

# Strategies for characterizing compositions of industrial pulp and paper sludge

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**Abstract.** The large quantities of waste sludge produced by the pulp and paper industry present significant environmental challenges. In order to minimize the amounts of waste, the pulp sludge should be utilized for productive applications. In order to find feasible solutions, the sludge need to be characterized. In this study, the potential of using acid pretreatment and ashing method to determine the chemical compositions of the sludge is investigated. This study shows that acid pretreatment could be used to dissolve and determine the composition of  $\text{CaCO}_3$  in the pulp sludge.  $\text{CaCO}_3$  removal also facilitates the measurement of fiber and ash (clay) contents by using the ashing method. The optimum acid concentration used to completely dissolve  $\text{CaCO}_3$  was determined using a titration method. Using this method, the measurement of the chemical composition of the sludge sample revealed that it consisted primarily of  $\text{CaCO}_3$  (55% w/w), clay (25%, w/w), and fibers (18%, w/w). Based on these chemical compositions, potential utilization for the sludge could be determined.

## 1. Introduction

In 2017, Indonesia is projected to produce 10 million tonnes of pulp and 17 million tonnes of paper [1]. Based on real pulp and paper production and sludge estimation, sludge production from pulp and paper production would be 0.20-0.27 million tonnes/year and 0.31-0.40 million tonnes /year [2]. This large quantity of pulp sludge causes environmental concerns. Currently, industrial pulp sludge is disposed of in landfills or used for land spreading, but this represents low-value use of the sludge [3]. Research has been done to produce value-added products from pulp sludge, including using sludge for the production of concrete block [4] chipboard [2], and cement composite [5]. Components in pulp sludge can also be separated and processed to produce other materials. Wajima and Ikegami [6] used paper sludge ash to synthesize zeolite. The valorization of pulp sludge depends on the compositions and physical properties of the sludge which in turn are affected by the raw materials, manufacturing process, and the types of final products [7, 8]. Pulp sludge is typically composed of water, organic materials such as cellulose fibres, and inorganic materials such as calcium carbonate ( $\text{CaCO}_3$ ) and Kaolin clay [9]. Thus, a characterization step is required to determine the types of value-added products that can be produced from a given pulp sludge. This work analyses a strategy to characterize the composition of pulp and paper sludge and discusses potential applications of the sludge based on the its compositions.



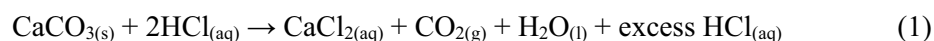
## 2. Materials and Methods

### 2.1. Material

The pulp sludge used in this work was obtained from PT Bukit Muria Jaya in Karawang regency, Indonesia. According to the company, the sludge consisted mainly of fibres,  $\text{CaCO}_3$ , and trace amounts of chemical additives used as coagulant and flocculating agents. The material contained 70 % moisture content. Prior to characterisation, materials were stored at 4°C.

### 2.2. $\text{CaCO}_3$ Removal and Quantification

Sludge samples (10 g wet weight) were mixed with 150 ml of HCl at concentrations ranging from 0.1 - 1.2M in order to find the optimum concentration needed to dissolve all  $\text{CaCO}_3$ . This mixture was stirred for 24 h with a magnetic stirrer at room temperature. After stirring, vacuum filtration was applied to separate the solid from the liquid fraction. The liquid fraction was analysed for pH and  $\text{CaCO}_3$  content. The pH of each filtrate was measured using a pH meter OHAUS ST3100-F. The  $\text{CaCO}_3$  content in the original sludge sample was quantified by titrating excess HCl in the filtrate with NaOH and 3 drops of phenolphthalein as an indicator. Filtrates from 0.8 – 1.2 M of HCl treatment were titrated using 0.47 M of NaOH, and filtrates from 0.6 M of HCl treatment were titrated using 0.02 M of NaOH. Prior to titration, NaOH solutions were standardised using 0.25 M of potassium hydrogen phthalate. The amount of  $\text{CaCO}_3$  was then calculated according to the Equations (1) - (3).



$$\text{CaCO}_3 \text{ Mass } \% = \frac{\text{Mass of CaCO}_3 (g)}{\text{mass of the sludge (g)}} \times 100\% \quad (3)$$

### 2.3. Measurement of Total Solids (TS) and Volatile Solids (VS)

The solid fraction after the HCl treatment was washed with tap water until the samples reached pH 7, indicating that the acid had been completely washed out. Distilled water was used as the final washing. Compositions of TS and VS in the solid fraction were determined by ignition at  $550^\circ\text{C} \pm 25^\circ\text{C}$  in a furnace [10]. A mass balance calculation was then carried out based on the ash and VS contents in the solid fraction after acid treatment. Samples were also analyzed for lignin and cellulose content. Lignin content was determined according to an NREL procedure [11]. Fibre samples were milled to 40 mesh fractions using Thomas Willey- mini cutting mills 1171H10. Milled fibres were subjected to acid hydrolysis with 72%  $\text{H}_2\text{SO}_4$  in order to release the sugars (hemicellulose and cellulose fractions). Upon separation, the solid residue was analysed for acid-insoluble lignin after drying and ignition at  $575^\circ\text{C}$ . The supernatant was analysed for acid-soluble lignin using UV-VIS spectrophotometer optima SP-3000 Nano at 280 nm. All lignin analyses were carried out in triplicates. Cellulose content in the solid fraction was carried out according to the standard anthrone method described by Hodge and Hofreiter [12]. The samples were mixed with  $\text{H}_2\text{SO}_4$  and anthrone reagent and then boiled. The mixture was cooled down and measured using UV-VIS spectrophotometer optima SP-3000 at 620 nm.

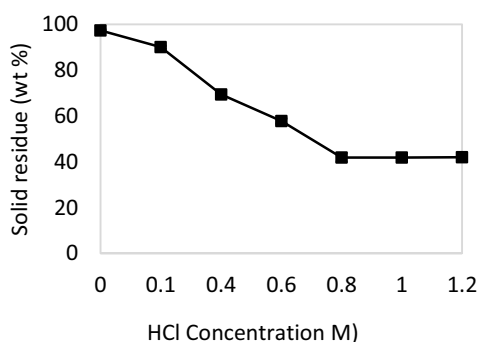
### 2.4. Fiber analysis

The fiber dimensions were analyzed by washing the sludge and separating the fibers manually. The fibers were then treated in a dilute HCl acid (0.1 M) to dissolve the residuals of the  $\text{CaCO}_3$  in the sludge in order to separate the fibers. The fiber lengths were measured by Olympus CX 22 RFS1 microscope, with LED illumination, using a millimeter paper (size: 1x1mm) at the background.

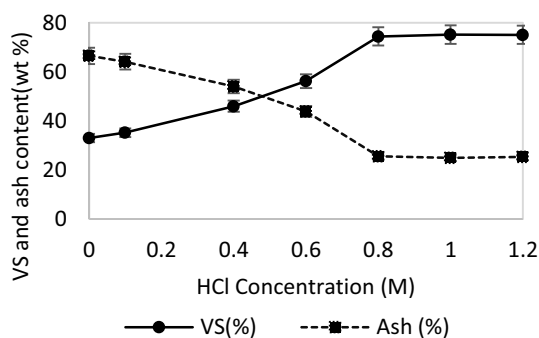
### 3. Results

#### 3.1. Optimization of the dissolution of $\text{CaCO}_3$ with HCl

Figure 1 shows the result of ignition loss expressed as a weight percentage (%wt) of the dry mass of insoluble residue after treatment with different concentrations of HCl. After washing and drying, the untreated sludge lost 2.63% in weight and had 97.3% insoluble residue. Increasing acid concentration from 0.1 to 0.8 M resulted in a steady decrease in the dry weight of the solid residue after the pretreatment (from 90.00% to 41.89%). The decrease in weight after HCl treatment may indicate the dissolution of  $\text{CaCO}_3$  from the pulp sample. An increase in HCl concentrations from 0.8 to 1.2 M did not result in any further change in the remaining percentage weight of solid residue after the treatment, which remained stable at 41.9 wt%. This indicated that there was an optimum HCl concentration for the dissolution of the total amount of  $\text{CaCO}_3$  at ~0.8M.  $\text{CaCO}_3$  dissolution after HCl treatment can also be confirmed by the ignition of the solid fraction at 550°C (Figure 2). The VS showed an increase from 33.1% for the untreated sludge to 74.1 wt % for the sample treated with 0.8 M HCl. Further increases in HCl concentration to 1.2 M did not significantly increase the VS content (75.1 wt%). Similarly, the ash content decreased from 66.6 wt% for the untreated sludge to approximately 25.5wt% for the 0.8M HCl and remained stable with further increases in HCl concentration beyond 0.8 M.



**Figure 1.** The percentage loss of the dry mass of the sludge solid residues after 24 h HCl treatment based on mass balance

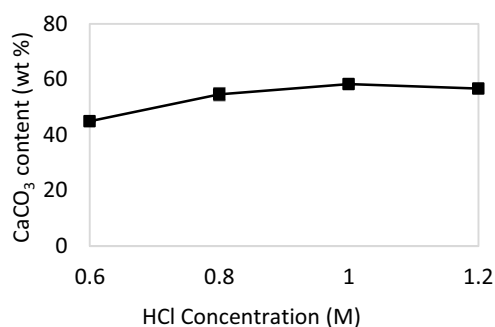


**Figure 2.** The loss of ignition of the solid residues after HCl treatment, expressed as volatile solid (VS %) and ash content (Ash%) of solid residues

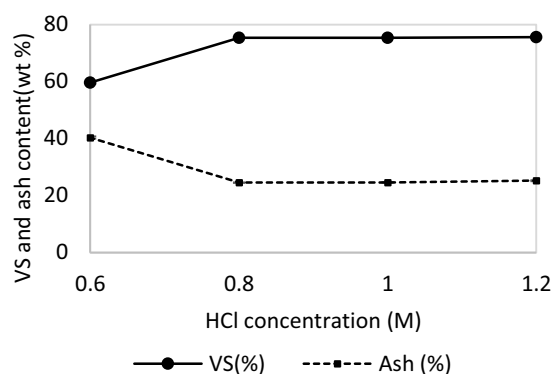
In order to confirm that weight loss after acid treatment was due to  $\text{CaCO}_3$  dissolution, the liquid fractions after treatments with HCl between 0.6 to 1.2M were analyzed using back titration with standardized NaOH. Figure 3 shows the calculated  $\text{CaCO}_3$  content using back titration method. The result showed that 0.6M HCl did not result in complete  $\text{CaCO}_3$  dissolution in the sludge, which is in accordance to with the result from previous method using mass balance of ignition loss of solid residue. The titration with 0.8M showed extensive fluctuation in the weight percent of  $\text{CaCO}_3$ . Repetition of the dissolution step with HCl after separation of the solid residual with acid concentration 0.8M for another 24 h did not significantly change the ash content of the solid residues, which remained stable at 24.5 % as shown in figure 4. The titration result on the other hand was more stable. This indicates that the HCl concentration at 0.8M was rather a transitional concentration for the  $\text{CaCO}_3$  dissolution rather than the optimum concentration for a complete  $\text{CaCO}_3$  dissolution. Further increases in HCl concentrations to 1 and 1.2M stabilized the titration result to 58.3 wt% to 56.7 wt% respectively (Figure 3). This shows that the optimum HCl concentration for dissolution of total  $\text{CaCO}_3$  in the sludge should be higher than 0.8M. This is also confirmed by the pH of the liquid fraction after the acid treatment (Figure 5) where pH decreased from 1.71 in the liquid residue treated with 0.8M HCl to less than 0.5 after treatment with 1.2M HCl. At higher HCl concentration all of the  $\text{CaCO}_3$  were dissolved and the excess unreacted acid in sample resulted in the low pH.

### 3.2. Fiber and clay content analysis

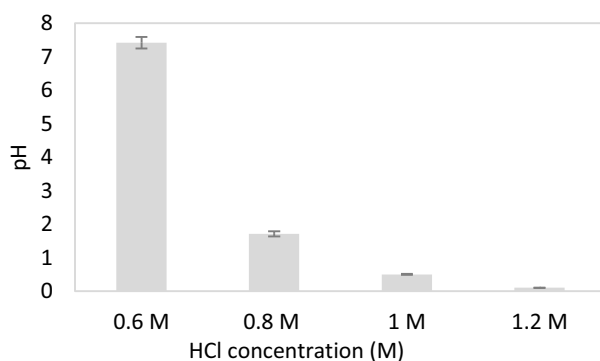
The ash contents in the solid fraction after HCl treatments at concentrations between 0.8 to 1.2M were shown to be stable between 24- 25 wt% (Figure 4). However, a change in the ash color from white gray to pink was observed with the samples treated at HCl concentrations between 0.6 to 1.2M (Figure 8). This color alteration could be caused by a lack of  $\text{CaCO}_3$  dissolution when the sludge samples were treated with HCl at concentrations below 0.8M. The remaining pink color ash could indicate the presence of clay in the pulp sludge.



**Figure 3.** Determination of  $\text{CaCO}_3$  content (wt %) with titrimetric method using standardized NaOH of the liquid filtrate after 24h HCl treatment at different concentration.



**Figure 4.** Titrimetric method - The loss of ignition of the solid fraction after HCl treatment, expressed as volatile solid (VS %) and ash content (Ash wt %) of solid residues



**Figure 5.** The pH of the liquid filtrate separated from the solid residue after HCl treatment at different concentrations

The ash content after combustion was used to indirectly determine the amount of organic matters (fiber) in the pulp sludge. In this case, the sample treated with 1.2 M HCl was used to ensure total  $\text{CaCO}_3$  dissolution from the pulp sample. The VS from the solid fraction were estimated to be 18.5 wt. % (Table 1). The VS of the pure pulp (the raw material) was determined to be 99.8% (wt%). In other words, the pure pulp had negligible ash content. Based on this information, we could ascribe the 18.5% VS from the solid fraction to be the fiber content in the pulp sludge. However, as some fiber might have been lost during acid treatment and filtration process, the percentage weight of the fibers could be slightly higher than the estimated 18 wt%.

The fibers dimension in the sludge was measured to be approximately around 1 mm to 2 mm shown in Figure 6. The acid treatment caused partial degradation of the cellulose fibers, which was lost during filtration process. Figure 6 shows the untreated sludge (6b), and acid treated sludge with 24 h (6c) and 48 h hydrolysis (6d). The 48h-acid treatment caused significant fiber damage while the fibers were more intact after 24h-acid treatment. No significant difference was observed in the ash and VS contents after 24h and 48h-acid treatment: 24 wt% and 75 wt%, respectively (Figure 7).

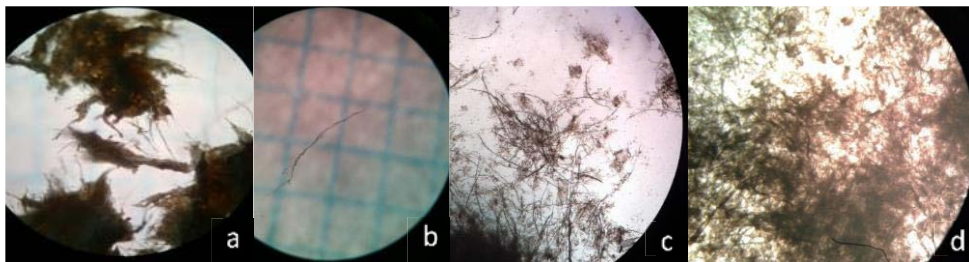
The cellulose content of the pure fibers was measured to be around  $94.6 \pm 5$  (%). The lignin content of the pure fibers was measured to be around  $6.32 \pm 0.33$ . The acid soluble lignin fraction of the fibers was shown to negligible. This indicates that the cellulose content in the untreated sludge should be somewhat higher than the measured value for the pure fibers.

**Table 1.** The result of percentage weight (wt %) of the fibers in the sludge treated with 1.2 M HCl and the volatile solid (VS), cellulose, total lignin and acid soluble lignin content in pure fibers

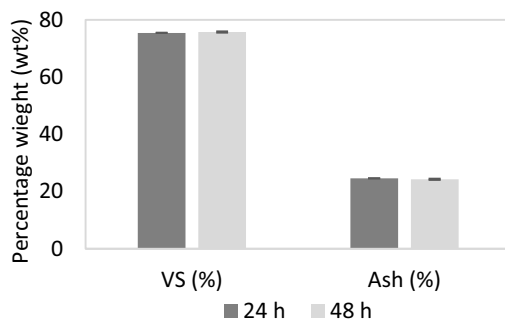
Components	Content (%)
Fibers <sup>a</sup>	$18.5 \pm 0.55$
Volatile solid (VS) <sup>b</sup>	$99.8 \pm 0.1$
Cellulose	$94.6 \pm 5.6$
Total Lignin	$6.32 \pm 0.33$
Acid soluble lignin	$0.044 \pm 0.0003$

<sup>a</sup> Calculated value based on mass balance after ignition loss of the solid residues after 1.2 M HCl treatment

<sup>b</sup> Determined based on pure fibers used in the paper making process.

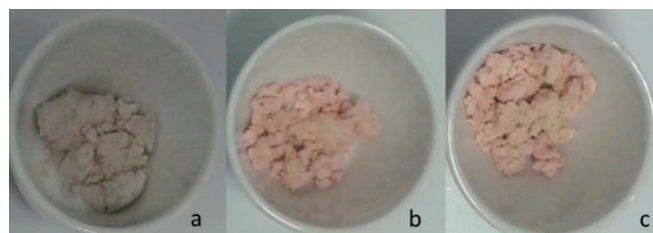


**Figure 6.** The fibers in the a) untreated sludge, b) Separated fibers from untreated sludge and oven dried at 7 °C, c) 24 h acid treatment with 0.8 M HCl and d) 48h acid treatment with 0.8 M HCl



**Figure 7.** Weight percentage of volatile solid (VS) and ash content of the solid residues after 24 h and 48 h of treatment with 0.8 M HCl





**Figure 8.** The colour of ash following ignition of solid residues at 550°C changed from white to pink as the solid residues were treated with increasing HCl concentrations: a) 0.6 M HCl, (white grey colour), b) 0.8 M HCl (pink color), c) 1.2 M HCl (pink colour)

#### 4. Discussion

The composition of the primary sludge from paper making process was analyzed using a combination of loss on ignition (LOI) method and titrimetric method after optimization of HCl concentration for the total amount of  $\text{CaCO}_3$  dissolution. The result shows that using these methods, compositions of  $\text{CaCO}_3$ , fiber, and ash in the pulp sludge could be determined.  $\text{CaCO}_3$  composition was measured between 56-58 wt%. Even though the composition of the sludge vary widely depending on the process, the results of compositional analysis in this study is close to other previous studies [13, 14].

As the decomposition and volatilization of  $\text{CaCO}_3$  usually occur above 600°C, combustion at 550°C would not affect  $\text{CaCO}_3$  content [15]. Therefore, an acid treatment step was required prior to LOI analysis to ensure total  $\text{CaCO}_3$  dissolution. The titrimetric method could be used to determine the optimum HCl concentration that would result in complete  $\text{CaCO}_3$  removal. Following complete  $\text{CaCO}_3$  dissolution, the clay and the fiber contents were measured using LOI to be at 24-25 wt % and about 18 wt%, respectively. This result implies that the simple methods described here can be used to determine the compositions of a typical pulp sludge.

Compositional analysis is important for determining potential utilization for the pulp sludge.  $\text{CaCO}_3$  seems to be the dominant part of our sludge sample (56-58 wt%), which could potentially be used as a soil amendment to balance the pH of acidic soil such as soil affected by coal mining operations [16]. The cellulosic fiber content in the sludge would also improve the ability of the soil to retain water [17]. This direct application of paper sludge on land is the preferred method of utilizing paper mill sludge due to its cost-effectiveness.

Applications of waste sludge in the construction industry, especially in the production of bricks and cement, have also been recognized. Using sludge with 13% ash content in cement tiles has been shown to increase plasticity, workability, strength, and waterproof property of the cement [18]. Sludge with 20% to 30% ash content may be used to produce a facing brick for commercial use [19, 20]. Another potential use of sludge is as filler in bio plastic production as the  $\text{CaCO}_3$  and the fibers work as a binding agent. Cellulose fibers are already known to improve the starch film performance [21] while  $\text{CaCO}_3$  could improve the homogeneity of the plastic by providing good thermal conductivity.

The cellulose fibers in the sludge also have potential applications. Utilization of the cellulose fibers may require separation of the fiber from other components in the sludge. The method described here could be used to remove  $\text{CaCO}_3$  from the sludge, increasing the proportion of the fiber in the treated sludge. The acid treatment to dissolve  $\text{CaCO}_3$ , however, may cause fiber damage, and thus the acid concentration needs to be optimized based on the requirements for the final application of the fiber. In addition, the economics of the process should be considered for such application especially when the cellulose fiber content is not very high.

Kaolin clay was another major fraction (24 wt%) in the sludge sample. The recovery of clay from paper mill sludge using wet air oxidation has been investigated earlier (28). However, it would be more cost effective and easier to separate the clay easily upon ignition after dissolution of the  $\text{CaCO}_3$  as almost all the cellulose fibers are volatilized. The clay component can be potentially be recycled into the papermaking process, used as a masonry additive, or for any other purposes [22, 23]. Kaolin is a natural pigment and the Kaolin clay in the sludge could have potential use for pigment recovery or dye in various application, even though no studies could be found for such application [24, 25].

## 5. Conclusion

This paper has described an inexpensive and easy-to-do method to determine the chemical compositions of a given pulp sludge. By using an acid treatment followed by ignition of the solid residues, the mass balance of  $\text{CaCO}_3$ , fiber, and ash (clay) could be determined. Understanding the chemical compositions of a pulp sludge is necessary to determine the possibility of producing value-added products from the sludge.

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