Investigation on Biometrical Properties and Mineral Content of Rice Residues and its Application in Pulp and Paper Production

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ABSTRACT
The aim of the study was to assess the variation of fiber biometrical properties and mineral content in three rice residues. Three types of rice stem residues such as Hashemi, Amrollah, and Neda harvested in the North of Iran. Then, fiber dimensions (fiber length, fiber diameter, cell wall thickness and lumen diameters), morphological properties (slenderness, flexibility, Runkel and rigidity coefficients) and mineral content (Zn, Mg, K, Ni, Fe, Cd, Cu and Pb) were investigated. The results of ANOVA indicated that the types of rice residues had effect significant on fiber dimensions, while the effect of this factor on the biometry properties weren’t significant. Hashemi rice residues showed the greatest average of fiber length. The lowest of fiber length and fiber lumen diameter values were found in Neda rice residues. The average of fiber diameter and cell wall thickness in Amorllahi rice is lower than other rice residues. The values of ash, K, Mg, Ni and Fe in Neda rice residues are higher than other rice residues. In general, results based on biometrical analysis and mineral content indicated that Iranian rice residues fibers aren’t promising fibrous raw material for the paper production.

INTRODUCTION

Wood has traditionally been the most widely used lignocellulosic matter in the production of pulp, furniture and boards of diverse types, as well as being a source for energy [1]. Increasing demand for these raw materials, together with economic and environmental factors, makes it necessary to research alternative sources of lignocellulosic matter [2]. Lignocellulosics includes wood, agricultural residues, water plants, grasses, and other plant substances [3]. Plant waste fibers have the composition, properties, and structure that make them suitable for uses such as composite, textile and pulp and paper manufacture. In addition, plant fibers can also be used to produce fuel, chemicals, enzymes and food, biomass, agricultural crops and residues. Forest resource and residues, animal and municipal wastes, are the largest sources of cellulose in the world [4].

There are numerous advantages in using wood for producing pulp than non-wood resources. The most important relate to the fact that it is a renewable resource which is ecologically friendly. The possibility of harvesting all year round is a very important point when compared to non-wood sources, which are usually harvested at a particular time of year. The higher density of wood is economically beneficial in relation to transport and storage of chips, and permits the design of larger and economically competitive mills. High ash and silica contents in non-wood plants make chemical recovery difficult, especially in the Kraft process [5].

Anatomical characteristics form the basis for lignocellulosic materials (wood and plant residues) utilization in pulp and paper making industry. The properties of paper depend on the fiber properties, anatomy and method of separation of the fibers. Fiber characteristics that influence the quality of paper are: length, fiber diameter, fiber lumen width, fiber cell wall thickness, Runkel ratio, Co-efficient flexibility and the relative fiber length [1, 6]. The fiber length is the number of bonding sites that is available on an individual fiber to form an interwoven network of fibers. It is measured from one end to another end. Long fiber lengths are preferable for manufacture of paper. Long fibers give a more open and less uniform sheet structure. Fiber length influences the tearing strength of paper. The higher of the fiber length had effect on the resistance of the paper to tearing [1, 7]. Fiber diameter is the diameter of fibre measured from side to side end and it is usually measured across the fiber length. The fibre lumen width is the diameter of the internal cavity. It is the distance between the inside diameter.
and the outer cavity. It is measured in a transverse direction. Faber lumen width affects the beating of pulp. The larger the fiber lumen width, the better will be the beating of pulp because of the penetration of liquids into empty spaces of the fibers [1, 6, 7]. Thick cell wall fibers adversely affect the bursting strength, tensile strength and folding endurance of paper. The paper manufactured from thick walled fibers will be bulky, coarse surface and contain a large amount of void volume. So, paper with thin walled fiber will be dense and well formed [1, 6].

There are different types of rice in Iran such as Khazar, Hashemi, Amrollahi, Neda, Tajen, Tarom, etc. Rice (Oryza sativa) is the second main food item in Iran, after wheat. It is farmed annually in large surface of Iranian northern lands, and as a consequence a large amount of straw is obtained. For example, rice cultivation area in Mazandaran province was for a account 239000 hectare in 2009 and we could be acquire rice straw for a account 1375906 ton. Therefore, the objective of this work was to characterize the fiber dimensions, morphological properties and mineral content of three types of rice residues (Amrollahi, Hashemi and Neda), with the aim of generating information to facilitate the incorporation of residues material in industrial processes.

MATERIALS AND METHODS

**Raw materials:**
Rice plant residues remaining after harvests were used. Three types of rice residues such as Hashemi, Amrollahi and Neda were selected from the north of Iran. Rice in Iran is scientifically classified into three categories, according to the physical grain shape, stem length and trade value are called Sadri, Champa and Gerdeh. The Hashemi and Amrollahi rice were first pattern (Sadri category) and Neda rice was in second category [1].

**Biometrical properties:**
The material was macerated using the Franklin method [8]. The pieces of fiber were cut with a scalpel and placed in test tubes in a solution of 1:1 acetic acid and oxygenated water of 30 volumes. The samples were dried in a stove at 60 °C for approximately 1 week. The disaggregated particles were washed in water, stained with aqueous safranin at 1% for 3 min, dehydrated with alcohol at 96% and xylol. Subsequently, the fibers were dried, placed on slides and fixed with Canada balsam. Sixty six (3 samples of rice residues × 23 fiber = 66 fibers) fibers were selected from three types of rice residues to determine fiber dimension (fiber length, fiber width, cell wall thickness and lumen diameter), which used from Leica Image Analyzer System. From the fiber features data, fiber morphological values were calculated according to the formula (RR: Runkel ratio, CWT: cell wall thickness, FD: fiber diameter, FR: Flexibility ratio, LD: lumen diameter, FL: fiber length, SR: Slenderness ratio, RC: Rigidity coefficient):

\[
RR = \frac{CWT}{LD}, \quad FR = \frac{LD}{FD} \times 100, \quad SR = \frac{FL}{FD}, \quad RC = \frac{CWT}{FD} \times 100
\]

**Ash content and mineral content:**
All of samples of rice residues were milled to flour for examine ash content. The value of ash content was determined according to TAPPI test methods [9]. Then, the mineral content such as Nickel (Ni), iron (Fe), copper (Cu), zinc (Zn), lead (Pb), potassium (K), magnesium (Mg), Cadmium (Cd) dissolved and separated from ash of rice flour by 63% nitric acid for an hour, mineral content identifications by atomic adsorption system (Varian AA240, Australia). All of measurements (mineral content and chemical properties) were repeated one time.

**Statistical analysis:**
A variance analysis (ANOVA) was made to establish the influence types of rice residues on fiber biometry properties and the differences were quantified through the Duncan test (p ≤ 0.05).

RESULTS AND DISCUSSIONS

1. **Biometrical properties:**
The analysis of variance results (ANOVA) indicated that the types of rice residues had significant effect on fiber length, fiber diameter, fiber lumen diameter and cell wall thickness, while hadn’t on the Runkel ratio, flexibility ratio, slenderness ratio and rigidity coefficient (Table 1).
Table 1: Statistical analysis of variance for fiber biometrical properties between all rice residues.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sum of squares between groups</th>
<th>Mean squares between groups</th>
<th>Sum of squares within groups</th>
<th>df</th>
<th>Mean squares within groups</th>
<th>F</th>
<th>Observed α</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL</td>
<td>0.692</td>
<td>2</td>
<td>0.346</td>
<td>1329</td>
<td>63</td>
<td>0.021</td>
<td>16.397</td>
</tr>
<tr>
<td>FD</td>
<td>82.412</td>
<td>2</td>
<td>41.206</td>
<td>399.122</td>
<td>63</td>
<td>6.335</td>
<td>6.504</td>
</tr>
<tr>
<td>LD</td>
<td>16.938</td>
<td>2</td>
<td>8.469</td>
<td>130.146</td>
<td>63</td>
<td>2.066</td>
<td>4.100</td>
</tr>
<tr>
<td>CWT</td>
<td>8.615</td>
<td>2</td>
<td>4.308</td>
<td>59.200</td>
<td>63</td>
<td>0.940</td>
<td>4.584</td>
</tr>
<tr>
<td>SR</td>
<td>2898.124</td>
<td>2</td>
<td>1449.062</td>
<td>39600.652</td>
<td>63</td>
<td>628.582</td>
<td>2.305</td>
</tr>
<tr>
<td>FR</td>
<td>551.000</td>
<td>2</td>
<td>275.500</td>
<td>7666.848</td>
<td>63</td>
<td>121.696</td>
<td>2.264</td>
</tr>
<tr>
<td>RR</td>
<td>1.760</td>
<td>2</td>
<td>0.880</td>
<td>20.184</td>
<td>63</td>
<td>0.320</td>
<td>2.746</td>
</tr>
<tr>
<td>RC</td>
<td>137.750</td>
<td>2</td>
<td>68.875</td>
<td>1916.712</td>
<td>63</td>
<td>30.424</td>
<td>2.264</td>
</tr>
</tbody>
</table>

a, significance level; * and ** are significant differences between the samples (P-value < 0.05 and 0.01). RR: Runkel ratio, CWT: cell wall thickness, FD: fiber diameter, FR: Flexibility ratio, LD: lumen diameter, FL: fiber length, SR: Slenderness ratio, RC: Rigididity coefficient

1.1. Fiber length:

The length and width of fiber have an effect on the bulk, burst, tear, fold and tensile strength of paper. For pulp and paper production, species with higher lengths are preferred since a better fiber length net is achieved, resulting in a higher resistance of the paper. The highest and lowest of fiber length values were found in Hashemi (0.989 mm) and Neda (0.743 mm), respectively (Figure 2). The Duncan's mean separation test shows that there is a significant difference in the fiber length between Hashemi and Amrollahi and between Hashemi and Neda rice residues. The average of fiber length in rice residues (0.843 mm) is lower than that of Bagasses (1.59 mm) [10], Canola (1.17 mm) [11], Tobacco (1.07 mm) [12], Bamboo (2.30 mm) [13], Corn (1.52 mm) [14], Sunflower (1.28 mm) [12], Cotton (1.32 mm) [12], wheat (0.851 mm) [14], Kenaf stalks (2.60 mm) [15], and softwood fibers (2.7-4.6 mm) [16] and close to minimum value of hardwood fibers (0.7-1.6 mm) [16].

Fig. 2: The fiber length values in three different rice residues.

1.2. Fiber width:

The highest and lowest of fiber width values were found in Hashemi (11.99 μm) and Amrollahi (9.45 μm), respectively (Figure 3). The Duncan's mean separation test shows that there is a significant difference in the fiber width between Hashemi and Amrollahi and between Hashemi and Neda rice residues. The average of fiber width in rice residues (10.30 μm) is lower than that of Bagasses (20.96 μm) [10], Canola (23.02 μm) [11], Tobacco (26.8 μm) [12], Bamboo (15.1 μm) [13], Sunflower (22.1 μm) [12], Cotton (29.3 μm) [12], Kenaf stalks (20 μm) [15], softwood fibers (32-43 μm) [16] and hardwood fibers (20-40 μm) [16] and is higher than that of Corn (8.4 μm) [14] and wheat (9.9 μm) [14].
Fig. 3: The fiber width in three different rice residues.

1.3. Lumen diameter:
The highest and lowest of lumen diameter values were found in Hashemi (5.26 μm) and Neda (4.04 μm), respectively (Figure 4). The Duncan’s mean separation test shows that there is a significant difference in the lumen diameter between Hashemi and Amrollahi and between Hashemi and Neda rice residues. The average of lumen diameter in rice residues (4.56 μm) is lower than that of Bagasses (9.72 μm) [10], Canola (12.50 μm) [12], Tobacco (16.3 μm) [12], Bamboo (6.9 μm) [13], Sunflower (15.6 μm) [12], Cotton (23 μm) [12], and wheat (6.8 μm) [14] and is higher than that of Corn (4.4 μm) [14].

Fig. 4: The lumen diameter in three different rice residues.

1.4. Single cell wall thickness:
Decrease in cell wall thickness has an important effect of physical resistance of paper. The highest and lowest of cell wall thickness values were found in Hashemi (3.36 μm) and Amrollahi (2.44 μm), respectively (Figure 5). The Duncan’s mean separation test shows that there is a significant difference in the cell wall thickness between Hashemi and Amrollahi and between Hashemi and Neda rice residues. The average of cell wall thickness in rice residues (2.86 μm) is lower than that of Bagasses (5.63 μm) [10], Canola (5.26 μm) [11], Tobacco (5.3 μm) [11], Bamboo (4.17 μm) [13], Sunflower (3.3 μm) [12], Cotton (3.6 μm) [12], and is higher than that of Corn (2 μm) [14] and wheat (1.6 μm) [14].
Fig. 5: The lumen diameter in three different rice residues.

1.5. Slenderness coefficient:

The highest and lowest of slenderness coefficient values were found in Amrollahi (98.88) and Neda (83.55), respectively (Figure 6). The average of slenderness coefficient in rice residues (88.95) is lower than that of Bamboo (152.31) [13], Corn (180.95) [14] and Kenaf stalks (130) [15] and is higher than that of Bagasses (75.85 μm) [10], Canola (50.82) [11], Tobacco (39.92) [12], Sunflower (57.91) [12], wheat (85.95) [14] and Cotton (45.05) [14].

Slenderness power is an important factor having positive effect on strength, tear, and burst strength according to physical test results of the paper. Generally, the acceptable value for this power of papermaking fibers are more than 33 [17] which these characteristics were found in three types of rice residues (Hashemi, Amrollahi and Neda).

Fig. 6: The slenderness coefficient in three different rice residues.

1.6. Flexibility ratio:

The highest and lowest of flexibility coefficient values were found in Amrollahi (47.79%) and Neda (41.11%), respectively (Figure 7). The average of flexibility coefficient in rice residues (44.58%) is lower than that of Bamboo (45.69%) [13], Corn (52.38%) [14], Bagasses (46.37%) [10], Canola (54.30%) [11], Tobacco (60.82%) [12], Sunflower (70.68%) [12], Wheat (68.68%) [14] and Cotton (78.49%) [12].

According to the flexibility ratio, there are 4 groups of fibers [18]: 1- high elastic fibers having elasticity coefficient greater than 75. 2- Elastic fibers having elasticity ratio between 50-75. 3- Rigid fibers having elasticity ratio between 30-50. 4- High rigid fibers having elasticity ratio less than 30. According to this, flexibility coefficient in Hashemi, Amorllahi and Neda rice residues were considered as rigid fibers. Rigid fibers
don’t have efficient elasticity, they aren’t suitable for paper production and they are used more on fiber plate rigid cardboard and cardboard production.

**Fig. 7:** The flexibility ratio in three different rice residues.

1.7. *Runkel ratio:*

The highest and lowest of Runkel coefficient values were found in Neda (1.57) and Amrollehi (1.19), respectively (Figure 8). The average of Runkel coefficient in rice residues (1.38) is higher than that of Wheat (0.47) [14], Bamboo (1.20) [13], Corn (0.90) [14], Bagasses (1.15) [10], Canola (0.84%) [11], Tobacco (0.65) [12], Sunflower (0.42) [12] and Cotton (0.31) [12].

Standard value of Runkel ratio is 1. Favorable pulp strength properties are usually obtained when value of Runkel ratio is below the standard value. In general, high Runkel ratio fibers are stiffer, less flexible, and form bulkier paper of lower bonded area than low Runkel ratio fibers. This effect is related to the degree of fiber collapse during paper drying, a phenomenon affected by the cell wall thickness and degree of refining that fibers undergo prior to papermaking [19]. From this point of view, the rice different fibers aren’t suitable for papermaking.

**Fig. 8:** The Runkel ratio in three different rice residues.

1.8. *Rigidity coefficients:*

The highest and lowest of rigidity coefficient values were found in Neda (29.44%) and Amrollehi (26.10%), respectively (Figure 9). The average of rigidity coefficient in rice residues (27.52%) is higher than that of Wheat (16.16%) [14], Corn (23.80%) [14], Bagasses (26.86%) [10], Canola (22.84%) [11], Tobacco (19.77%) [12],
Sunflower (14.93%) [12] and Cotton (12.38%) [12] and is a little lower than that of Bamboo (27.61%) [12]. High of this rate effects tensile, tear, burst and double fold resistance of paper negatively [20].

**Fig. 9:** The rigidity ratio in three different rice residues.

2. **Ash and mineral content:**

The average of ash and mineral content for three rice residues are shown in Table 2. The values of ash, K, Mg, Ni and Fe in Neda rice residues are higher than other rice residues, while, Hashemi rice residues have a highest of Cu and Cd. There are higher values of Zn and Pb content in Amrollahi rice residues than other rice residues. Results of mineral content showed that the value of ash in rice residues is higher than hard wood (0.2-0.8%) and softwood (0.2-0.4%) [21]. The silica content in rice residues (14.9%) [22] is higher than hardwood and softwood (below 0.1%).

**Table 2:** Values of mineral content in three rice residues.

<table>
<thead>
<tr>
<th>Mineral content</th>
<th>Neda</th>
<th>Hashemi</th>
<th>Amrollahi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (%)</td>
<td>6.76</td>
<td>6.45</td>
<td>6.41</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>2.105</td>
<td>1.077</td>
<td>2.257</td>
</tr>
<tr>
<td>K (ppm)</td>
<td>2008</td>
<td>1948</td>
<td>1574</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>1433.9</td>
<td>678.9</td>
<td>890.2</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>0.618</td>
<td>0.359</td>
<td>0.275</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>5.216</td>
<td>2.112</td>
<td>2.633</td>
</tr>
<tr>
<td>Cd (ppm)</td>
<td>0.038</td>
<td>0.064</td>
<td>0.051</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>0.348</td>
<td>0.361</td>
<td>0.307</td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>0.005</td>
<td>0.008</td>
<td>0.014</td>
</tr>
</tbody>
</table>

**Conclusion:**

This work focused on the main biometry properties and mineral content of rice residues in the north of Iran (Mazandaran province). The analysis of variance showed that the types of rice residues had significant effect on fiber length, fiber width, thickness cell wall and lumen diameter, while the effect of this factor weren’t significant on the SR, RR, RC and FR. The highest of fiber dimension was found in Hashemi rice residues. Lowest of fiber length and fiber lumen diameter values were found in Neda rice residues, while the values of fiber width and cell wall thickness in Amrollahi rice is lower than other rice residues. Most of mineral content in Neda rice residues is higher than other rice residues such as K, Mg, Ni and Fe. The differences among rice residues in fiber biometrical properties and mineral content could be related to different stem length and grain shape. Because of the Neda rice residue classify in Champa category and Hashemi and Amrollahi residues classify in Saderi category.

Fiber biometrical indexes showed that the rice residues due to high of mineral content, low fiber length and unfavorable biometrical coefficients are not suitable for paper production. The higher of mineral content cause a lot of disadvantages such as corrosion of paper equipment, decreasing of the adhesive joining quality in particleboard, making of color form group in paper. By using rice residues for paper production, it is necessary to use anthraquinone in pulping process [23] and etc. This work increased cost of paper production in industries. Therefore, we only can to use from non-wood fibers in mixture with wood pulp, could become an important component of paper raw material market in the future.
REFERENCES


