line with the circular economy and explains why, in recent years, biorefinery of lignocellulosic materials has aroused great interest within the pulp and paper industry [33–35].

This research has studied the use of PEO, PAC and poly-DADMAC on black liquor, obtained after a pulping process, with the aim of analysing its effect on COD, turbidity and total solids. Moreover, the calorific value of the solid fraction separated through coagulation–flocculation processes (rich in lignin) has been determined, in order to assess and compare its possible energetic valorization.

Materials and Methods

Materials

Cereal straw used in pulping processes, at laboratory scale, was supplied by the company Ecopapel S.L. (Écija, Spain). The straw was manually sampled so as to eliminate the undesired material (mainly stones and seeds) and was stored in plastic bags, at room temperature, until it was pulped in the reactor.

To perform this work, different coagulants were used. Poly (dimethyl diallyl ammonium chloride) (poly-DADMAC, solution 20 wt% in weight) with a high molecular weight (average 400–500 kDa) was purchased in Sigma-Aldrich (Madrid, Spain). Poly (ethylene oxide) (PEO, 600 kDa) was also obtained from Sigma-Aldrich (Madrid, Spain). Poly aluminium chloride solution (PAC, 10%) was provided by Brenntag (Seville, Spain).

Pulping Process

To conduct the pulping process, a 15-L batch cylindrical reactor (Metrotec®, Guipúzcoa, Spain) was heated by an outer jacket heater and connected to a rotary axle to provide proper agitation. This reactor monitored pressure, temperature, and cooking time. Wheat straw was cooked under the following operating conditions: 7% NaOH (over dried material) at 100 ± 1 °C for 150 min, and the liquid/solid ratio was 10:1. These operating conditions are the same as those used in the industrial process (Specel®) performed by Ecopapel S.L.

After performing the pulping process, the liquid fraction (black liquor) was separated from the solid (unbleached wheat straw pulp), through a sieve with 2-mm holes. The characteristics of the wheat straw pulp obtained have been previously reported [9].

Coagulation–Flocculation

After recovering the wheat straw pulp, the black liquor generated in this process was treated with different coagulation–flocculation processes in order to minimize its toxicity. Also, the by-product obtained was used to produce energy.

On the basis of the complexation of lignin with coagulants, such as PEO/poly-DADMAC/PAC, showing our previous study [36] and different works of literature [22, 23, 37–40], the experimental design of this study has been raised with different conditions (pH and concentration of reagent) under which these coagulants could be most effective for the reduction of the environmental impact of this type of waste. To this end, three coagulants were added to the black liquor under different conditions: PEO (1200, 1500, and 1714 mg/L), poly-DADMAC (191, 250, 308 and 364 mg/L) and PAC (990, 1190, 1575, 1961 and 2913 mg/L). These concentrations were selected based on the previous results, as well as the different pretreatments performed before the flocculation–coagulation treatments previously reported in the literature, using PEO [22, 23, 37], poly-DADMAC [38, 39] and PAC [26, 40]. In some of the five tests performed, a previous acidification of the black liquors was carried out to achieve the optimum conditions of flocculants (see Table 1). This acidification entails the addition of sulphuric acid, to the initial solution of black liquors, to reach pH 2.

After the coagulation–flocculation processes, the different solutions were centrifuged for 20 min at 8000 rpm and the supernatant (liquid fraction) was recovered. The insoluble fraction was dried in an oven at 60 °C overnight and weighed. Additionally, a diagram of the configuration of the process to improve the removal of the chemical oxygen demand (COD), turbidity and total solids is presented in Fig. 1.

Liquid Fraction Characterization

The analysis of physical and chemical parameters of the different liquid fractions obtained after the flocculation process, and the initial black liquor as well, were performed in duplicate. The density was determined by dividing their total mass by their total volume. The turbidity was measured using a HI 93703 Turbidimeter (HANNA instruments, Guipúzcoa, Spain) at room temperature (UNE-EN 7027:2001). COD was determined by the standard dichromate method (UNE 77004:2002). Dry matter was evaluated based on its weight loss (determined as the steady weight) at 105 °C for 24 h (UNE 77030:2015). Volatile Solids (VS) and ash content were obtained based on their weight loss after combustion at 575 °C for 3 h. Finally, the pH and the electrical conductivity were analysed with a meter of pH and conductivity (Crison Instruments, Barcelona, Spain).

Table 1 Experimental conditions of the coagulation–flocculation processes

Tests	Coagulant/flocculant	Previous acidification	Time (min)	Stirring (rpm)
1	PEO	No	30	100
2	PEO	Yes	30	100
3	Poly-DADMAC	Yes	10	150
4	PAC (10%)	No	2/8	150/50
5	PAC (10%)	Yes	2/8	150/50

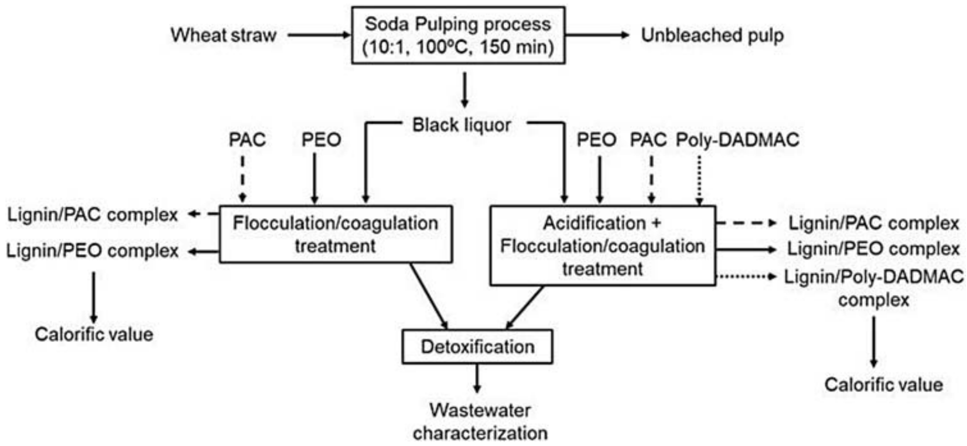


Fig. 1 Diagram of the whole process

Solid Fraction Calorific Value

The data refers to a base constant calculation; all operations were referred to on a dry basis (moisture-free). The moisture content was determined applying the standard UNE 77030:2015 (dried in an oven at 105 °C for 24 h).

The gross heating values (constant volume) were determined according to "CEN/TS 14918:2005 (E) Solid biofuels—"Method for the determination of calorific value" and UNE 164001 EX standards by using a Parr 6300 automatic isoperibol calorimeter (bomb calorimeter). Sample pellets of 1.0 g were used for each analysis. A cotton thread was attached to a platinum wire of ignition and placed in contact with the pellet. The bomb (a stainless steel box) of the calorimeter was filled with oxygen at 25 °C and 1.0 cm^3 of water was added to it. The bomb was then placed inside the isothermal jacket of the calorimeter, with an air-gap separation of 10 mm between the jacket wall surface and the bomb wall surface. The electrical energy for ignition was determined according to the change of potential through a 1256 or 2900 µF capacitor when discharged from about 40 V through a platinum wire. The calorimeter jacket was maintained at a constant temperature making the water flow at 27 °C.

Results and Discussion

Initial Characterization of the Liquid Fraction

Before the coagulation–flocculation treatments, the physicochemical properties of the black liquor were analysed. Results are presented in Table 2. The percentage of total solids was significant in the liquid fraction and more than 50%, dry weight were volatile solids. In turn, most of these volatile solids correspond to the lignin in the black liquors (16 g/L) as described in our previous study [36]. These results can explain that the values of turbidity and COD were high. In any case, the data obtained is between the levels of the paper-industry liquors, studied by other authors and to which the same coagulants and flocculants were applied [24, 41].

Effectiveness of Coagulation–Flocculation Processes

Effect of PEO Dosage on the Parameters of the Process at Acid and Neutral pH of Black Liquor

Figure 2 shows the percentage of removal of total solids and the percentages of COD and turbidity reduction in the black liquor after its treatment with different proportions of PEO at pH 7.0 and 2.0.

Amongst the treatments with the same pH, the increase of the proportions of PEO did not result in significant differences of the percentage of total solids removed; nevertheless, this behaviour was different when we compare tests with different pH values. Acidification resulted in a higher removal of total solids (around 20 percentage points) than with the treatments with neutral pH. These results can be explained by the synergy of two factors, to be taken into account in processes at low pH levels: (1) PEO reacts with the phenolic groups of the lignin inducing the formation of stable complexes with a high molecular weight that end up

Table 2 Physicochemical characteristics of the black liquor from the pulp process results correspond to the average and the standard deviation (n = 2)

	pH	Total solids (%)	Volatile solids (%)	Ash (%)	Turbidity (NTU)	COD (mg/L)	Lignin (g/L)
Black liquor	7.05 ± 0.05	4.01 ± 0.05	2.35 ± 0.06	1.65 ± 0.01	3112.33 ± 60.81	35,733.99 ± 1123.01	16.06 ± 0.10

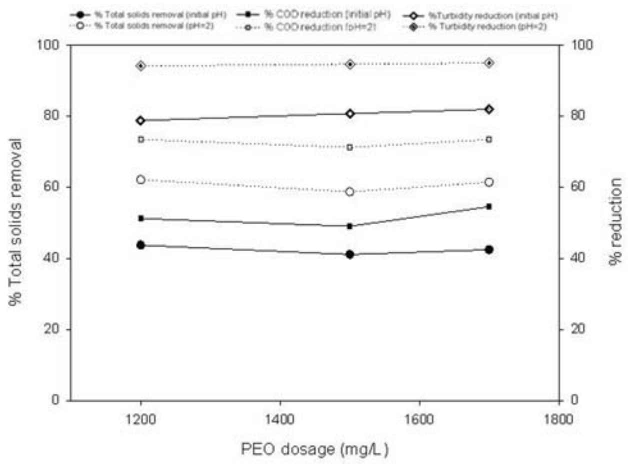


Fig. 2 Effect of the PEO dosage on the total solids, COD and turbidity of the liquid fraction with neutral pH ad with pH 2.0

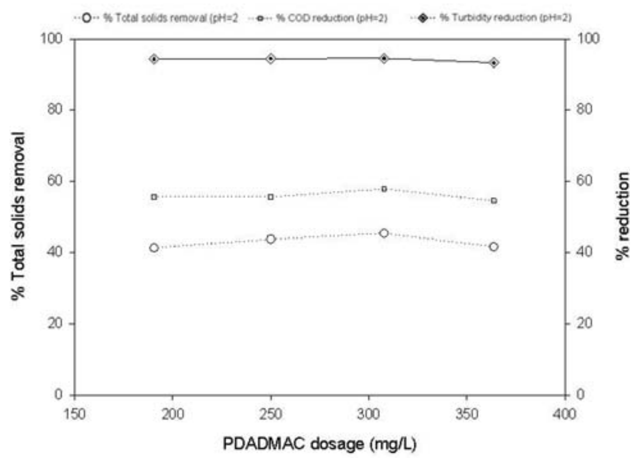


Fig. 3 Effect of the dosage of poly-DADMAC on the total solids, COD and turbidity of the liquid fraction, at pH 2.0

precipitating [22, 42, 43]; and (2) anionic organic molecules interact with metallic cations which form insoluble metallic complexes that remain stable [44]. The highest percentage of removal of total solids (66% approximately) was achieved when adding 1200 mg/L of PEO (pH 2.0).

Regarding the evolution of the percentages of COD and turbidity reduction, results proved that there were no major differences observed when increasing PEO proportions between experiments at the same pH. Nevertheless, when comparing experiments with different pH, the highest removal percentages were observed at pH 2 (around 20 percentage points for COD and around 15 percentage points for turbidity). Literature comprehensively explains the reduction of COD at acid pH, based on the sum of two effects (1) the interaction of PEO with the oxygen atoms in the phenolic, carboxyl and hydroxyl groups of organic species, such as the lignin; and (2) the acidic environment creates a screen effect on some of the anionic charges in the structure of lignin macromolecules, increasing the interaction amongst them and the lignin/PEO complexes [23]. The most significant percentages of reduction (75%, COD and 95% turbidity) were obtained with the proportion 1200 mg/L of PEO (pH 2.0). This COD reduction was significantly higher than the maximum percentage (32%) that Shi et al. [37] reached when applying 400 mg/L PEO (molecular weight, 800 kDa) on liquors obtained from pulping kraft processes.

Effect of Poly-DADMAC Dosage on the Parameters of the Process at Acid pH of Black Liquor

PDADMAC molecular weight and pH have a notorious impact on the efficacy of the flocculation process. Several authors point out that performing flocculation processes with low-molecular-weight PDADMAC and with high pH values (> 9.0) are not optimum conditions for the treatment of black liquors of the paper industry [38, 39]. In this study, the liquid fraction of the black liquor was acidified to pH 2 with concentrated sulphuric acid and, later, with different proportions of high-molecular-weight PDADMAC ($40 \cdot 10^4$ g/mol). Figure 3 shows the percentage of total solids removed and the percentages of COD and turbidity reduction in 4 tests with different dosages of PDADMAC. With the operating conditions established for the tests, there were no significant differences amongst the parameters being studied, except in the case with the highest proportion of PDADMAC, where a slight decrease of the efficacy of the process was observed.

PDADMAC has a high-density cationic charge which becomes neutralized by the density of negative charges of species, such as the lignin, in these kinds of black liquors [45]. Nevertheless, in the event of an excess of PDADMAC, a re-stabilisation of positive charges can occur and, with it, repulsion phenomena may appear [46]. This can explain the behaviour of the test with the highest amount of flocculant.

With the dosages of PDADMAC applied (between 191 and 364 mg/L) at pH 2.0, a reduction on the content of total solids, COD, and turbidity was achieved, reaching average percentage values of 42%, 57% and 94%, respectively. These values are similar to the ones obtained in other studies on paper-industry black liquors treated with PDADMAC of different molecular weights, with proportions between 0.4–160 mg/L [38, 39].

Effect of PAC Dosage on the Parameters of the Process at Acid and Neutral pH of Black Liquor

Figure 4 shows the effects on the parameters of evaluation of coagulation processes on black liquors, to which different proportions of PAC were applied, with the original pH (7.0) and with pH 2.0. Overall, the results revealed that the acidification of the environment fostered the indicators of the process when the dosage of PAC was $\leq$ 1960 mg/L; whereas with 2913 mg/L, the efficacy of the treatment experienced an increase with a neutral pH. This behaviour was similar to the one revealed by the studies of Ahmad et al. [47] with the same type of waste, to which different dosages of PAC (200–1400 mg/L) were applied with pH levels between 5 and 10.

Amongst the experiments at acid pH, there were no significant differences in the results for the process indicators, except in the case with the highest dosage (2913 mg/L), where a slight decrease of the percentages of COD and turbidity reduction was observed. This result may be due to the important role performed by pH on metallic hydroxides with a positive charge originated by the hydrolysis of the metallic coagulant dissolved in water, according to Eq. 1 [48].

$$xM^{3+} + yH_2O = M_x(OH)_y^{(3x-y)+} + yH^+ \tag{1}$$

It is known that these metallic species are hydrophobic and, moreover, these are adsorbed to the surface of anionic organic particles, diminishing their solubility. Specifically, the aluminium species formed in the solution of PAC has a strong trend towards the formation of insoluble complexes with a number of ligands, especially, with polar molecules and with functional groups containing oxygen, such as the hydroxyl or carboxyl groups [49]. This reaction (Eq. 1) is shifted towards the left, as pH decreases; and protons occupy the positions of negative-charge density of the organic molecules, reducing the coagulant efficacy [50, 51].

In our study, with acid pH (2.0), the average values of the percentages of total solids removal, COD and turbidity

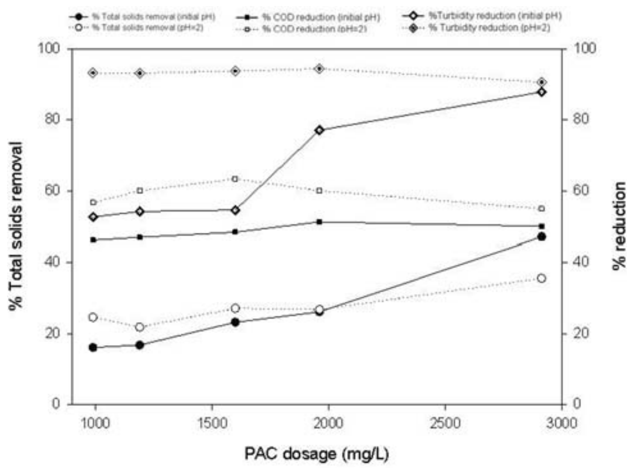


Fig. 4 Effect of the dosage of PAC on total solids, COD and turbidity of the liquid fraction, at neutral pH and at pH 2.0

reduction were 27.2%, 59.0% y 92.9%, respectively. This COD reduction was similar to the one achieved by Felissia et al. [13] in their study on the efficacy of this type of coagulant on paper-industry black liquors with pH 5.0 and a far superior dosage (6000 mg/L) than the one used in our study; nonetheless, in Srivastava et al. [40] with a dosage of 3000 mg/L PAC and with pH 3, a higher percentage of COD reduction was achieved (approximately 20 percentage points more).

As per the treatments at neutral pH, a significant decrease in the content of total solids and turbidity was observed with the highest proportions of PAC (1961 mg/L and 2913 mg/L); whereas COD barely varied. Overall, the highest efficacy was achieved with a dosage of 2913 mg/L of PAC (reduction of total solids, COD and turbidity around 47%, 50% and 88%, respectively). This reduction of COD noticeably surpassed (approximately 35 percentage points) the one achieved by the work of Irfan et al. [26] with a dosage of 800 mg/L of PAC on black liquors, at neutral pH.

Solid Fraction Recovery and Calorific Potential

The effects of PEO dosage on the amount of precipitate of black liquor is presented in Fig. 5a. With both neutral pH and pH 2, it was observed that the increase in the amount of PEO did not cause any significant differences amongst the quantity of precipitated mass in the different tests. Nevertheless, overall, the treatment with pH 2.0 achieved an increase of the precipitated mass, of 22 g/L approximately, compared to the one with neutral pH.

The amount of precipitate from the black liquor treated with poly-DADMAC at pH 2 is presented in Fig. 5b. When increasing the concentration of poly-DADMAC, the amount of precipitate reached its maximum (27 g/L) with 308 mg/L of poly-DADMAC. Furthermore, it was observed that an increase exceeding 308 mg/L of poly-DADMAC had a negative effect on the lignin complexes formation; a fact that has been previously reported [46, 52]. Consequently, the optimum dosage of PDADMAC at pH 2 was 308 mg/L because lower or higher dosages mean lower reductions of COD, total solids as well as the amount of precipitate (Fig. 3). Accordingly, for this dosage (308 mg/L), the amount of precipitate at the neutral pH was also measured (5.1 g/L) (data not shown), and it was much lower than the one obtained at pH 2 (27 g/L), as well as the turbidity, COD or total solids removal (data not shown). For this reason, this experiment was discarded.

The effects of PAC on the process of coagulation–flocculation are represented in Fig. 5c. At both conditions of pH, it was observed that increasing the dosage of PAC made the amount of solid fraction separated larger. This reality was more pronounced with the highest dosage of

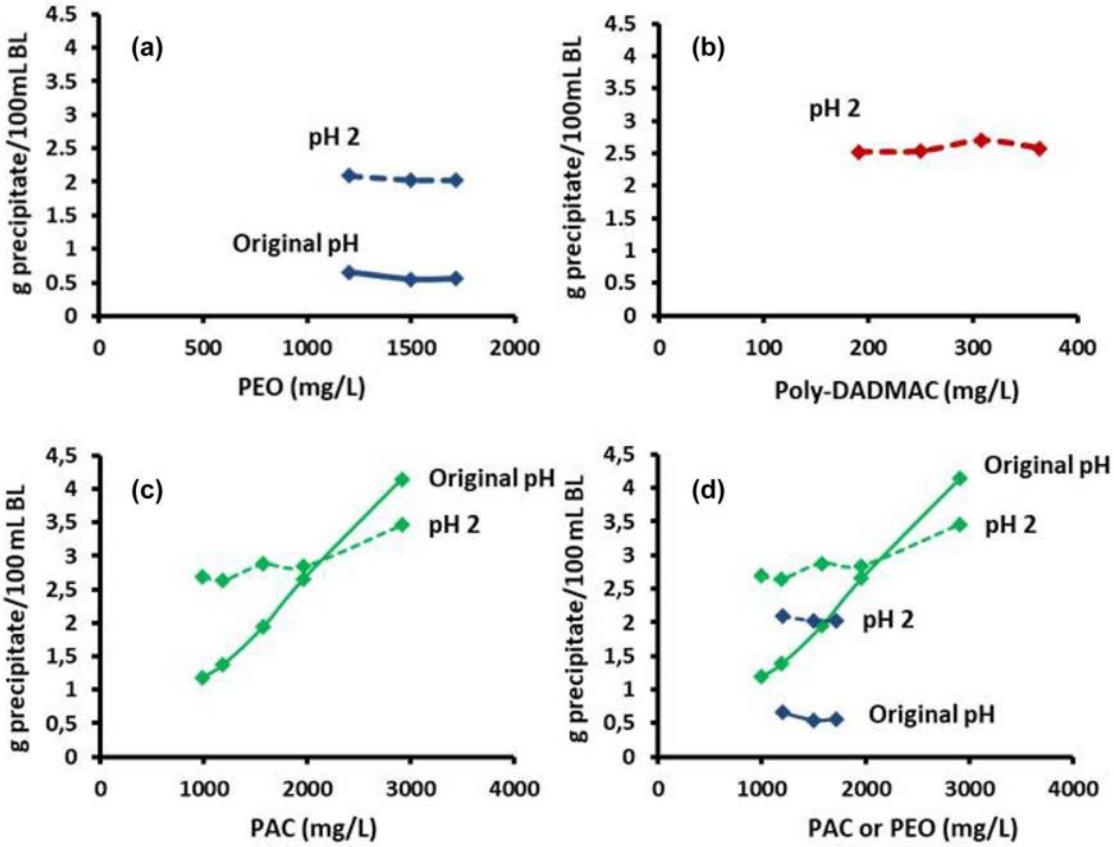


Fig. 5 Recovered solid fraction of the coagulation–flocculation processes

PAC (2913 mg/L) with neutral pH, obtaining a precipitation of around 42 g/L of the solid fraction. Finally, a comparison between PEO and PAC is presented in the Fig. 5d to observe the effects of both treatments with and without acidification.

Once the solid fraction was separated through the different processes of coagulation–flocculation, an analysis to study the calorific potential of that fraction (rich in lignin) was performed. Figures 6, 7, and 8 show the calorific value versus the concentration (mg/L) used for each flocculant that was tested. Regarding the calorimetric determinations, they have been obtained according to the elementary-type compositions provided in the CEN/TS 14918:2005 standard for the determination of the calorific value in solid biofuels. As per the units used (J/g), it is considered that an internal error in the replicates of 120 J/g is within the accuracy margin of the method. The results offered are averages of at least two replicates that meet this criterion.

In the coagulation–flocculation experiments performed with PEO at the original pH, very low flocculation efficiency was observed (Fig. 6). The residues after combustion represented between 12.3 and 23.4%, which would explain the substantial drop in the calorific value with regard to the acidified black liquor, due to the lower relative presence of organic matter. In the case of the experiments conducted by combining acidification up to pH 2 and PEO addition, an increase between 43.4 and 54.4% is observed compared to those with the mere addition of the flocculant.

The results obtained, using poly-DADMAC, are presented in Fig. 7. An important rise in the calorific value was found when the concentration increased from 191 to 250 mg/L. Nevertheless, with higher concentrations, there weren't any significant differences amongst the tests.

The results of the experiments performed with PAC are presented in Fig. 8. With the use of this flocculant a great precipitate was obtained at its highest concentration (Fig. 2c). However, the increase of the concentration of PAC had a slight negative impact on the calorific value, mainly due to the inorganic character of this compound. Indeed, after the combustion, the final residue ranged from 14.4 to 24.4% when the experiment was performed at the original pH of the black liquor and 6.9 to 16.3% when the black liquor was previously acidified, up to pH 2.0. Furthermore, combining the previous acidification of the black liquor with the PAC addition resulted in higher values of the calorific value of the precipitate.

Fig. 6 Calorific value achieved using poly (ethylene oxide) (PEO)

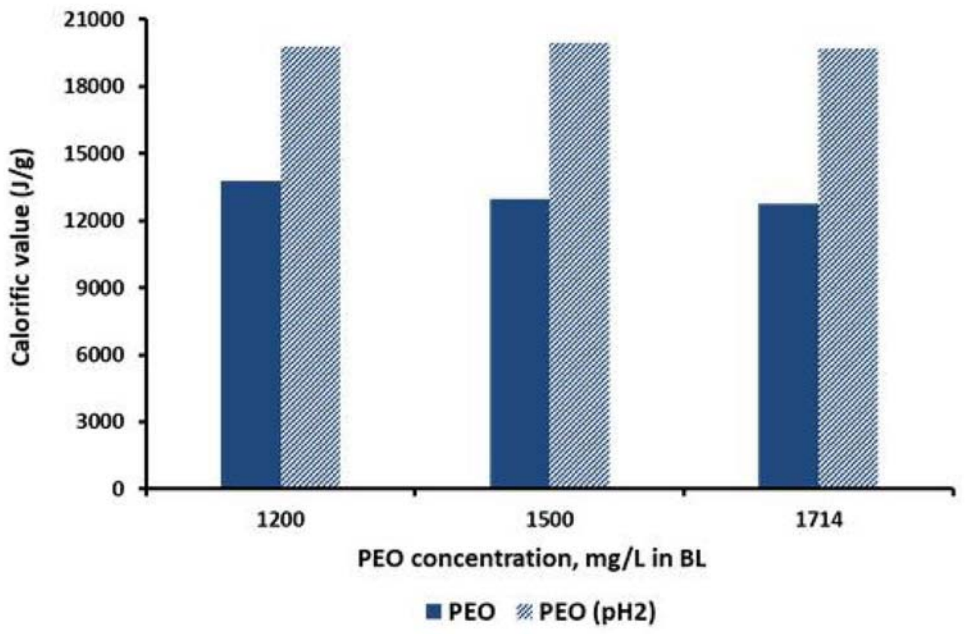
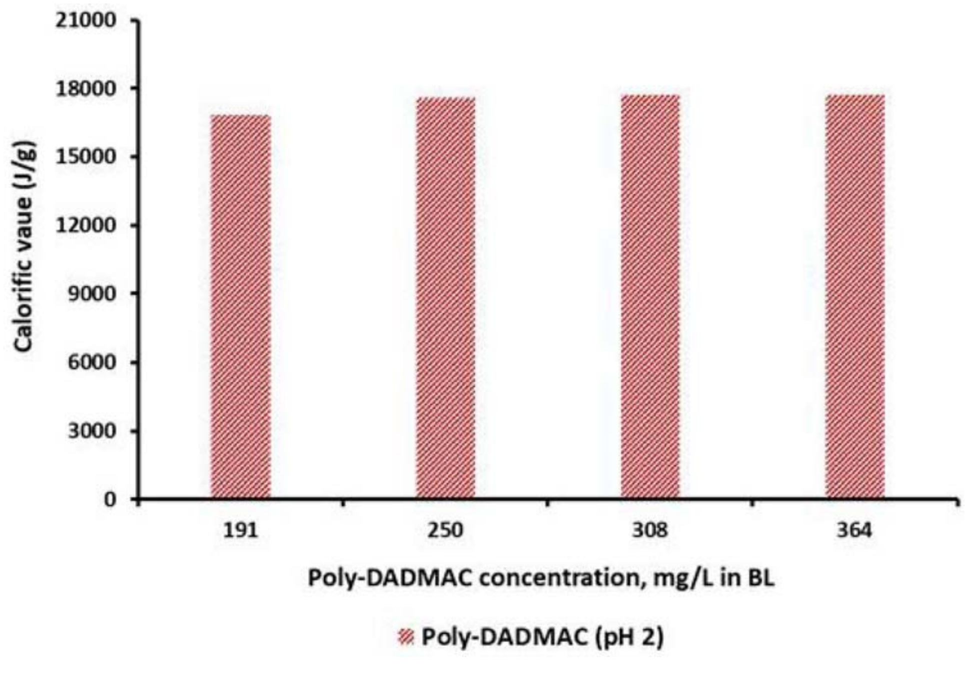


Fig. 7 Calorific value achieved using poly (dimethyl diallyl ammonium chloride) (poly-DADMAC)



Furthermore, Table 3 shows selected gross heating values reported by several authors [53–56]. In short, softwood and related materials typically have values in the area of 20.0 MJ/kg, and hardwood such as that from *Eucalyptus globulus* generate about 18.0 MJ/kg, whereas other deciduous plants (and their residues) give lower values.

Regarding the calorific potential of each test, the best results were obtained with the solid fraction that was separated with the addition of PEO at pH 2.0 (19.7–19.9 MJ/kg) and the one obtained with poly-DADMAC (16.8–17.7 MJ/kg). Comparing these results with the gross heating values of many lignocellulosic materials, provided by different authors (see Table 3), it is observed that, in the first case, the values were similar to the data obtained in conifer species or their by-products; and, in the second one, the calorific value range was similar to the one obtained with hardwood species such as the *E. globulus*.

Taking into account the information provided in Figs. 5, 6, 7, 8 and Table 4 shows the inferior and superior limits obtained for the calorific value of the solid fraction per litre of black liquor, treated in each test. Results indicated that with dosages of 2913 mg/L of PAC (pH 2.0 and 7.0), of 308 mg/L of PDADMAC (pH 2.0) and of 1200 mg/L of PEO (pH 2.0) the most significant performance was achieved, with regard to the gross calorific values of the solid fraction obtained per litre of treated black liquor (0.59 MJ, 0.53 MJ, 0.48 MJ and 0.45 MJ, respectively).

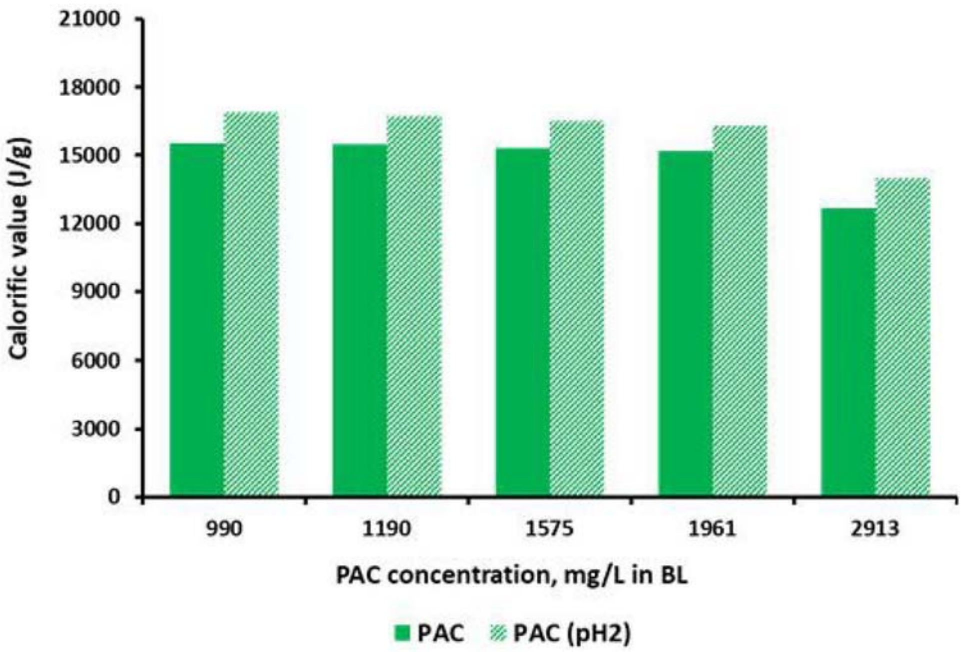


Fig. 8 Calorific value achieved using poly aluminium chloride (PAC)

Table 3 Gross heating values for different raw materials

Raw material	Gross calorific value (MJ/kg)	References
Pine cone	27.4	Brebu et al. [54]
Wood bark, Agba, Iroko, Atlas cedar, wheat straw	20.5–20.3	Demirba [53], Telmo et al. [56]
Spruce wood, softwood, common douglas fir, pinewood	20.1–19.6	Demirba [53], Telmo et al. [56], Satyanarayan et al. [55]
Hazelnut shell, Hazelnut seedcoat, beech wood, narrow-leafed ash, Jatobá, olive husk, Sapele, *Ailanthus* wood	19.3–19.0	Demirba [53], Telmo et al. [56]
Populus euro-americana, hardwood, English oak, *Castanea sativa*, Sycamore maple, Sweet cherry, Babylon willow	18.8–18.2	Demirba [53], Telmo et al. [56]
Corn stover, tobacco stalk, *Eucalyptus globulus*, tobacco leaf, tea waste	17.8–17.0	Demirba [53], Telmo et al. [56], Satyanarayan et al. [55]
Timothy grass, barley straw	16.7–15.7	Satyanarayan et al. [55]

Table 4 Inferior and superior limits of the calorific value in each test

	PEO pH 7.0	PEO pH 2.0	PDADMAC pH 2.0	PAC pH 7.0	PAC pH 2.0
Gross calorific value (MJ) of the fraction of precipitate per litre of treated black liquor	(0.07–0.11)	(0.39–0.45)	(0.42–0.48)	(0.19–0.53)	(0.44–0.59)

Conclusions

Black liquors, treated with different coagulants/flocculants (PEO, poly-DADMAC and PAC) with different proportions and pH (7.0, 2.0), had their content of total solids (15–66%), COD (45–75%) and turbidity (50–95%) reduced. Overall, under the operating conditions established for the different tests, the efficacy of the treatment was higher with an acid pH (2.0) and regardless of the dosage used; with the exception of the PAC, where the higher the dosage used with a neutral pH, the more effective the treatment was.

With regard to the calorific value of the precipitated solid fraction, the decrease of pH to 2 achieved the best results (> 15 MJ/kg) in all cases; with the exception of the treatment with PAC with the highest dosage (2913 mg/L) due to the pronounced inorganic nature of this coagulant.

The use of 1200 mg/L of PEO with pH 2.0 achieved the most significant results of removal of total solids (66%), COD reduction (75%), turbidity decrease (95%) and calorific value of the precipitated solid fraction (19.9 MJ/kg). Nevertheless, with this test, the calorific value (0.45 MJ) of the gross precipitated mass (20 g/L) per litre of black liquor treated was lower than with the dosages of 2913 mg/L of PAC with pH 2 and 7 (0.59 MJ and 0.53 MJ, respectively).

As an overall conclusion, it can be claimed that the treatments applied, under the operating conditions established, would allow for a noticeable reduction of the contamination of the black liquors generated by the paper industry and for the energetic valorization of the solid fraction recovered.

Acknowledgements The authors wish to acknowledge BASF Corporation for providing us with different coagulant samples to use in this study. The authors would also like to thank Ministry of Economy & Competitiveness of Spain (Project CTQ2013-46804-C2-2R), University of Córdoba (RNM 2323) and University Pablo de Olavide (PPI 1401) and, finally, we would like to thank MatchBetter Translations, namely, Carmen Torrella, for reviewing and translating our papers.

Compliance with Ethical standards

Conflict of interest All the co-authors, and the responsible authorities as well, have agreed on and authorized the publication of this manuscript upon the final revised version. There is no conflict of interest. This work has not been published previously, and it is not under consideration for publication elsewhere. Furthermore, if accepted, it will not be published elsewhere either, in English or in any other language, including electronically, without the written consent of the copyright-holder.

References

1. Liguori, R., Faraco, V.: Biological processes for advancing lignocellulosic waste biorefinery by advocating circular economy. Bioresour. Technol. **215**, 13–20 (2016)
2. Liguori, R., Amore, A., Faraco, V.: Waste valorization by biotechnological conversion into added value products. Appl. Microbiol. Biotechnol. **97**, 129–6147 (2013)
3. Salehian, P., Karimi, K., Zilouei, H., Jeihanipour, A.: Improvement of biogas production from pine wood by alkali pretreatment. Fuel **106**, 484–489 (2013)
4. RISI, Inc.: Annual review of global pulp & paper statistics (2014)
5. RISI, Inc.: World dissolving pulp monitor (2014)
6. López, F., García, M.M., Yánez, R., Tapias, R., Fernández, M., Díaz, M.J.: Leucaena species valoration for biomass and paper production in 1 and 2 year harvest. Bioresour. Technol. **99**, 4846–4853 (2008)
7. Jiménez, L., Serrano, L., Rodríguez, A., Sánchez, R.: Soda-anthraquinone pulping of palm oil empty fruit bunches and beating of the resulting pulp. Bioresour. Technol. **100**, 1262–1267 (2009)
8. Requejo, A., Rodríguez, A., Colodette, J.L., Gomide, J.L., Jiménez, L.: TCF bleaching sequence in kraft pulping of olive tree pruning residues. Bioresour. Technol. **117**, 117–123 (2012)
9. Vargas, F., González, Z., Sánchez, R., Jiménez, L., Rodríguez, A.: Cellulosic pulps of cereal straws as raw material for the manufacture of ecological packaging. BioResources **7**, 4161–4170 (2012)
10. Huang, G., Shi, J.X., Langrish, T.A.G.: A new pulping process for wheat straw to reduce problems with the discharge of black liquor. Bioresour. Technol. **98**, 2829–2835 (2007)
11. Monte, M.C., Fuente, E., Blanco, A., Negro, C.: Waste management from pulp and paper production in the European Union. Waste Manag. **29**, 293–308 (2009)
12. Miège, C., Choubert, J.M., Ribeiro, L., Eusèbe, M., Coquery, M.: Removal efficiency of pharmaceuticals and personal care products with varying wastewater treatment processes and operating conditions-conception of a database and first results. Water Sci. Technol. **57**, 49–56 (2008)
13. Felissia, F.E., Barboza, O.M., Bengoechea, D.I., Area, M.C.: Reduction of the recalcitrant COD of semi-chemical pulp effluents by chemical precipitation. Rev. Cienc. Tecnol. **13**, 36–42 (2010)
14. Koyuncu, I., Yalcin, F., Ozturk, I.: Color removal of high strength paper and fermentation industry effluents with membrane technology. Water Sci. Technol. **40**, 241–248 (1999)
15. Shawwa, A.R., Smith, D.W., Sego, D.C.: Color and chlorinated organics removal from pulp mills wastewater using activated petroleum coke. Water Res. **35**, 745–749 (2001)
16. Thompson, G., Swain, J., Kay, M., Forster, C.F.: The treatment of pulp and paper mill effluent: a review. Bioresour. Technol. **77**, 275–286 (2001)
17. Sreekanth, D., Sivaramakrishna, D., Himabindu, V., Anjaneyulu, Y.: Thermophilic treatment of bulk drug pharmaceutical industrial wastewaters by using hybrid up flow anaerobic sludge blanket reactor. Bioresour. Technol. **100**, 2534–2539 (2009)
18. Ji, J., Qiu, J., Wai, N., Wong, F.S., Li, Y.: Influence of organic and inorganic flocculants on physical–chemical properties of biomass and membrane-fouling rate. Water Res. **44**, 1627–1635 (2010)
19. Khosravi, M., Badalians, G., Soltanzadeh, A., Riahi, R., Reza, H.: Membrane process design for the reduction of wastewater color of the Mazandaran pulp-paper Industry. Iran. Water Resour. Manag. **25**, 2289–3004 (2011)
20. Liu, T., He, Z., Hu, H., Ni, Y.: Treatment of APMP pulping effluent based on aerobic fermentation with *Aspergillus niger* and post-coagulation/flocculation. Bioresour. Technol. **102**, 4712–4717 (2011)
21. Xu, G., Yan, G., Yan, J.: An integrated green process for beneficial utilization of pulping black liquor. Waste Biomass Valor. **4**, 497–502 (2013)
22. Negro, C., Fuente, E., Blanco, A., Tijero, J.: Flocculation mechanism induced by phenolic resin/PEO and floc properties. AIChE. J. **51**, 1022–1031 (2005)

23. Shi, H., Fatehi, P., Xiao, H., Ni, Y.: A combined acidification/PEO flocculation process to improve the lignin removal from the pre-hydrolysis liquor of kraft-based dissolving pulp production process. Bioresour. Technol. **102**(8), 5177–5182 (2011). https://doi.org/10.1016/j.biortech.2011.01.073
24. Garg, A., Mishra, I.M., Chand, S.: Effectiveness of coagulation and acid precipitation processes for the pre-treatment of diluted black liquor. J. Hazard. Mater. **180**(1–3), 158–164 (2010). https://doi.org/10.1016/j.jhazmat.2010.04.008
25. Wong, S.S., Teng, T.T., Ahmad, A.L., Zuhairi, A., Najafpour, G.: Treatment of pulp and paper mill wastewater by polyacrylamide (PAM) in polymer induced flocculation. J. Hazard. Mater. **135**, 378–388 (2006)
26. Irfan, M., Butt, T., Imtiaz, N., Abbas, N., Khan, R.A., Shafique, A.: The removal of COD, TSS and colour of black liquor by coagulation–flocculation process at optimized pH, settling and dosing rate. Arab. J. C. **10**, 2307–2318 (2013). https://doi.org/10.1016/j.arabjc.2013.08.007
27. Leschinsky, M., Zuckerstätter, G., Weber, H.K., Patt, R., Sixta, H.: Effect of autohydrolysis of *Eucalyptus globulus* wood on lignin structure. Part 1: comparison of different lignin fractions formed during water prehydrolysis. Holzforschung **62**, 645–652 (2008)
28. Coimbra, R.N., Paniagua, S., Escapa, C., Calvo, L.F., Otero, M.: Thermal valorization of pulp mill sludge by co-processing with coal. Waste Biomass Valor. **7**, 995–1006 (2016)
29. Stewart, D.: Lignin as a base material for materials applications: chemistry, application and economics. Ind. Crops Prod. **27**, 202–207 (2008)
30. Domínguez-Robles, J., Tarrés, Q., Delgado-Aguilar, M., Rodríguez, A., Espinach, F.X., Mutjé, P.: Approaching a new generation of fiberboards taking advantage of selflignin as green adhesive. Int. J. Biol. Macromol. **108**, 927–935 (2017)
31. Van Heiningen, A.: Converting a kraft pulp mill into an integrated forest biorefinery. Pulp Pap. Can. **107**, 38–43 (2006)
32. Domínguez-Robles, J., Sánchez, R., Díaz-Carrasco, P., Espinosa, E., García-Domínguez, M.T., Rodríguez, A.: Isolation and characterization of lignins from wheat straw: application as binder in lithium batteries. Int. J. Biol. Macromol. **104**, 909–918 (2017)
33. Amidon, T.E., Wood, C.D., Shupe, A.M., Wang, Y., Graves, M., Liu, S.: Biorefinery: conversion of woody biomass to chemicals, energy and materials. J. Biobased Mater. Bioenergy **2**, 100–120 (2008)
34. Saeed, A., Jahan, M.S., Li, H., Liu, Z., Ni, Y., Van Heiningen, A.: Mass balances of components dissolved in the pre-hydrolysis liquor of kraft-based dissolving pulp production process from Canadian hardwoods. Biomass Bioenergy **39**, 14–19 (2010). https://doi.org/10.1016/j.biombioe.2010.08.039
35. Yu, Y., Zeng, Y., Zuo, J., Ma, F., Yang, X., Zhang, X., Wang, Y.: Improving the conversion of biomass in catalytic fast pyrolysis via white-rot fungal pretreatment. Bioresour. Technol. **134**, 198–203 (2013)
36. Domínguez-Robles, J., Espinosa, E., Savy, D., Rosal, A., Rodríguez, A.: Biorefinery process combining specel® process and selective lignin precipitation using mineral acids. BioResources **11**, 7061–7077 (2016)
37. Shi, H., Fatehi, P., Xiao, H., Ni, Y.: Optimizing the poly ethylene oxide flocculation process for isolating lignin of prehydrolysis liquor of a Kraft-based dissolving pulp production process. Ind. Eng. Chem. Res. **51**(14), 5330–5335 (2012). https://doi.org/10.1021/ie300141k
38. Razali, M.A.A., Ahmad, Z., Ahmad, M.S.B., Ariffin, A.: Treatment of pulp and paper mill wastewater with various molecular weight of polyDADMAC induced flocculation. Chem. Eng. J. **166**(2), 529–535 (2011). https://doi.org/10.1016/j.cej.2010.11.011
39. Sun, Y., Liu, Z., Fatehi, P.: Flocculation of thermomechanical pulping spent liquor with polydiallyldimethylammonium chloride. J. Environ. Manag. **200**, 275–282 (2017). https://doi.org/10.1016/j.jenvman.2017.05.042
40. Srivastava, V.C., Mall, I.D., Mishra, I.M.: Treatments of pulp and paper mill wastewaters with poly aluminium chloride and bagasse fly ash. Colloids Surf. A. **260**, 17–28 (2005)
41. Dashtban, M., Gilbert, A., Fatehi, P.: A combined adsorption and flocculation process for producing lignocellulosic complexes from spent liquors of neutral sulfite semichemical pulping process. Bioresour. Technol. **159**, 373–379 (2014). https://doi.org/10.1016/j.biortech.2014.03.006
42. Xiao, H.N., Pelton, R., Hamielec, A.: The association of aqueous phenolic resin with polyethylene oxide and poly (acrylamide-*co*-ethylene glycol). J. Polym. Sci. A **33**, 2605–2612 (1995)
43. Takase, H., Van de Ven, T.G.M.: Effect of a cofactor on polymer bridging of latex particles to glass by polyethylene oxide. Colloids Surf. A. **118**, 115–120 (1996)
44. Kumar, P., Teng, T., Chand, S., Wasewar, L.: Treatment of paper and pulp mill effluent by coagulation. Int. J. Civil Environ. Eng. **3**, 222–227 (2011)
45. Fatehi, P., Shen, J., Hamdan, F., Ni, Y.: Improving the adsorption of lignocelluloses of prehydrolysis liquor on precipitated calcium carbonate. Carbohydr. Polym. **92**, 2103–2110 (2013)
46. Gregory, J., Duan, J.: Hidrolyzing metal salts as coagulants. Pure Appl. Chem. **73**(12), 2017–2026 (2001)
47. Ahmad, A.L., Wong, S.S., Teng, T.T., Zuhairi, A.: Improvement of alum and PACl coagulation for the treatment of pulp and paper mill wastewater. Chem. Eng. J. **137**(3), 510–517 (2008). https://doi.org/10.1016/j.cej.2007.03.088
48. Stumn, W., Morgan, J.J.: Chemical aspects of coagulation. J. Am. Water Works Assoc. **54**, 971–994 (1962)
49. Licsko, I.: Dissolved organics removal by solid-liquid phase separation (adsorption and coagulation). Water Sci. Technol. **27**, 245–248 (1993)
50. Randtke, S.J.: Organic contaminant removal by coagulation and related process combinations. J. Am. Water Works Assoc. **80**, 40–56 (1988)
51. Ching, H.W., Tanaka, T.S., Elimelech, M.: Dynamics of coagulation of kaolin particles with ferric chloride. Water Res. **28**, 559–569 (1994)
52. Wang, Q., Jahan, M.S., Liu, S., Miao, Q., Ni, Y.: Lignin removal enhancement from prehydrolysis liquor of kraft-based dissolving pulp production by laccase-induced polymerization. Bioresour. Technol. **164**, 380–385 (2014)
53. Demirba, S.A.: Calculation of higher values of biomass fuels. Fuel **76**, 431–434 (1997)
54. Brebu, M., Ucar, S., Vasile, C., Yanik, J.: Co-pyrolysis of pine cone with synthetic polymers. Fuel **89**, 1911–1918 (2010)
55. Satyanarayan, N., Vaibhav, V.G., Prasant, K.R., Kathlene, J., Ajay, K.D.: Characterization of Canadian biomass for alternative renewable biofuel. Renew. Energy. **35**, 1624–1631 (2010)
56. Telmo, C., Lousada, J., Moreira, N.: Proximate analysis, backwards stepwise regression between gross calorific value, ultimate and chemical analysis of wood. Bioresour. Technol. **101**, 3808–3815 (2010)

Affiliations

Juan Domínguez-Robles[1] · **Mª del Valle Palenzuela**[2] · **Rafael Sánchez**[1] · **Javier Mauricio Loaiza**[3] · **Eduardo Espinosa**[1] · **Antonio Rosal**[2] · **Alejandro Rodríguez**[1]

[1] Chemical Engineering Department, University of Córdoba, Campus de Rabanales, Córdoba, Spain

[2] Molecular Biology and Biochemical Engineering Department, University Pablo de Olavide, 41013 Sevilla, Spain

[3] Chemical Engineering Department, University of Huelva, Campus El Carmen, 21007 Huelva, Spain