Cellulose, hemicelluloses, lignin and ash content of some organic materials and their suitability for use as paper pulp supplements

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Abstract

Freshwater algal biomass and orange and lemon peels were assessed as tissue paper pulp supplements. Cellulose and hemicellulose contents of algal biomass were 7.1% and 16.3%, respectively, whereas for citrus peels cellulose content ranged from 12.7% to 13.6% and hemicellulose from 5.3% to 6.1%. For all materials, lignin and ash content was 2% or lower, rendering them suitable for use as paper pulp supplements. The addition of algal biomass to paper pulp increased its mechanical strength significantly. However, brightness was adversely affected by chlorophyll. The addition of citrus peels in paper pulp had no effect on breaking length, increased bursting strength and decreased tearing resistance. Brightness was negatively affected at proportions of 10%, because citrus peel particles behave as coloured pigments. The cost of both materials is about 45% lower than that of conventional pulp, resulting in a 0.9–4.5% reduction in final paper price upon their addition to the pulp.

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1. Introduction

World paper consumption was about 300 million tons in 1996/97 and is expected to rise above 400 million tons by the year 2010 (Hurter and Riccio, 1998). In view of the shortage of conventional raw materials for pulping and the increasing demand for paper products, new raw materials for pulp production such as non-wood fibers are being investigated worldwide (Ververis et al., 2004). Some of the new materials are either filamentous algae that can be used as the main raw material for papermaking (Kiran et al., 1980; Sakai et al., 1996; Chao et al., 2000) or algal biomass used as a supplement in softwood or hardwood pulps (Nicolucci et al., 1994). The major problems in producing paper from filamentous algae are (i) the isolation of certain species and growth of biomass in culture solutions inevitably increase the process cost and (ii) the relatively poor mechanical strength of the algal pulps (Chao et al., 2000). On the other hand, mixing algal biomass with conventional paper pulp seems a more promising method for exploiting algae from eutrophic waters (Nicolucci et al., 1994). Slime that develops at sewage treatment works is composed of over 50% freshwater algae (Shelef et al., 1978a), and is known to cause plugging of certain biological treatment systems in sewage and wastewater plants. Thus, it is usually removed/collected using various methods (Masters, 1998). Shelef et al. (1978b) proposed an intensive algal wastewater treatment system, where algal biomass removes N and P from wastewaters and is finally harvested and used as a protein source in animal feeds. More recently, similar systems called ATS (Algal Turf
Scrubbers) have been proposed by Craggs et al. (1996) and Mulbry and Wilkie (2001). These algal turfs are effective in removing nutrients and a variety of pollutants from wastewaters, while at the same time the harvested algal biomass can be used as a soil compost or livestock feed. Despite the fact that there are about 300 sewage treatment plants in Greece, there is no exploitation of freshwater algal biomass for any commercial application at this time.

Other organic materials that pose an environmental risk are citrus peels from processing plants for juice production. Leachates from citrus plants or from disposed citrus peels can cause serious organic pollution problems due to the high BOD of these materials (Braddock and Crandall, 1981). Citrus peels have traditionally been dried and marketed as cattle feed or used in the production of by-products for the food industry (Braddock and Cadwallader, 1992). However, only a small fraction of the 35000 tons (dry weight) of citrus peels produced each year in Greece is used as cattle food (Manganari, 1996). The rest is usually disposed of at landfill sites, where it can cause serious organic pollution problems.

In 1998, Greece imported about 170000 tons of tissue paper and related products at a cost of about €130 million (Greek National Statistical Service, 1999). Thus, the objective of the present study was to examine the suitability of algal biomass and citrus peels as paper pulp supplements. This was done by (a) determining chemical constituents that are of special interest for paper chemistry, namely cellulose, hemicelluloses, ash and lignin in the above organic materials, (b) examining the effects of their addition in small (2.5–10%) proportions on basic paper pulp properties and (c) assessing the economic potential of adding these materials to conventional softwood and hardwood pulp in tissue paper manufacture.

2. Methods

2.1. Raw materials

Whole orange (Citrus sinensis L. cv. Valencia) and lemon (Citrus limon L. cv. Meyer) peels were collected from a process plant and air-dried. Both varieties are commonly used for juice production in Greece (Manganari, 1996). Freshwater algal biomass (slime) was collected from two sedimentation tanks of a municipal wastewater treatment plant, at Keratea, a small town, 50 km SE from the city of Athens. The biomass was collected in sterile bottles and was air-dried for five days. Representative samples were examined under a compound microscope for eukaryotic organism identification to the genus level.

2.2. Chemical analysis

2.2.1. Citrus peels

Orange and lemon peels were analysed for cellulose, hemicelluloses, (acid insoluble) lignin and ash using the method developed by Aravantinos-Zafiris et al. (1994). The method is based on the initial treatment of the samples with dilute nitric acid to extract pectin according to the procedure by Aravantinos-Zafiris and Oreopoulou (1992), followed by treatment with aqueous ethanol (determination of total sugars) and successive treatment with protease (to remove proteins), extraction with NaOH (hemicelluloses) and treatment with H2SO4 (cellulose, lignin and ash). The method also allows for the determination of proteins and pectins in the citrus peels. Four samples from each material (orange and lemon peels) were analysed.

2.3. Algal biomass

Ash, lignin, cellulose and hemicellulose contents of algal biomass were determined as follows: four samples of air-dried, ground (0.5 mm) algal biomass (0.7 g each) were boiled with 5 mL of 72% w/w H2SO4 solution for 4.5 h in order to hydrolyse the cellulose and hemicellulose. The suspension remaining after the above treatment was filtered through a crucible and the solid residue dried at 105 °C for 24 h and weighed (W1). The residue was then transferred to a pre-weighed dry porcelain crucible and heated at 600 °C for 5 h. After cooling down, it was weighed (W2) and ash content (%) was determined. Acid insoluble lignin was then calculated by the difference (W1 − W2). The filtrate from the H2SO4 treatment that contained the sugars released from cellulose and hemicellulose was thoroughly stirred and homogenized. Glucose (C1) and reducing sugar (C2) concentrations in the filtrate were determined according to a glucose oxidase–peroxidase assay kit (Biosis TM, Athens, Greece) and the DNS method (Miller, 1959), respectively. Following these measurements, the cellulose content in the starting material was calculated using the following equation:

\[
\% \text{ w/w cellulose content} = \left( \frac{0.9}{0.96} \right) \times C1 \times \left( \frac{V}{M} \right) \times 2 \times 100,
\]

where 0.9 is the coefficient that results from the molecular weight ratio of the polymer and the monomer hexose. The saccharification yield was taken as 0.96, C1 as the glucose concentration (g/L), V the total volume of sugar solution (L), M the dry weight of the algal biomass sample (g) and \(x\) the dilution of the sample (if any).

The hemicellulose content was calculated from the following equation:

\[
\% \text{ w/w hemicelluloses} = \left( \frac{0.88}{0.93} \right) \times (C2 – C1) \times \left( \frac{V}{M} \right) \times 2 \times 100,
\]

where 0.88 is the coefficient that results from the molecular weight ratio of the polymer and the monomer pentose, 0.93 is the saccharification yield of xylan to xylose, C2 is the determined reducing sugars concentration (g/L) from the DNS method, C1 the glucose concentration (g/L) from above, V the total volume of sugar solution (L), M the dry weight of the algal biomass sample (g) and \(x\) the dilution of the sample (if any).
2.4. Mechanical and optical properties of paper pulp

The effects of adding citrus peels and algal biomass to paper pulp on basic paper properties were examined. Three mechanical properties (breaking length, bursting strength and tearing resistance) and one optical (brightness) were selected for the study. Breaking length was determined using the ISO 1924/1 method (International Organization for Standardization, 1983a,b) and a Lawrence Wetter pendulum-type tensile tester; bursting strength (burst index) by the ISO 2758 method (International Organization for Standardization, 1983a,b) and a Mullen tester (serial 67C 185 Drive 6162); tearing resistance (tear index) by the ISO 1974 method (International Organization for Standardization, 1985) and a Lawrence Wetter 4-1 APP 971 tear tester; and brightness by the ISO 2470 method (International Organization for Standardization, 1977) and an Elepho 3000 EL 493 brightness tester. Grammage (g/cm²) was also determined using the ISO 536 method (International Organization for Standardization, 1976). Paper samples (160 mm × 160 mm) were prepared using a standard hand sheet press. Air-dried orange and lemon peels and algal biomass were ground using a Fritsch pulverisette-6 lab mill and sieved to produce <20 µm particle diameter size powder. The powder was then incorporated into virgin conventional paper (50% softwood–50% hardwood) pulp used for tissue paper production. Each material was added separately to the pulp at proportions (dry weight basis) shown in Table 1. Combinations of the three materials (orange–algal, lemon–algal and orange–lemon) were also added at 5% each. Blank samples (e.g., samples containing only conventional pulp) were also prepared. Instrument readings were corrected for grammage using the following formulae:

- Breaking length: \( (A \times 1000) / (15 \times B) \), where \( A \) is the instrument reading in kg;
- Bursting strength: \( (A \times 70.3 \times 0.098) / B \), where \( A \) is the instrument reading in psi;
- Tearing resistance: \( (A \times 98.07) / B \), where \( A \) is the instrument reading and \( B \) the grammage (g/cm²) of each sample in all measurements.

2.5. Statistical analysis

Collected data was subjected to analysis of variance (ANOVA, \( P < 0.05 \)) using appropriate statistical software. Sources of variation were the various organic materials and their mixing proportions with the conventional pulp. Error bars in all graphs refer to 95% Just Significant Confidence Intervals. This approach is less prone to type II error in multiple comparisons and therefore the preferred method when many means are to be compared (Snedecor and Cochran, 1980).

3. Results and discussion

3.1. Algal biomass community

Microscopic examination of slime revealed a natural assemblage of organisms in which freshwater green algae predominated. Filamentous species included Ulothrix sp., Microspora sp., Stigeoclonium sp. and Oedogonium sp. along with Chlorella sp. and Scenedesmus sp. (ellipsoidal cells). Cyanobacteria were represented by Hydrocoleus sp. and Oscillatoria sp. whereas diatoms were represented by Nitzschia sp. and Gomphonema sp.

Most of the above species are very common in aeration ponds and ATS systems in sewage treatment plants (Cantar-Lund and Lund, 1998). Scenedesmus sp. usually predominates in spring, whilst Ulothrix sp., Stigeoclonium sp. and Chlorella sp. predominate during autumn and winter (Canovas et al., 1996; Craggs et al., 1996). However, the presence of algae and other organisms is controlled by a large number of factors including irradiance, predation, pH, toxicity tolerance, etc. (Pearson et al., 1987).

3.2. Chemical analysis

Results of chemical analyses for the various organic materials examined are presented in Table 2. Cellulose, hemicellulose, lignin and ash contents for orange peels were close to those reported by Aravantinos-Zafiris et al. (1994). Lemon peels had somewhat lower cellulose and hemicellulose content, but had lower lignin content as well. The cellulose content of freshwater algal biomass was about half that of citrus peels and 1% higher than the cellulose content of seawater algal biomass reported by Nicolucci et al. (1994). However, the hemicellulose content of algal bio-

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Table 1

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<thead>
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<th>Materials</th>
<th>Proportions (%)a</th>
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<tr>
<td>Conventional pulp/algae biomass</td>
<td>97.5/2.5</td>
</tr>
<tr>
<td>Conventional pulp/algae biomass</td>
<td>95/5</td>
</tr>
<tr>
<td>Conventional pulp/algae biomass</td>
<td>90/10</td>
</tr>
<tr>
<td>Conventional pulp/orange peels</td>
<td>97.5/2.5</td>
</tr>
<tr>
<td>Conventional pulp/orange peels</td>
<td>95/5</td>
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<tr>
<td>Conventional pulp/orange peels</td>
<td>90/10</td>
</tr>
<tr>
<td>Conventional pulp/lemon peels</td>
<td>97.5/2.5</td>
</tr>
<tr>
<td>Conventional pulp/lemon peels</td>
<td>95/5</td>
</tr>
<tr>
<td>Conventional pulp/lemon peels</td>
<td>90/10</td>
</tr>
<tr>
<td>Conventional pulp/orange peels/lemon peels</td>
<td>90/5/5</td>
</tr>
</tbody>
</table>

a Dry weight basis.

Table 2

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical components</th>
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<tbody>
<tr>
<td></td>
<td>Cellulose (%)</td>
</tr>
<tr>
<td>Algal biomass</td>
<td>7.10 ± 0.2</td>
</tr>
<tr>
<td>Orange peels</td>
<td>13.61 ± 0.6</td>
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<tr>
<td>Lemon peels</td>
<td>12.72 ± 0.5</td>
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± Standard deviation.
mass was about three times higher than that of citrus peels. Due to the relatively low cellulose content of the organic materials compared to that of the bleached commercial pulp, it was decided to keep their maximum proportion at 10% when mixing with the pulp. It is worth noting that all the materials contained low (2% or less) lignin and ash and this makes them suitable as pulp supplement materials.

3.3. Addition of organic materials to paper pulp: effects on basic properties

The effect of adding organic materials on breaking length is shown in Fig. 1. Algal biomass increased the breaking length significantly compared to that of the conventional pulp. This was probably due to the proteins, which usually account for over 45% of the algal cells dry weight (Shelef et al., 1978a). Struszyk (2001) has reported a significant enhancement of paper breaking length when proteins along with chitin polymers were added to paper pulp. Chitin is also a common constituent of green algal biomass, so the increased mechanical strength could be attributed to the combination of proteins with chitin, which acts as a natural binding agent. This seems to have had a positive effect on other mechanical properties as well (see below). Detailed microscopic observation of paper samples tested for breaking length revealed the absence of whole algal cells in the fiber matrix. This means that algal cells broke down during the mixing of algal biomass with paper pulp and released all of their contents (especially chitin and proteins) into the pulp. The same effect was observed when algal biomass was added along with citrus peels. Pectins may play the role of chitin here, as they also act as natural glues. Citrus peels contain as much as 25–30% (dry weight) pectins (Aravantinos-Zafiris et al., 1994).

The addition of citrus peels seems to have had no significant effect on breaking length. Paper strength was generally maintained at satisfactory levels indicating that as far as breaking length is concerned, a small proportion (up to 10%) of citrus peel biomass can successfully replace conventional pulp.

Fig. 2 shows the effect of organic materials on bursting strength. All materials (except for orange peels at a proportion of 2.5%) give statistically significant higher values for bursting strength compared to those of conventional pulp. Algal biomass gave the highest values followed by combined materials and citrus peel addition. Increased bursting strength after the addition of citrus peels may also be attributed to small particles being embedded among paper fibers; the embedded particles make the fiber matrix more resistant to the stresses exerted by the Mullen tester, especially close to the rupture area, where pressure is higher.

Tearing resistance data is presented in Fig. 3. Added algal biomass increased tearing resistance significantly, whereas the addition of citrus peels seems to have had the opposite effect. It is evident that the mixing of citrus peels resulted in lower mechanical strength compared to that of algal biomass for all the paper strength properties examined. As far as tearing resistance is concerned, this may happen due to the occasional presence of citrus peel

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**Fig. 1.** The effect of organic materials on breaking length. A = algal biomass, L = lemon peels, O = orange peels, A–O = algae and orange, A–L = algae and lemon, O–L = orange and lemon, CP = conventional pulp. Numbers refer to % proportion (dry weight basis). Error bars refer to 95% JSCI.

**Fig. 2.** The effect of organic materials on bursting strength. A = algal biomass, L = lemon peels, O = orange peels, A–O = algae and orange, A–L = algae and lemon, O–L = orange and lemon, CP = conventional pulp. Numbers refer to % proportion (dry weight basis). Error bars refer to 95% JSCI.

**Fig. 3.** The effect of organic materials on tearing resistance. A = algal biomass, L = lemon peels, O = orange peels, A–O = algae and orange, A–L = algae and lemon, O–L = orange and lemon, CP = conventional pulp. Numbers refer to % proportion (dry weight basis). Error bars refer to 95% JSCI.
particles on and between fiber surfaces and the hindering of bond formation between them. This results in easier fiber separation (collapse) and subsequently in lower tearing resistance values of the samples.

Fig. 4 presents the effects of added organic materials on brightness, an important optical property especially for tissue paper in the Greek market. The addition of citrus peel in 2.5% and 5% proportions did not affect pulp brightness significantly. Detailed microscopic investigation showed that only a small percentage of citrus peel cells broke down during mixing and released pigments, dyeing the fibers. However, mixing proportions of 10% or those of orange–lemon peel combinations deteriorated brightness significantly, because the added material contained coloured pigments (Scott et al., 1995). The addition of algal biomass (at a proportion higher than 2.5%) caused a significant fall in brightness. This was because the algal cells broke down, releasing chlorophyll, and the final effect on brightness was similar to that caused by the addition of a green dye (Scott et al., 1995). Generally speaking, the algal biomass, which dramatically enhanced the mechanical strength of paper, also caused a significant deterioration of brightness. There seems to be a conflict between desired properties of tissue paper when using algal biomass as a supplement, but this could be overcome by appropriate advertising of the final product. A new brand of tissue paper called “naturally” or “ecologically” dyed could be sold successfully in the Greek market. Further research on other properties (e.g., opacity) may reveal the suitability of the organic materials examined as supplements in the production of printing and writing papers.

3.4. Cost considerations for using organic materials to supplement conventional pulp in tissue paper production

Calculation of cost for citrus peels in Greece is given in Table 3. A total cost for using citrus peels as pulp supplement is about €250/tn. Taking into account that imported virgin, conventional pulp cost is currently around €400–€450/tn (Ververis et al., 2004) citrus peels are 45% cheaper, so mixing them with pulp may lower final tissue paper prices from 0.9% to 4.5% depending on the mixing proportion (2.5–10%). As far as the algal biomass is concerned, there has not been any experimentation in Greece with the commercial exploitation of this material. Calculations on the ATS average productivity (dry weight) vary between 35 g m$^{-2}$ day$^{-1}$ (Craggs et al., 1996) and 5 g m$^{-2}$ day$^{-1}$ (Mulbry and Wilkie, 2001). Final production of algal biomass will depend on the area of the substrate of the ATS, which can typically be hundreds of m$^2$. Other authors (Shelef et al., 1978b) calculated an algal biomass production of over 2500 tons/year (dry weight) for municipalities of 100,000 inhabitants using the IAWTS system. Thus, available technologies for algal biomass production can certainly produce adequate amounts for the paper industry. American companies currently producing and processing algal biomass for fish feed using the ATS technology sell it at $300/tn ($240/tn) (W.H. Adey, personal communication). Adding the transportation costs, the final price of algal biomass could be very close to that of citrus peels resulting in similar reductions in final tissue paper prices. Assuming a 10% proportion of mixing, there could be a 17,000 tons annual reduction in imports of tissue paper pulp in Greece.

### 4. Conclusions

Organic materials (algal biomass from sewage treatment plants and citrus peels) can be used as supplements for tissue paper manufacture. Their cellulose and hemicellulose content allows them to be mixed with pulp in low proportions (2.5–10%), whereas their lignin and ash contents (≤2%) are also favourable. The addition of algal biomass to paper pulp significantly increased its mechanical strength, probably due to the binding properties of the proteins and chitin of the algal cells. However, brightness deteriorated severely due to chlorophyll, which acts as a natural green dye.

The addition of citrus (orange and lemon) peels to paper pulp had a neutral effect on breaking length, a positive effect on bursting strength and a negative effect on tearing resistance. Brightness was negatively affected at proportions of 10%, because citrus peel particles behave as coloured pigments. Overall, algal biomass seems to be a
better supplement material for conventional pulp, provided that appropriate marketing strategies will overcome the problem of decreased brightness.

The cost of both materials is about 45% lower than that of virgin conventional pulp, so a 0.9–4.5% reduction in final paper price could be achieved by using them as supplements (at 2.5–10% proportions) in tissue paper manufacture.

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