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Production of metakaolin from industrial cellulose waste

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Abstract Research focused on the transformation and utilization of industrial wastes into products of commercial interest plays an increasingly important role. Residual pulp can become useful in the manufacture of different materials, providing high value to this waste and reducing its environmental impact when disposed of improperly in the environment. The main constituents of this waste are kaolin and calcium carbonate ($CaCO_3$). Starting from kaolin, metakaolin can be produced by calcination of the residue at 630 °C for 2 h in a rotary reactor with air flow, followed by solubilization with hydrochloric acid to remove the $CaCO_3$. The development of technological alternatives aimed at the reuse of certain wastes can result in applications of real economic interest to the chemical industry and ceramics and glass, which is the case in this study. The raw material and metakaolin obtained were analyzed by thermogravimetric analysis and derivative thermogravimetric analysis, X-ray diffraction, and X-ray fluorescence spectroscopy with promising results. This is because metakaolin was obtained free of contamination by other materials.

Keywords Cellulose residue · Calcium carbonate · Metakaolin

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Introduction

Industrial waste is becoming a serious problem because inadequate disposal causes environmental degradation and the contamination of soil and water sources. The reuse of industrial waste at the productive chain has emerged as an alternative for minimizing the damage that industrial waste can generate.

The paper industry in Santa Catarina State in Brazil has special prominence nationally, occupying the second-largest area of the country forested with *Pinnus elliotii* trees, and is third in paper production and fourth in cellulose production. The paper and cellulose industry of Santa Catarina State is distributed over a great territorial space, with 246 companies located in 71 municipalities, mainly in the micro-regions of the central area and in the west of the State [1]. In 2008, Brazil rose from sixth to fourth place among world producers of cellulose pulp, with 12.7 million tons produced, and advanced from twelfth to eleventh place among the main world producers of paper with 9.4 million of tons. Furthermore, Brazil registered an increase of 5% in paper consumption per capita, which rose from 44.0 to 46.2 kg/hab.

White paper pulping is one process of the pulp and paper industry that produces a byproduct in the form of a mixed material of mineral origin consisting of kaolin and $CaCO_3$ and approximately 10% cellulose.

Kaolins are crystallized, hydrated aluminosilicates that have a chemical composition that approaches $Al_2Si_2O_5(OH)_4$, which corresponds to a theoretical chemical composition (mass%) of 46.54% SiO_2, 39.50% Al_2O_3, and 13.96% H_2O [2]. Upon annealing at approximately 560 °C, dehydroxylation occurs through the loss of –OH groups from the crystal structure, forming amorphous metakaolin.

With paper production increasing and an improvement in product quality sought, the paper industry has generated large amounts of waste that have become an environmental and economical concern. To address this situation, several alternatives for the full or partial recovery of this waste have been studied with the aim of reducing the impact caused.

One studied alternative is the utilization of kaolin as a metakaolin source, which has many applications in several industrial areas, including building construction [3].

Metakaolin, a pozzolana with high reactivity and efficiency, can be used as a modifier additive for the mechanical and chemical performance of concretes and other cementitious products or as a substitute in significant proportions of Portland cement [4, 5]. Several studies have been developed in the field of calorimetry of Portland cements containing different mineral additives [6–8]. It is believed that the metakaolin will present a very intense rate of growth in world production volume over the next two decades. The world consumption of metakaolin could reach hundreds of millions of tons annually in the next two decades. In Brazil, the potential demand for metakaolin exceeds one million tons, which makes it a candidate to dominate a significant part of the world market because of reserves of kaolin in the Amazon region [9].

The use of metakaolin as a supplementary material for preparing cements and mortars has been studied [10], as well as its characteristics and the influence of the end products on its properties [11–15]. In the last few years, the use of metakaolin, obtained from natural kaolin, as a mineral additive for the durability and strength of concretes has grown [16]. And many other papers have studied the characteristics and properties of kaolin and metakaolin [17–20].

This work had as mainly objective the metakaolin free of contaminants producing, using a thermal treatment step followed by a solubilization with HCl, the first step (calcination at 630 °C for 2 h) intended the organic matter oxidation; the second step (solubilization with HCl) had the objective of remove the reminiscent $CaCO_3$ at the annealed material, for a free contaminants metakaolin production. After these steps the CaO (mass%) decreased from 33.76% until 11.93%. The Al_2O_3 (mass%) contend increased from 10.8% until 32.05% and SiO_2 increased from 13.3% until 41.85%. These high contends of Al_2O_3 and SiO_2 indicate a good material for utilization as raw material at the building industry as a pozzolana, which was indentified with the XRD results.

Materials and methods

The solid waste used for metakaolin production originated from the cellulose industries of the middle west of Santa Catarina State. This waste is composed of 45% $CaCO_3$, 45% kaolin, and 10% cellulose.

Obtaining annealed waste cellulose

The waste was annealed at 630 °C for 2 h in a rotary reactor Grion brand, with a capacity of 5 L, in the presence of air provided from a compressor. This annealed step aimed at removing the organic matter from the sample as well as causing the decomposition reaction of kaolin to metakaolin. The waste mass annealed was 0.5 kg. The rotary reactor was build specifically for this work, and it had: temperature, time, rotation velocity, and air flow controls. The air pressure at the reactor was controlled at 101,325 Pa with a typical N_2 (79 vol.%) and O_2 (21 vol.%) ratio.

Annealed waste solubilization

After calcination, the material was subjected to solubilization with 1 M hydrochloric acid (HCl), with the objective to remove the $CaCO_3$ present in the annealed material [21]. Four experiments were done varying the sample mass. All experiments were done with mechanical agitation (300 rpm) for 1 h during which the annealed sample was solubilized with 1 M HCl using the same amount for the four experiments (0.1 L). The first experiment (sample 1) was performed with 5 g of material annealed at 323 K. The second (sample 2) was done using 7.5 g of material annealed at 323 K. The third experiment (sample 3) was done using 10 g of material annealed at 50 °C. The fourth and last experiment (sample 4) was done with 5 g of material without annealing (the sample temperature was 23 °C). After the stipulated time for each solubilization (1 h), the solutions were filtered, and the remaining material was dried in a furnace at 100 °C. After 24 h, the samples were withdrawn from the drying furnace and weighed. The waste was used as the raw material in this study, and the annealed material and the four resulting samples of the described experiments above were characterized by thermogravimetric analysis (TG) and differential

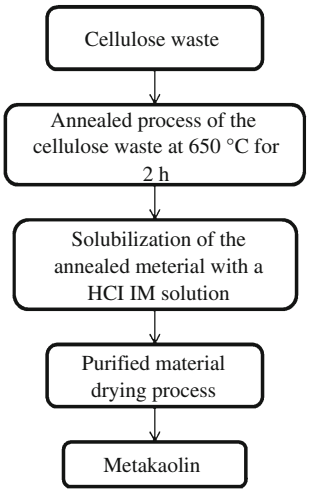

Fig. 1 Flowchart of the experimental procedure steps

thermogravimetric analysis (DTG) using a TA instrument (Q500), 20–1200 °C, 10 °C/min, sample mass of 18.225 mg and Al_2O_3 crucible. X-ray diffraction (XRD) was performed using a Shimadzu instrument (XRD-6000), a current of 30 mA, operating voltage of 30 kV, speed of 2°/min and angle for 5 to 80°. The chemical analysis was performed by X-ray fluorescence spectroscopy (XRF) using a PHILIPS instrument (2400 kVA), with molten sample (lithium tetra borate). Figure 1 shows a flowchart of all of the steps.

Results and discussion

The used waste from the paper industry contained, initially, $CaCO_3$, kaolin, and cellulose. This material, after thermogravimetric analysis (Fig. 2), presented the starting of the cellulose oxidation at 250 °C, finishing at 350 °C. At 400 °C, occurs the dehydroxylation of the kaolin, to form metakaolin. At a temperature near 650 °C, the $CaCO_3$ starts it decomposition to CaO and CO_2. The temperature used at the thermal treatment step was 630 °C and as was expected, the metakaolin and $CaCO_3$ was verified after this step. The cellulose initially present at the samples was removed by oxidation and the kaolin decomposed in metakaolin. As was expected by the thermogravimetric analysis, not was verified the $CaCO_3$ decomposition (CaO forming). Calcium as $CaCO_3$ is preferable for a better yield at the solubilization step with HCl. The objective is the metakaolin enrichment at the final product obtained.

The determination of the $CaCO_3$ amount was done using the molecular mass of CaO and CO_2. Figure 2 shows that 21.02% $CaCO_3$ was detected; dividing by the molecular mass of CO_2 (44%) the mass% of $CaCO_3$ present in the annealed sample can be determined. Therefore, the product of the annealing process is $CaCO_3$ (47.8 mass%) and metakaolinite (52.2 mass%) from the kaolinite dehydroxylation.

In Fig. 3, the XRD spectra of the waste before (a) and after (b) after annealing are presented. The presence of crystalline phases corresponding to calcite, kaolinite and cellulose are observed in the waste.

Figure 4 presents the thermogravimetric analysis of the annealed material. At approximately 400 °C, dehydroxylation of a small amount of kaolinite, which still remained in the annealed sample, takes place. From 600 °C, the

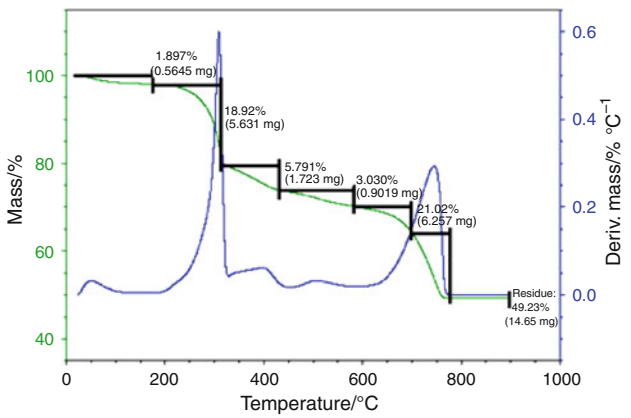

Fig. 2 Thermogravimetric analysis of the cellulose waste

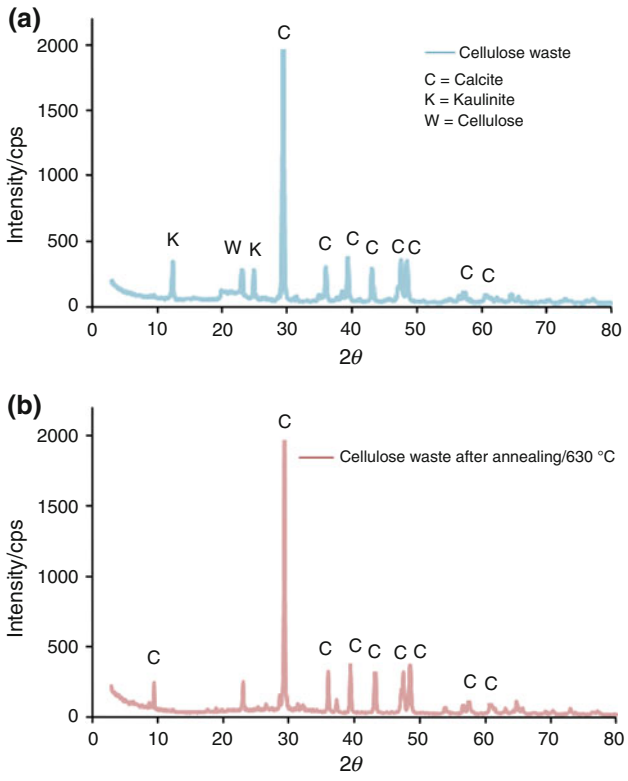

Fig. 3 XRD spectra of the waste **a** before and **b** after annealing

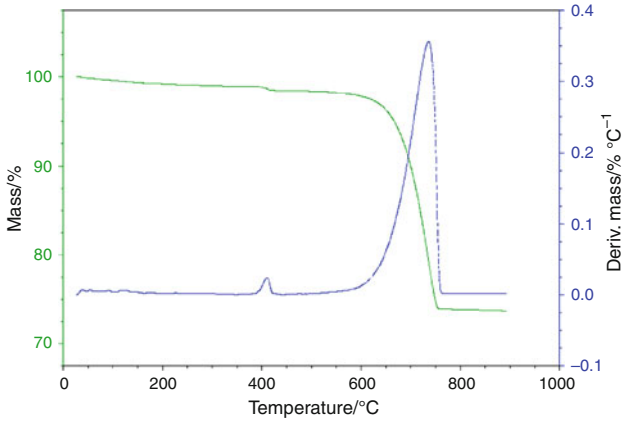

Fig. 4 Thermogravimetric analysis of the annealed (630 °C) material

Table 1 Solubilization results

Sample	Initial solid material/g	Solubilized solid material/mass%	Final solid material/g
1	5	68.6%	3.43
2	7.5	50.1%	3.76
3	10	33.3%	3.33
4	5	65.2%	3.26

$CaCO_3$ starts transforming into CaO, liberating CO_2. The annealing parameters used in this work yielded good results because most of the organic matter was removed at the applied annealing temperature.

The removal of $CaCO_3$ was performed by solubilization with HCl (1 M). Table 1 shows that the best solubilization condition occurred with sample 2 for which the solubilization of 7.5 g of annealed material was performed at 50 °C. For sample 1, because of an excessively high HCl/annealed material ratio, compounds other than $CaCO_3$ were solubilized; the same occurred with sample 4. Sample 3 presented low solubilization of the desired compound.

Comparing the amount of solubilized material at the samples 1 and 4, can be concluded that a 25 °C difference in the temperature does not interfere significantly at the yield of solubilization of the material.

Table 2 reports the presence of other oxides found in the annealed sample, however, in low amounts. The chemical analysis of the cellulose waste before the annealed step, after annealing and after solubilization with 1 M HCl, is also presented. This analysis showed that the main oxides present in the waste are aluminum, silicon and calcium.

The amount of aluminum oxide and silicon oxide increase gradually with each processing step. After annealing, these amounts increase due to cellulose oxidation. After the solubilization process with $CaCO_3$, traces of other elements and residual $CaCO_3$ remained in the final metakaolinite sample.

Table 2 Chemical analysis of the cellulose waste before annealing and after solubilization with HCl

Oxide/ composition	Waste before the annealing process	Annealed waste	After solubilization with HCl/50 °C
Al_2O_3	10.8	18.56	32.05
CaO	33.76	33.57	11.93
Fe_2O_3	0.32	0.48	0.96
K_2O	0.154	0.25	0.56
MgO	0.56	1.22	1.40
MnO	0.01	N.D.	0.01
Na_2O	0.08	0.20	0.35
P_2O_5	0.08	0.15	0.25
SiO_2	13.03	25.08	41.85
TiO_2	0.24	0.55	1.08
Cr_2O_3	<0.1	<0.1	<0.1
SrO	<0.1	<0.1	<0.1
ZnO	<0.1	<0.1	<0.1
LOI	40.79	19.80	9.38

The XRF analysis (Table 2) also indicated that the solubilization process yield was near 66%. The yield determination was done taking into account the calcium amounts before and after the solubilization step with HCl.

Conclusions

The utilization of experimental procedures that allow an extrapolation for the processing of large amounts of material is interesting, fitting for this proposal the rotary reactors, which can process large amounts of waste and with a good quality.

The experiments conducted in a rotary reactor with intake air during the entire processing time confirmed that it is perfectly feasible to obtain metakaolinite with a good yield.

It is also concluded that the optimum ratio for the solubilization step is 75 g/L (annealed waste/1 M HCl solution).

The solubilization yield was 66% based at XRF results, being the process temperature a parameter without significant influence.

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