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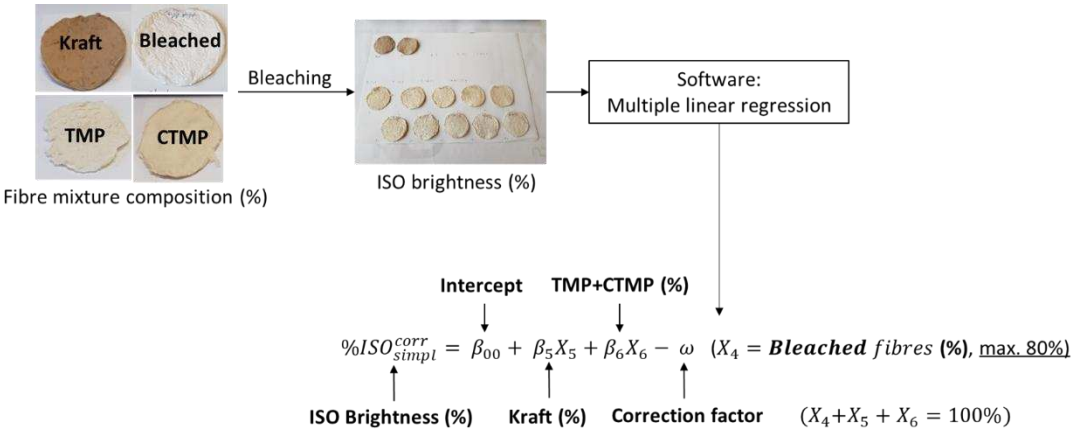
Abstract

Waste paper is recovered and bleached to produce recycled newsprints and magazines. It is composed of a fibre mixture from different wood pulping processes. Each type of fibre shows a different reactivity towards bleaching. Consequently, if the composition of waste paper changes over time, the actual industrial bleaching process may no longer be suitable to achieve the intended brightness. This study aims to develop a multiple linear regression that correlates brightness and fibre composition to determine in advance whether a waste paper stream can achieve the intended brightness. Several samples of four of the most representative fibre types were bleached under specific laboratory conditions, and the resulting brightness was used to develop the regression. The resulting model is valid and consistent when the amount of bleached fibre chemically pulped type in the mixed fibre stream does not exceed 80%. Waste samples with a known fibre composition were then bleached to verify the model. The measured brightness followed the same trend predicted by the regression but was lower at a constant value. The use of a correction factor allowed for a good fit. The cause of this discrepancy could be the differences between the reference fibre mixtures and waste paper pulp not included in the model (e.g., contaminants or collapsed fibres). This work is a first step to develop a simple statistical tool to estimate the brightness of waste paper pulp, despite some limitations.

Keywords

Waste paper, bleaching, multiple linear regression, pulping, brightness, wood fibres

Graphical Abstract



Introduction

The necessity to achieve a circular economy for sustainable development is pushing the attention of the researchers to the purification (Vilardi et al. 2020) and valorisation of wastes and side streams (Rispoli et al. 2021a). Paper and board production (more than 400 million tons/y), and their recycling is globally a large waste generating activity (Martin and Haggith 2018). Therefore, intensive research was performed for the valorisation of waste paper by the production of valuable chemicals (Tofani et al. 2020), materials (Tofani et al. 2021a) and energy (Rispoli et al. 2021b; Vilardi and Verdone 2022). However, the primary use of recovered paper is in producing newsprints, magazines, and cardboards. In this field, the optimisation of paper recycling is a crucial step towards a circular economy. In this manuscript, the focus is on the bleaching process.

Waste paper may originate from paper obtained by different pulping processes and is generally brightened or bleached to impact or remove the chromophore structures to produce newsprints and magazines, respectively. The applied technology consists of a single bleaching step with hydrogen peroxide, followed by an optional treatment with sodium dithionite (Suess 2010). However, two aspects of the incoming "waste paper streams" can have a negative impact on these standard bleaching techniques. First, the composition of the collected recovered paper changes over time. For example, packaging paper production increases over the years, while graphical paper consumption decreases (CEPI 2020). The second issue is the heterogeneity of the recovered paper. In paper manufacturing, each type of pulping process (i.e., mechanical and chemical) delivers fibres of different morphology, molecular structure, and lignin content (Adamoupolos and Oliver 2006, Suess 2010). These two aspects affect the bleaching by variations in types and amounts of chromophores (Ek et al. 2009, Sixta 2006). Fibres from mechanical pulping contain chromophores in free-form or terminal groups of the lignin, such as coniferaldehyde-like structures (Ek et al. 2009). The chromophores present after chemical pulping also contain internal groups in the residual lignin structure, such as stilbene-like structures between two branched phenolic groups (Lange et al. 2013). In addition, novel inks make the recycled paper more heterogeneous and influence bleaching by forming a layer around the fibres that prevents interaction with the bleaching agents (Holik 2013).

Current technologies are limited to the analysis of outer layers of waste paper products in order to sort out the suitable waste paper to achieve a target brightness of the final product, without considering the inner layers (Bajpai 2014, Rahman et al. 2014). The development of a model to predict the optical properties of the waste paper mixture before bleaching could be an alternative. Statistical techniques have been previously applied in paper recycling

studies to predict the product's physical properties (Adamopoulos et al. 2016) and the flotation deinking step (Pauck et al. 2014). Moreover, a model-based optimisation of the bleaching stage was studied by Lenz et al. (2005). They studied the development of a Gaussian model to find a balance between cost and brightness during a hydrogen peroxide bleaching step of deinked recycled paper. The model described the influence of hydrogen peroxide and sodium hydroxide dosage on brightness. The authors demonstrated that the same final brightness value could be reached by different concentration combinations of the two chemicals. However, the authors did not study which types of fibre were present in the pulp. Burnet et al. (2007) showed the influence of the fibre composition on the brightness using bleached chemical pulp, unbleached TMP (thermomechanical pulp) and bleached TMP as reference samples. Their work demonstrated that the major type of fibre that affects the brightness is the unbleached TMP. However, the application of a mathematical model to describe their findings was not investigated. Pourmosa (2015) studied how the optical properties of deinked paper pulp (DIP) were affected by the amount of mechanical and chemical pulps present in the recovered paper. It was demonstrated that the presence of collected waste paper from the mechanical pulp was more detrimental for the brightness than recovered paper from the chemical pulp. The limit of their study is that the starting material consisted only of the recovered paper used for tissue products (high brightness material). It is also not described whether the mechanical pulp studied was composed of bleached or unbleached fibres or a mixture. In a preceding work (Tofani et al. 2021b), the variation of hydrogen peroxide consumption according to the fibre type was found to affect the bleaching process. However, only virgin fibres were studied.

This study aims to develop a multiple linear regression (MLR) as a tool to determine whether a particular recovered paper can reach a target brightness under specific bleaching conditions based on its fibre composition. This is a first approach in that direction. Four types of fibres were used to build the model. However, the predictability and accuracy entirely depend on the history of the fibres (i.e., the type of wood where the fibres come from, the original pulping process to extract the fibres from wood, how many times the fibres were recycled and the type of final product where the fibres were used). Therefore, the actual model has to be seen as a first step will have to be validated and expanded by future work.

Materials and Methods

Starting materials, reagents, and solvents

Pulp samples and sodium silicate (Grade 200-5052, sodium disilicate $Na_2O \cdot 2SiO_2$ Mw: 182, dry material 0.45%) were provided by a paper mill located in Belgium. Reference samples: unbleached Chemical Pulp (Kraft, consistency (K, dry mass of the pulp divided by the wet mass of the pulp, 46.3%), unbleached Thermo-Mechanical Pulp (TMP, K 32.7%), unbleached Chemo-Thermo-Mechanical Pulp (CTMP, K 28.8%) and deinked copy paper made with Bleached chemical pulp ("Bleached fibres", K 26.5%). Waste paper samples: Old Corrugated Cardboard (OCC, K 30%, ratio chemical: mechanical fibres 78:22), DeInked Pulp for newsprints (DIP2, K 17.5%) and DeInked Pulp for magazines (DIP1, K 30.7%). Their composition of fibres is reported in Table 1. Other chemicals and materials were purchased from Acros Organics. When it is not specified, deionized water was used.

Preparation of model samples having a known composition of fibres

The four reference fibres were used to prepare twenty-two model samples with known reference fibres percentages

(Table 1A, **Supplementary Information**). Six different concentrations were used for each reference fibre. Afterwards, the model samples were bleached using the sequence P10 (section *Bleaching sequence P10*). Finally, the reference samples were weighed using a scale with a level of accuracy of ±0.0005.

Neutral washing

Twenty-five grams of dry fibres were diluted up to 700 g using water to reach a consistency (K) of 3.6%. The mixture was heated until 50°C and stirred for 1 h. At the end of the treatment, the mixture was filtered using a 0.16 mm pore size filter and washed twice using water (700 ml x 2). After, the fibres were diluted in water to reach a consistency of around 2-2.5%. Fifty grams of the resulting pulp were passed through a Büchner filter and dried at 60°C. A disc of around 1 g and a diameter of around 45 mm was made and dried at 60°C until constant weight. The brightness was measured according to the standard procedure ISO 2470-1:2016 (2016).

Alkaline extraction

Eighteen grams of dry OCC pulp were diluted in a volume of 500 ml using water with 6 ml of NaOH 2 M and 136 mg of $MgSO_4$ to reach a pH of 11.9. The mixture was heated at 100°C for 1 h in a 1 L closed Parr reactor. In the end, the mixture (final pH more than 10.5) was filtered using a filter with a pore size of 0.16 mm and washed twice using water (700 ml x 2). Afterwards, the fibres were diluted until the consistency of 2-2.5%.

Alkaline solution and fibre discs

An alkaline solution composed of sodium silicate and sodium hydroxide was prepared. Forty-six grams of silicate solution were dissolved in 250 ml of sodium hydroxide 2 M. The final volume of the solution was 275 ml. The alkaline solution contains 0.0018 mol (0.072 g) of NaOH and 0.0004 mol (0.073 g) of silicate for each millilitre. The molar ratio of NaOH: silicate is 4.5:1. As reported in section *Neutral washing*, 15 g of the resulting pulp were used to make a disc. The brightness of the disc was measured.

Bleaching sequence P10

Bleaching (P10x1): the bleaching reaction was performed in a beaker of 1000 ml at 600 rpm using an overhead stirrer. Ten grams of dry fibres were diluted up to 500 g using water to reach a consistency of 2%. The mixture was heated to 80°C, and 2.86 g of hydrogen peroxide was added (10% odf, on dry fibres). The alkaline solution was added to adjust the pH between 10.2 and 10.5. The reaction was stopped after 1.5 h or at the total consumption of hydrogen peroxide. One hundred grams of the treated pulp was filtered using a filter of 0.16 mm and washed twice using water (100 ml x 2). The fibres were diluted again up to 100 g using water. Fifty grams of the resulting pulp were used to make a disc, as reported in section *Neutral washing.* The brightness of the disc was measured.

Bleaching (P10x1+Y): the other 50 g of washed pulp were bleached using sodium dithionite. The reaction was performed in a beaker of 200 ml at 100 rpm using a magnetic stirrer. The pH was regulated using sulfuric acid and sodium hydroxide to reach a pH between 5 and 7. The pulp was heated until 60°C, and 35 mg of sodium dithionite was added. The reaction was stopped after 1 h. It was filtered using a filter of 0.16 mm and washed twice using water (50 ml x 2). The fibres were diluted again in 50 g of water and used to make a disc as reported in section Neutral washing.

Bleaching (P10x2): the 400 g of non-washed treated pulp from P10x1 were heated to 80°C, and 2.29 g of hydrogen peroxide was added (10% odf). The reaction was performed in a beaker of 1000 ml at 500 rpm using an overhead stirrer. The reaction conditions, the procedure to take the 100 g of sample, wash it and prepare a fibre disc of around 1 g using 50 g of washed pulp are the same as reported in Bleaching (P10x1).

Bleaching (P10x2+Y): the other 50 g of washed pulp were bleached using sodium dithionite following the procedure described in Bleaching (P10x1+Y).

Bleaching (P10x3): same conditions of Bleaching (P10x2) using 300 g of non-washed treated pulp from P10x2 and 1.72 g of hydrogen peroxide (10% odf). The reaction was performed in a beaker of 1000 ml at 300 rpm.

Bleaching (P10x3+Y): The other 50 g of washed pulp were bleached using sodium dithionite following the procedure described in Bleaching (P10x1+Y).

Bleaching (P10x4): same conditions of Bleaching (P10x2) using 200 g of non-washed treated pulp from P10x3 and 1.14 g of hydrogen peroxide (10% odf). The reaction was performed in a beaker of 400 ml at 400 rpm.

Bleaching (P10x4+Y): the other 50 g of washed pulp were bleached using sodium dithionite following the procedure described in Bleaching (P10x1+Y).

Bleaching (P10x5): same conditions of Bleaching (P10x2) using 100 g of non-washed treated pulp from P10x4 and 0.57 g of hydrogen peroxide (10% odf). The reaction was performed in a beaker of 400 ml at 200 rpm.

Bleaching (P10x5+Y): The other 50 g of washed pulp were bleached using sodium dithionite following the procedure described in Bleaching (P10x1+Y).

Kappa number

The amount of oxidizable material present in the pulp before and after bleaching was determined following the standard Tappi procedure “T 236 om-99, Kappa number of pulp” (1999).

The Kappa number was measured using part of the dried discs collected during the bleaching

Molisch’s test

Molisch’s test evaluated the cellulose decomposition of the “Bleached fibres” during bleaching. A bleaching reaction was performed in similar conditions of P10 on the “Bleached fibres”. The resulting liquid phases obtained after filtration of the pulp during each P10 stage were analysed by Molisch’s test (Pavia et al. 2011).

Results and Discussion

The development of the statistical tool and its study was done considering the following steps:

1. Selection of the reference fibres.
2. Selection of the waste paper samples.

3. Bleaching of reference fibres and samples using the sequence P10 and study decomposition and side reactions.
4. Mutual or not-mutual influence of fibres in mixture on the bleaching.
5. Development of MLR using the ISO brightness data on reference fibres from point 3.
6. Simplification of the MLR excluding the neglectable variables.
7. Application of the simplified model on waste paper samples.
8. Definition of the limitations and restrictions of the MLR.
9. Application of the model to predict the usefulness of a waste stream to reach a set-point in brightness.

Selection of the reference fibres (1)

Based on the literature (Sixta 2006, Belgacem and Pizzi 2016, Popa 2013), the four most used types of fibres in paper and cardboard production were selected:

1. Thermo-Mechanical Pulp (TMP) for the virgin fibres generated by mechanical pulping: used for printing paper products and the corrugated medium or liner board of the packaging products.
2. Unbleached Kraft fibres generated by chemical pulping of wood: used for cardboard production.
3. Chemo-Thermo-Mechanical Pulp (CTMP) for the virgin fibres generated by semi-mechanical pulping: used for both printing and corrugated medium production.
4. "Bleached fibres" are generated from copy paper pulp after cleaning by chemical pulping and bleaching. Bleached chemical fibres are used for printing products.

The four fibres were washed and analysed to determine their ISO brightness and Kappa number (Table 2). For the "Bleached fibres", the Kappa number at the start is not significantly different from zero because oxidizable materials were not detected. As a consequence, the "Bleached fibres" shows the highest brightness. Based on the literature review and the data in Table 2, two main differences can be identified between the Kraft fibres and the TMP/CTMP fibres:

1. Types of chromophores (Figure 1). The chromophores in Kraft fibres are present as internal and terminal groups of the lignin structure (Lange et al. 2013). Although Kraft fibres present the lowest starting brightness and starting Kappa number (Table 2), they also show different types of chromophores with respect to the TMP and CTMP. The chromophores in TMP and CMP fibres are present as lignin terminal groups and in free form (Ek et al. 2009). Besides this comparable chromophore structure of TMP and CTMP, the data of Table 2 also reveal similar ISO brightness and Kappa number. This makes us conclude that they also have a similar concentration of chromophores.

2. Fibre's morphology. The fibres from chemical pulping present a higher porosity than fibres after mechanical pulping due to the lignin removal (Sixta 2006). The lignin removal is confirmed by the lower Kappa number of the Kraft fibres with respect to the TMP/CTMP fibres (Table 2).

Selection of waste paper samples (2)

The industrial unbleached waste paper samples studied in this research were:

1. DeInked Pulp 1 (DIP1): deinked recycled paper for magazine production.
2. DeInked Pulp 2 (DIP2): deinked recycled paper for newsprint production.
3. Cardboard (OCC): recycled cardboard for cardboard production. Pre-treated by neutral washing (OCC wash) and alkaline treatment (OCC alkali).

Alkaline treatment of the OCC is applied to remove contaminants (e.g., dyes, residual lignin, waxes, and glues) that should typically not be present in the waste paper (Freeland 1999, Hagiopol and Johnston 2012). This treatment improves bleachability because the removal of contaminants from the fibre's surface made the fibres more accessible to the bleaching agents. The fibre's composition and starting brightness of the three samples are reported in Table 1.

The main differences between virgin fibres and waste paper pulp are two:

1. The waste paper contains a higher amount of non-fibrous material, such as ink, than virgin fibres pulp. (Bajpai 2015, Hagiopol and Johnston 2012, Holik 2013).
2. Once virgin pulps are dried, the fibres collapse, making their internal layers inaccessible to bleaching agents. This collapse is called hornification (Fernandes Diniz et al. 2004) or flattening (Howard and Bichard 1992).

The Kraft, TMP and CTMP fibres applied in this research were provided wet and kept wet. It means that the amount of collapsed fibres is minimal. On the other hand, the "Bleached fibres" is composed of dry recovered fibres. Therefore, they contain collapsed fibres. However, the impact of the "Bleached fibres" on the bleaching efficiency is minimal because it contains a minimal amount of chromophores (Kappa number < 1, Table 2).

Bleaching using the sequence P10 and study of decomposition and side-reactions (3)

The conditions were kept constant during bleaching and were the same for all the samples studied to have comparable data for all fibres. The ISO brightness of reference fibres and model samples during the subsequent bleaching steps are reported in Table 2A and Table 3A of **Supplementary Information**.

During the bleaching, hydrogen peroxide can decompose as well as cause unwanted side reactions with lignin and cellulose (Ek et al. 2009, Sixta 2006, Suess 2010). Therefore, specific precautions were selected to decrease the effect of these undesirable reactions. The temperature was kept below 90°C to limit decomposition (Sixta 2006), and the pH was around 10-11 to reduce Fenton and Fenton-like reactions (Jung et al. 2009, Wang 2008). Moreover, the pulps were stored in the fridge to reduce the impact of microorganisms (Suess 2010). The pulps were pre-heated to 80°C to deactivate any enzymes present in the pulp (Bajpai 2014).

The following tests were performed to estimate the impact of the unwanted reactions on the peroxide bleaching:

1. Kappa number to indicate chromophore formation. In Table 2, the Kraft fibres show a continuous decrease in the Kappa number, while the other three fibres manifest a slight increase. The latter can be correlated to the chromophore formation by side reactions in TMP and CTMP fibres during bleaching.

2. Mass loss during P10x5 to estimate the fibre degradation. Kraft fibres undergo a low mass loss (≈1%) (Table 3). On the other hand, a mass loss of about 14% for "Bleached fibres", 22% for TMP and 8% for CTMP is estimated.

3. Molisch test on the "Bleached fibres". The presence of glucose (cellulose degradation product) was detected in the P10x3 (4.5 h of reaction) by the pink ring (Figure 2) (Pavia et al. 2011). This cellulose degradation due to prolonged reaction times is described in the literature (Sixta 2006, Suess 2010).

Also, sodium dithionite bleaching was studied. A washing step between peroxide bleaching and the addition of dithionite enabled the removal of the soluble chromophores and the residual hydrogen peroxide. Based on the literature, the dithionite bleaching is performed in slightly acid conditions and low temperature (pH ≈ 6, < 60°C) to avoid alkaline degradation of lignin and reduce other side reactions (Gierer 1990).

Brightness variation when fibres are mixed (4)

As far as we know, a detailed study about the presence or absence of a mutual influence between different fibres during bleaching is not reported in the literature. However, several authors observed a linear behaviour of the ISO brightness as a function of the fibre's composition. Burnet et al. (2007) observed that unbleached mechanical pulp has a strong negative influence on the brightness with respect to the bleached chemical pulp (max. 85%). Ibrahim (2003) observed a positive linear trend in brightness with the proportion of unbleached fibres from chemical pulping when mixed with fibres from recycled cardboard and a negative trend when mixed with recycled newsprints and recycled magazines. Fišerová et al. (2013) observed a linear decrease in brightness with the proportion of recycled cardboard fibres mixed with unbleached Kraft fibres. Based on these findings, it was decided to consider a non-mutual influence between fibres when developing an MLR in the present research.

Development of MLR on the ISO brightness obtained after bleaching (5)

The ISO brightness data obtained by the bleaching of the reference fibres and the waste paper samples having known composition are reported in Table 1A, Table 2A and Table 3A of the **Supporting Information** and were used to develop an MLR. The regression is defined as:

$$\%ISO_{full} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 \quad (1)$$

where $\%ISO_{full}$ is the dependent variable, i.e. the ISO brightness at P10x1 or P10x1+Y, …. The independent variables are X_1 for Kraft, X_2 for TMP, X_3 for CTMP, X_4 for "Bleached fibres", corresponding to the mass % of the fibres. β_0 is the intercept, and β with i=1,2,3,4 corresponds to the coefficients of the independent variables**.**

The coefficients and their confidence intervals are reported In Table 4. The coefficients reported in Table 4 are negative because the chromophores present in the fibres reduce the brightness. The values after peroxide bleaching with and without the combination with dithionite are comparable. Because the resulting coefficients β_4 for the "Bleached fibres" were almost zero; they are omitted from Table 4. Omitting the $\beta_4 X_4$ term in Equation 1, i.e., $\beta_4 = 0$, the same final brightness was obtained while still considering the "Bleached fibres" composition percentage. The coefficients of Kraft, TMP and CTMP fibres stayed the same. A continuous decrease in the impact of the Kraft fibres on the brightness throughout the subsequent bleaching steps can be observed. All MLR coefficients

of the TMP and CTMP fibres are similar and lower in absolute values than most Kraft fibre coefficients. Table 5 presents the statistical data for each model equation. The significance p values are less than 0.05. The MLR models are significant.

Simplification of the MLR excluding the non-necessary variables (6)

The similar coefficients between TMP and CTMP fibres indicated that the regression could be simplified, combining the two fibres in one parameter. Equation 2 was used instead of Equation 1. This simplification is reasonable from a chemical perspective because TMP and CTMP fibres show similar characteristics (*Selection of the reference fibres (1)*).

$$\%ISO_{simpl} = \beta_{00} + \beta_5 X_5 + \beta_6 X_6 \quad (2)$$

where $\%ISO_{simpl}$ is the dependent variable, i.e. the ISO brightness at P10x1 or P10x1+Y, P10x2.… The independent variables, i.e., X_5 for Kraft, X_6 for TMP and CTMP (named Mech.), corresponding to the fibres' mass percentage. β_{00} is the intercept, and β with i=5,6 are the coefficients corresponding to the independent variables. "Bleached fibres" content (X_4) has still to be considered for mass balance.

The coefficients, the R^2, F values and significance p values for each model equation 2 are reported in Table 6 and Table 7. The significance p values are less than 0.05, meaning that the model equations are significant. Moreover, the values after peroxide bleaching with and without the combination with dithionite are comparable.

The reliability of the model simplification by combining the TMP and CTMP fibres in one variable was statistically evaluated using the F-test (Horn 1987). The complete procedure is reported in the **Supporting Information F-test** (Table 4A). The results allowed us to conclude that the simplified model describes the data and the original model. Furthermore, the sensitivity of the MLR was verified and reported in the **Supporting Information, Sensitivity of the simplified model** (from Table 5A to Table 8A). Finally, the results showed that the model could be implemented by adding samples having a high concentration of "Bleached fibres".

The behaviour of the fibres from the perspective of their molecular structure can be evaluated using the coefficient's absolute values β of Equation 2 reported in Figure 3. The fibres having the highest amount of chromophores have the most significant negative impact on the final brightness. Kraft fibres coefficients show the highest value at the start of the bleaching and a decreasing trend in the following bleaching steps. As reported in the literature (Sixta 2006), the Kraft fibres are more porous than the fibres from mechanical pulping. It can be assumed that in the early stages (P10x1 and P10x2), the porosity of Kraft fibres makes a high amount of chromophores available to the bleaching; in the next bleaching steps, the lower amount of residual chromophores has fewer chances to react with hydrogen peroxide, reducing the impact of the Kraft fibres on the ISO brightness. The continuous decrease of the coefficient throughout the bleaching process can also be interpreted by the absence or no significant presence of side reactions between hydrogen peroxide and lignin, as confirmed by the low mass loss (Table 3) and the decrease in the Kappa number (Table 2). In the case of TMP and CTMP fibres, the coefficients only show a substantial decrease from the starting point to P10x1. This indicates the removal of a significant amount of chromophores. In the subsequent bleaching steps, these coefficients are almost constant and lower with respect to the coefficients of Kraft fibres. The formation of new chromophores can justify this

behaviour because of side reactions and is supported by the mass loss (Table 3) and the increase of the Kappa number from stage P10x3 (Table 2).

The MLR model (Equation 2) can describe the ISO brightness linearity with the proportion of Kraft fibres in the mixture as long as the "Bleached fibres" does not exceed 80%. This result confirms the observations mentioned in the literature (Burnet et al. 2007) and the data reported in the **Supporting Information** (Figure 1A, Figure 2A and Figure 3A). This limitation can be assigned to the non-linear correlation between brightness and chromophores concentration (Ek 2009).

Application of the simplified model for waste paper samples (7)

The waste paper samples (DIP1, DIP2, OCC washed, and OCC alkali) were bleached, applying P10 and P10+Y sequences. The fibre compositions of the waste paper pulps are reported in Table 1. These values were applied as the independent variables in the MLR Equation 2, together with the model coefficients obtained for the reference fibres (Table 6), to predict ISO brightness. The predicted values for the samples OCC washed and OCC alkali-treated are the same because pre-treatment is not included in the model. The predicted and measured ISO brightness of the waste paper samples are presented in Figure 4 and Figure 5. The data are reported in Table 9A and Table 10A in the **Supporting Information**. Equation 2 predicts a similar influence of fibre composition on the ISO Brightness as the measured data both after the peroxide bleaching and the combination of peroxide with dithionite. However, the values are higher than the measured data (Figure 4 and Figure 5). It means that phenomena not included in the MLR negatively influence bleaching. Therefore, the model is not exhaustive in predicting the bleaching of waste paper samples. Another interesting aspect is the difference in ISO brightness between alkali-treated and washed OCC. The OCC alkali-treated reached higher values than OCC washed. It can be correlated to removing contaminants by alkali action, such as saponification reactions of the fats and oils, that just washing cannot do (Freeland 1999, Hagiopol and Johnston 2012). Therefore, pre-treatment is another aspect that has to be considered.

The differences between the predicted and measured ISO brightness values of waste paper samples after each step are reported in Figure 6 for comparison. The hydrogen peroxide bleaching of OCC wash showed a higher difference, and the model was therefore significantly less efficient in describing the data than for the other samples. The average and the estimated error for all differences, except for the deviating "OCC wash", were determined (Table 8). The standard deviation shows that the difference between measured ISO brightness values and predicted using Equation 2 is almost constant for the three waste paper samples. It was decided to use the average value reported in Table 8 as a "correction factor" (called ω) to adapt the model to fit the experimental data of the waste paper samples. This parameter ω is used to account for significant phenomena not included in the regression. The MLR was modified, leading to Equation 3:

$$\%ISO_{simpl}^{corr} = \beta_{00} + \beta_5 X_5 + \beta_6 X_6 - \omega \quad (3)$$

with a correction factor ω that equals 8.

Figure 7 and Figure 8 show that the values predicted ISO brightness by the new model Equation 3 and the measured data are comparable. However, the values after P10 bleaching are slightly lower than the values obtained

with the P10+Y sequence. The data can be found in Table 11A and Table 12A in the **Supporting Information**.

Equation 3 describes a good agreement between the achieved ISO brightness and the original fibre composition of waste paper. As far as we know, no other correlation has been reported in the literature before. Lenz et al. (2005) developed a Gaussian process model to describe the final brightness of waste paper as a function of the concentration of hydrogen peroxide and sodium hydroxide. However, this model does not consider the fibre composition of waste paper and is therefore efficient only on a certain type of waste paper. Burnet et al. (2007) and Pourmosa (2015) described the effect of the bleaching of different types of fibres from mechanical pulping and bleached fibres from chemical pulping together with the effect of the applied dosage of chemicals (hydrogen peroxide and sodium hydroxide). The authors observed that the unbleached fibres from mechanical pulping had a major effect on the final brightness. This result agrees with the data obtained during the research described in this manuscript. However, the presence of unbleached fibres from chemical pulping (ex. Kraft fibres) in the waste paper was not considered. Nonetheless, it is a crucial variable because of the increase in its content in the waste paper (CEPI 2020) and its high influence on bleaching, as described by its high coefficient in Equation 3 (Table 6). Moreover, a mathematical model to predict brightness was not yet developed.

Definition of the limitations and restrictions of the MLR (8)

The use of a correction factor was necessary. The possible causes of the difference between predicted and measured values are twofold: (1) "differences between reference fibres and recycled paper fibres" and (2) "limits of the model". Differences between reference fibres and recycled paper fibres:

1. The recycled samples contain contaminants and additives that are not present in samples composed of virgin wood fibres (Holik 2013).
2. The recycled fibres are collapsed due to the continuous circle, pulping-drying processes (Fernandes Diniz et al. 2004). As a result, the internal layers of the fibres have less chance to interact with bleaching agents.

It is possible to consider that the factor ω added in Equation 3 corrects these limitations.

Limits of the model:

1. A correction factor is necessary.
2. The regression is valid until the bleached fibres do not exceed 80%.
3. The amount and type of reference samples in the model are limited because the same called thermomechanical pulping or kraft process can be performed in different conditions depending on the paper mill.
4. Pre-treatments are not considered in the constructed model.
5. The model is applicable for the specific bleaching sequence used.

Application of the model to predict the usefulness of a waste stream to reach a set-point in brightness (9)

Equation 3 could be used in the paper industry using the coefficients reported in Table 6 and ω being equal to 8. For example, a waste paper has to be selected because it will be used as starting material to produce newsprints (target ISO brightness of 55% according to Ek et al. 2009) using the bleaching conditions of the stage P10x1. In this case, six hypothetical waste paper streams having a known fibre composition are provided (Table 9). These values can be inserted in Equation 3 to predict the % of ISO brightness after P10x1 (Table 9). The pulp nr. 5

shows the highest ISO brightness value (60 %) despite a similar starting ISO brightness compared to other waste streams. Consequently, this approach allows the selection of the best waste stream from the six proposed. Pulp nr. 5 makes it possible to obtain a paper product with a higher ISO brightness than required or apply a "softer" bleaching condition (ex. using a lower amount of hydrogen peroxide) than P10x1, reducing the costs.

However, it must be stressed that Equation 3 only permits an estimation of the ISO brightness. Further studies to improve this research are reported in the section **Future research**.

Future research

Further research must be addressed to resolve the limits of the model. The regression can be improved by constructing a model without needing an experimental "correction factor". In order to achieve this, the impact of collapsed fibres and contaminants (inks and fillers) have to be quantified and evaluated.

Also, it is necessary to improve the accuracy of the limit of bleached fibres where the model is valid. In this work, the limit was estimated at 80%. Therefore, it is necessary to prepare more samples with percentages of bleached fibres having values between 70 and 90% to improve the predictability and accuracy.

Moreover, other mechanical and semi-mechanical pulps must be studied to confirm that these fibres can always be lumped in one single variable. The regression can also be improved by adding samples with lower levels of Kraft, TMP and CTMP fibres to determine for which compositions the linearity of the model is still viable. Moreover, the influence of the fibre pre-treatment process can be improved by testing different processes, such as deinking and alkaline treatment, on different fibre samples.

Another approach to overcome the problem of the presence of a correction factor can be to develop the regression to predict the optical density based on the fibre's concentration. The optical density is equal to the logarithm of the inverse of the brightness. It is a parameter that can be easily measured in a paper mill using a densitometer. The application of optical density is reasonable because it can be correlated with the chromophore concentration through the Beer-Lambert law that describes a linear relationship between the two parameters (Biermann 1996).

The chemistry behind bleaching can be understood more in detail by studying lignin and chromophores during bleaching. The modification on the molecular structure of soluble chromophores and lignin can be determined using different techniques such as HPLC, GC-MS, NMR and FTIR (Ahvazi et al. 2016). In this way, it would be possible to estimate the functional groups present in the fibres at the start of the process and the functional groups formed during bleaching. Furthermore, if it became possible to estimate the concentration of chromophores in the fibres, it would be possible to develop an alternative MLR.

As written in the introduction, the predicting power of the model and its accuracy entirely depend on the history of the fibres. This paper describes a first approach where four fibre samples were investigated. However, the development of a general model requires fibres acquired from all different types of pulping processes (mechanical, chemical, semi-chemical, semi-mechanical and organosolv) and from all different types of paper products that can be present in the waste paper (sorted office paper, old newsprints, magazines, old corrugated contains and paperboard). Moreover, it should be taken into account that some countries have a paper industry that relies on grass and agricultural residues as a source of fibre, usually extracted by soda pulping (Abd El-Sayed et al. 2020).

This type of biomass presents a higher amount of ashes than wood. Moreover, the lignin structure of this type of biomass is different from wood lignin because it contains p-coumaric acid and ferulic acid residues linked to the main structure of lignin through ester linkages (Lin and Dence 1992). Therefore, it is necessary to include another type of fibre in the regression. Furthermore, the changes in bleaching and printing technologies must be considered. The reaction conditions of the bleaching, such as the concentration of hydrogen peroxide, and the development of new inks and dyes can influence the brightness of the final paper product. As a consequence, a vast amount of data must be collected to enable the construction of such a general model.

Conclusion

In this work, a multiple linear regression (Equation 3) estimates the ISO brightness of paper pulps bleached using hydrogen peroxide by knowing the fibre composition. As far as we know, this model-based approach for setting limitations to the fibre composition of waste paper stocks for bleaching was never reported in the literature.

Equation 3 contains two independent variables, i.e., the percentage of Kraft fibres and the overall percentage of TMP and CTMP fibres. “Bleached fibres” type is not present in Equation 3, but its quantity has to be taken into account for the mass balance. Therefore, this model is valid when the fraction of the “Bleached fibres” does not exceed 80%. Moreover, the addition of a “correction factor” is required, as reported in Equation 3.

Further studies are necessary to improve Equation 3, as reported in the **Future research** section. However, the model constructed in this paper could already estimate the ISO brightness of waste paper mixtures bleached under the reaction conditions reported in this study.

Supplementary Information: available

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Conflict of interest The authors declare that they have no conflict of interest.

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Table 1 Fibre types and composition of waste paper samples

Sample	ISO Brightness	Bleached chemical		Unbleached chemical		Mechanical	
	%	%	CI(σ)±[a]	%	CI(σ)±	%	CI(σ)±
OCC	23/25[b]	25	1	53	1	22	1
DIP1	59	69	2	0	-	31	2
DIP2	51	58	2	0	-	42	2

[a]CI(σ)±=Confidence interval 1 sigma; [b]23% after alkaline treatment, 25% after washing

Table 2 ISO brightness and Kappa number (KN) of reference samples[a]

Step	ISO Bright.	ISO CI(σ)±[a]	Start KN[b]	CI(σ)±	P10x1 KN	CI(σ)±	P10x3 KN	CI(σ)±	P10x5 KN	CI(σ)±
Kraft	17	2	52	1	38	1	25	1	21	1
TMP	60	2	103	1	95	1	81	1	83	1
CTMP	50	2	115	1	100	1	95	1	98	1
Bleached	87	2	n.d.[c]	0.1	n.d.	0.1	3	1	3	1

[a]CI(σ)±= Confidence interval 1 sigma; [b]The Kappa number was measured twice, [c]n.d.=not determined

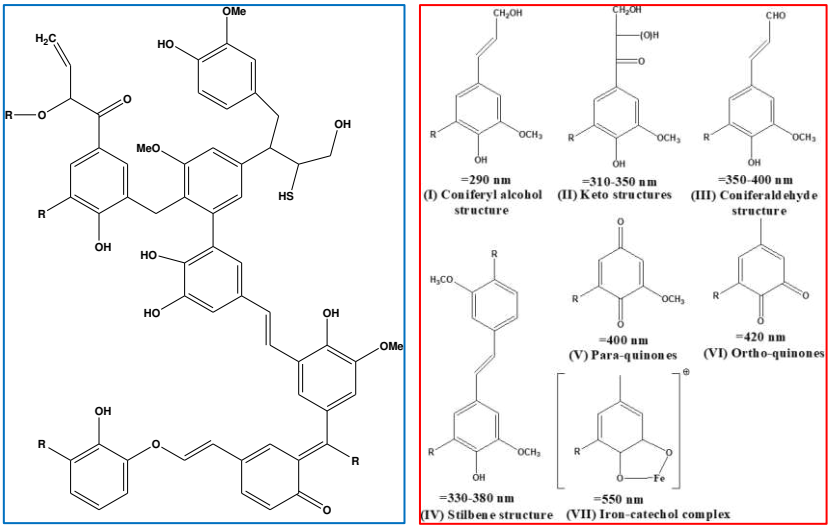

Figure 1 Chromophores present in Kraft fibres (left) (Lange et al. 2009) and TMP and CTMP fibres (right) (Ek et al. 2009)

Table 3 Mass loss[a] (%) measured during the P10x5 for the four types of reference fibres

Step	Mass loss P10x1 (%)	CI(σ)±[b]	Mass loss P10x5 (%)	CI(σ)±
Kraft	n.d.[c]	0.1	1	0.1
TMP	14	4	22	4
CTMP	5	1	8	1
Bleached	9	4	14	4

[a]the mass loss was measured twice, weighing the dried solid after filtration and washing,
[b]CI(σ)±= confidence interval 1 sigma; [c]not determined.

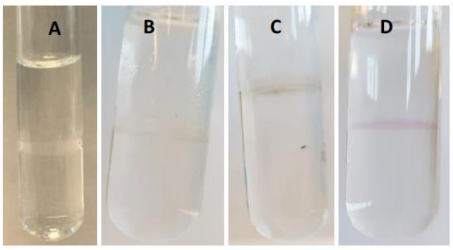

Figure 2 Molisch's test. A) P10x0. B) P10x1. C) P10x3. D) P10x5

Table 4 Coefficients of the MLR on ISO brightness as a function of the fibre composition (Equation 1) for each bleaching step

Step	Intercept β_0	CI(σ)±[a]	Kraft (X_1)	CI(σ)±	TMP (X_2)	CI(σ)±	CTMP (X_3)	CI(σ)±
Start	74	2	-0.60	0.04	-0.15	0.04	-0.25	0.04
P10x1	80	3	-0.58	0.03	-0.13	0.04	-0.17	0.04
P10x2	85	2	-0.45	0.02	-0.15	0.03	-0.18	0.03
P10x3	86	1	-0.35	0.02	-0.16	0.02	-0.17	0.02
P10x4	88	1	-0.28	0.02	-0.20	0.02	-0.18	0.02
P10x5	88	1	-0.21	0.02	-0.20	0.02	-0.18	0.02
P10x1+Y	82	2	-0.51	0.03	-0.09	0.03	-0.13	0.03
P10x2+Y	86	1	-0.38	0.02	-0.11	0.02	-0.15	0.02
P10x3+Y	90	2	-0.32	0.02	-0.14	0.02	-0.17	0.02
P10x4+Y	91	1	-0.26	0.02	-0.16	0.02	-0.17	0.02
P10x5+Y	92	1	-0.23	0.02	-0.18	0.02	-0.19	0.02

[a]CI(σ)= confidence interval 1 sigma

Table 5 R square, F and Significance p values of Equation 1

Step	R square	CI(σ)± of the regression[a]	F	Significance p
Start	0.932	5	119.284	3E-15
P10x1	0.943	5	144.262	3E-16
P10x2	0.952	3	171.005	3E-17
P10x3	0.937	3	129.380	1E-15
P10x4	0.915	3	93.668	5E-14
P10x5	0.884	2	66.213	3E-12
P10x1+Y	0.950	4	163.343	6E-17
P10x2+Y	0.939	3	133.117	7E-16
P10x3+Y	0.919	3	98.559	3E-14
P10x4+Y	0.905	3	82.988	2E-13
P10x5+Y	0.899	2	77.213	4E-13

[a] CI(σ)= confidence interval 1 sigma

Table 6 Coefficient of the MLR for each bleaching step Equation 2

Step	Intercept β_{00}	CI(σ)±[a]	Kraft (X_5)	CI(σ)±	Mech (X_6)	CI(σ)±
Start	74	3	-0.60	0.04	-0.20	0.04
P10x1	80	2	-0.58	0.03	-0.15	0.03
P10x2	85	2	-0.45	0.02	-0.17	0.02
P10x3	86	1	-0.34	0.02	-0.16	0.02
P10x4	88	1	-0.28	0.02	-0.19	0.02
P10x5	88	1	-0.21	0.02	-0.19	0.02
P10x1+Y	82	2	-0.51	0.03	-0.11	0.03
P10x2+Y	86	2	-0.38	0.02	-0.13	0.02
P10x3+Y	90	2	-0.32	0.02	-0.15	0.02
P10x4+Y	91	1	-0.26	0.02	-0.17	0.02
P10x5+Y	92	1	-0.23	0.02	-0.18	0.02

[a]CI(σ)= confidence interval 1 sigma

Table 7 R square, F and Significance p values of the Equation 2

Step	R square	CI(σ)± of the regression[a]	F	Significance p
Start	0.919	6	153.010	2E-15
P10x1	0.941	5	216.612	2E-17
P10x2	0.949	3	249.209	4E-18
P10x3	0.937	3	201.374	6E-17
P10x4	0.912	3	139.361	6E-15
P10x5	0.883	2	101.419	3E-13
P10x1+Y	0.947	4	239.016	7E-18
P10x2+Y	0.932	3	184.579	2E-16
P10x3+Y	0.912	3	139.429	6E-15
P10x4+Y	0.904	3	126.652	2E-14
P10x5+Y	0.897	2	118.100	4E-14

[a] CI(σ)= confidence interval 1 sigma

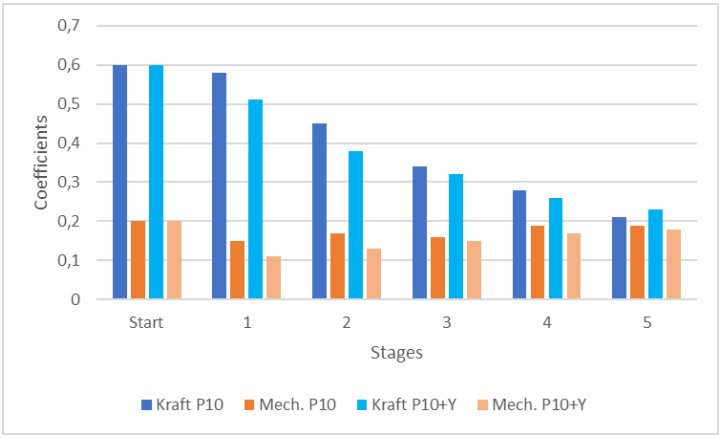

Figure 3 Coefficient's β of Equation 2 in absolute values

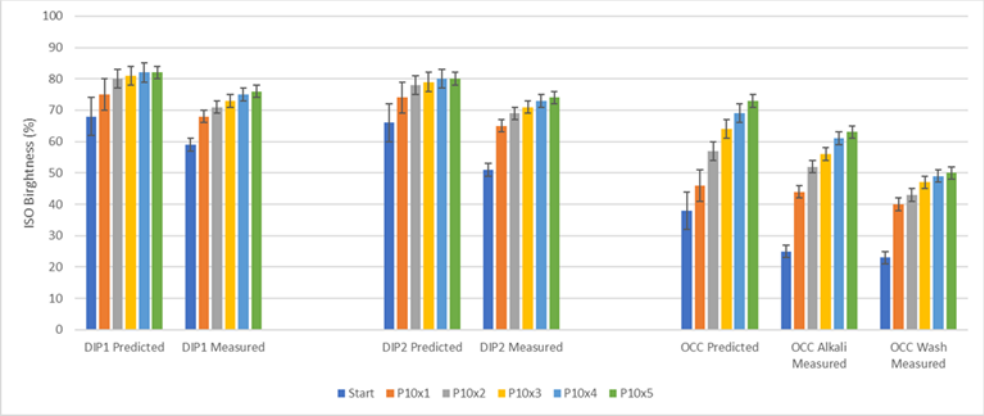

Figure 4 Comparison between measured values and predicted values during peroxide bleaching P10

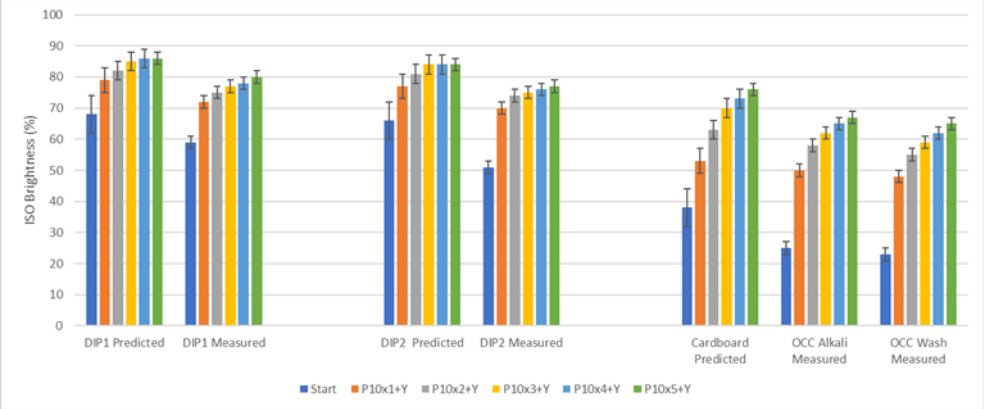

Figure 5 Comparison between measured values and predicted values during peroxide bleaching P10+Y

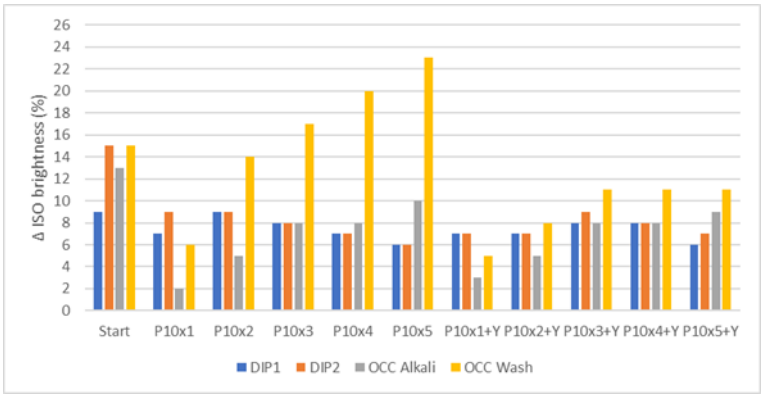

Figure 6 Difference between predicted and measured ISO brightness values, in P10 and P10 +Y

Table 8 Average and standard deviation of the differences between predicted and measured brightness

	Average (%)	CI(σ)±[a]
P10	8	3
P10+Y	8	3

[a]CI(σ)±=confidence interval 1 sigma

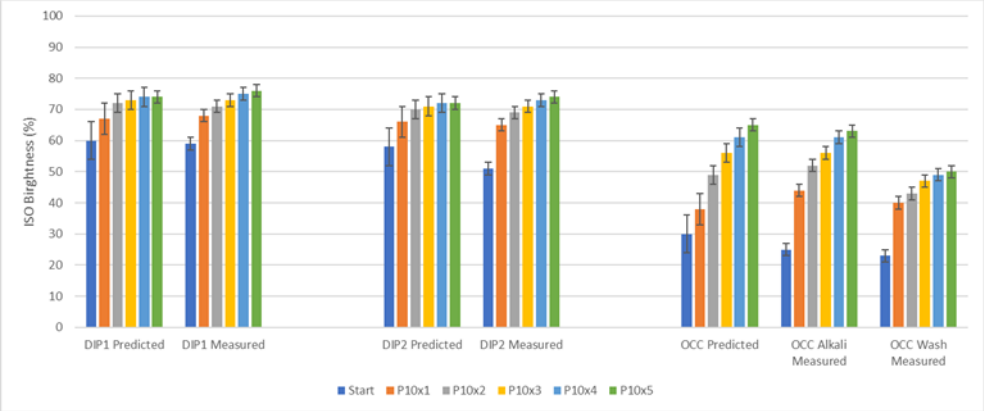

Figure 7 Comparison between measured values and predicted values during bleaching sequence P10 after correction

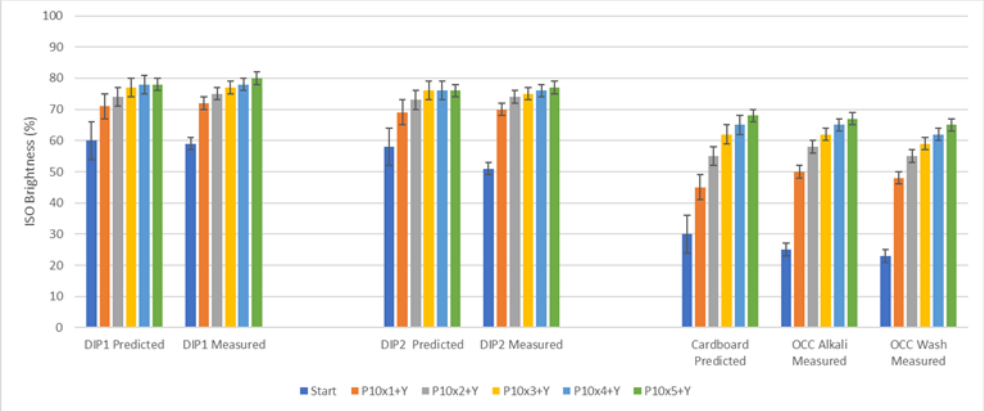

Figure 8 Comparison between measured values and predicted values during bleaching sequence P10+Y after correction

Table 9 Estimated brightness after P10x1 of hypothetical waste paper pulps

Example nr.	Kraft (%)	Mech. (%)	Bleached (%)	Start ISO (%)[a]	ISO P10x1 (%)
1	30	30	40	42	50
2	30	0	70	48	55
3	5	75	20	48	58
4	25	5	70	50	57
5	0	80	20	50	60
6	15	40	45	49	57

[a]The ISO values were predicted using Equation 3 with a confidence interval of 6 for the Start ISO and 5 for ISO P10x1