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Deinking Effect of Paper-Cartons Wastes on Calorifique Value of Combustibles Briquettes

Alexis Dzokom[1], Joël Tize Koda[2], Roger Djoulde Darman [3]
[1]Department of Environmental Sciences, National Advanced School of Engineering, University of Maroua, Cameroon
[2]Department of Renewable Energy, National Advanced School of Engineering, University of Maroua, Cameroon
[3]Department of Agriculture Animal Husbandry and By-Products, National Advanced School of Engineering, University of Maroua, Cameroon

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ABSTRACT
Pre-treatment of paper waste cartons for making briquettes fuels that can be used in substitution of safe firewood for the environment is one of the means of management efficient waste. The objective of this work is the pre-treatment of paper and cardboard waste with locally available products. The stadium preliminary waste pre-treatment paper-cardboard consisted for a time of average maceration of 84.21 hours in NaCl (0.1mol, pH 5) to separate the particles coarse paper fiber. De-inking with weak acid solutions (CH_3COOH, 0.1 mole/liter, Ph 3), strong acid (H_2SO_4, 0.1 mole/liter, Ph 4) and weak alkali solutions (NaOH, 0.1 mole/liter, Ph 8) have made it possible to obtain the same level of average deinking which is 45, while in a strong alkali solution (NaClO, 0.1 mole/liter, Ph 9), the de-inking proved to be a little more important of the average order of 57. The ratio COD/BOD_5 between 3.39 and 14.96 allowed to consider a physico-chemical pretreatment. The leachate resulting from de-inking has been decontaminated using the filters and have been reused or discarded without major danger to the environment while the polluting residues were buried in the unload. Fuel briquettes made from untreated paper-cardboard have a power calorific value is 12.53 MJ / Kg, very close to those completely deinked which is 12.65 MJ/Kg.
Keywords: Pretreatment, bleaching, de-inking, recovery, waste paper

I. INTRODUCTION

Best available techniques for reducing waste means minimizing its production first, to recover them then, and finally to recycle and enhance them. The recycling is part of a comprehensive system comprising different stages all interdependent others. Indeed, the process of managing household waste allows product management used which are the result of processing or final consumption of households and businesses (Revipac, 2008). Thus, pasta factories and papers treat the wastewater from the process before discharging them into the environment and respect the regulations in force (Larouche, 2015). The flow of used products has historically been disposed of without no other prior processing operation. In indeed, it is necessary to carry out the characterization of the effluent to assess its polluting potential (Boudrant, et *al.*, 1994). This defines an equivalent pollution of all effluent compounds (Cindy, 2007). The problem would be that of emissions of harmful fumes during combustion and the presence of chemical elements such as cobalt in paper packaging, brochures, magazines; copper in inks, varnishes; the lead and zinc in printing inks; the manganese in special waste (batteries); the molybdenum in plastics and metals (Meou and Le Clerc, 1999; Report, 2002; François, 2004; Aloueimine, 2006). Attempts to produce solid biofuel from waste paper in to explore other alternative sources to wood heating in the Sahelian zone revealed a potential very satisfactory energy (Tizé et *al.*, 2020). However, the dangerous chemical elements contained in the paper and cardboard unsuitable for this valuation if they are not removed of these. This work was initiated with the aim of reduce the polluting potential of paper waste and cardboard boxes that are recycled through the production of biofuel for household use. It is de-inking the printed paper.

II. MATERIAL AND METHODS

2-1-Sorting and categorization

The very selective sorting of the raw material is preferably done manually, thanks to personal protective equipment (Dzokom et *al.*, 2021).

Following sorting, the A_4 format paper, mainly, was chosen for de-inking. Paper waste and boxes, printed on both sides were cut in small pieces of 0.4 × 29.7cm² with a pair of chisel in small piece of 0.6 x 29.7cm².

2-2- Soaking time and pulping of soaked papers

The determination of the soaking time of each sample of paper and cardboard is made according to a given sample volume. Then to get the necessary time, it was set up the equation:

$y = \frac{p}{s} + \text{In}(e^{10v_{eau}})$, (1)

With P=unit weight; S=unit contact surface; x=number of sheets of the raw material imbibed; y=soaking time; ln=natural logarithm

Soaking facilitates the deformation of the cardboard paper, the release of coarse pollutant (and inking) and the work of shredding, crushing, pressing. Grinding (or mixing) of printed waste paper and their suspension was carried out using an electric kitchen mixer. Spinning through a 0.25 mm/mm a mesh size sieve been done to definitively separate the paper pulp of the solution which floats on the mixture. When trituration, the paper separates into different constituents: fibers, fillers, inks and contaminants (Pelletier,1992).

2-3-De-inking

i)-Preliminary stage

De-inking by combining the flotation and washing is suitable for papers with a size of 5 to 100 µm, imbibed as part of this work. The first wash was made with sodium chloride (NaCl) solution. To do this, an electronic scale was used precision 0.1 grams to quantify NaCl. The maceration solution prepared at the stage preliminary is a solution based on water and salt NaCl. It was weighed 25 grams of NaCl (1 mole/dm^3) which has been dissolved in 500 milliliters of distilled water (H_2O_2). Thus, it was consequently prepared 5 liters of a NaCl solution (0.1 mole/liter) used for soaking and maceration of waste paper boxes. Then followed the peroxide treatment hydrogen (H_2O_2, 3%) to release the agent's large pollutants of lipid origin (oils) from the lignin of the paper, for 4 hours. The treatment for 4 hours with water to cleanse more inks and metals was carried out. The ink particles can be washed away (European Commission, 2001).

ii) - PHASE 1: Washing with acid solution

The first phase as described by Galland (2001), aims to win and eliminate ink on papers printed with water, and some metal ions. This first phase has consisted of washing with an acid solution consisting of 12.5ml of hydrogen peroxide (H_2O_2), and 37.5ml of the acid solution (H_2SO_4, CH_3COOH, 0.5 mole/liter, pH between 4-8). This solution was brought to 50°C.

iii) - PHASE 2: Washing with basic solution

The second phase inspired by the method described by Galland (2001) aims to unhook and to eliminate ink. This is a step for adjusting the pH of the dough by adding liquor alkaline and without addition of alkaline earth ions (Devenyns et *al.*, 2002). The first phase interacts with the second to allow the elimination of ink particles. The dough partially deinked and thickened (by filtration) to a concentration of 15%, had addition of alkaline solution diluted in hydrogen peroxide giving rise to a alkali solution consisting of 12.5ml of peroxide of hydrogen (H_2O_2), and 37.5 ml of the base (NaOH or NaCl, 0.5 mole/liter, pH between 7-14). This solution was brought to 50°C in an oven.

iv)-Measurement of the level of laundering and pastry color

The level of coloration was measured thanks to a portable colorimeter, which uses the principle of mathematical calculations carried out from reflectance values of its filters to obtain in phase 1 the X, Y and Z stimuli such as:

X=(0.782RF9+0.198RF11);

Y=RF10;

Z=1.181RF11.

The values of X, Y and Z then make it possible to evaluate the color coordinates L*(luminosity), a*(hue green- red) and b*(blue-yellow tint) of the system CIE standard (Pelletier C., 1992).

$L^*=[(116)(Y/100)^{1/3}]-16$ (2)

$a^*=500[(X/98.041)^{1/3} - (Y/100)^{1/3}]$ (3)

$b^*=200[(Y/100)^{1/3} - (Z/118.103)^{1/3}]$ (4)

These coordinates make it possible to quantify the tints paper from the CIE LAB graph (Pelletier,1992).

2-5- Treatment of contaminated process water

Drainage allows the papers to obtain a better water clarification. In the case of a deinking by washing, solids can be removed of the filtrate in a separate flotation unit inspired by the methodological approach of Lifestraw (2019) which has two floors (Jay et *al.*, 2013): The first stage consists of a sieve whose bottom was covered with a membrane cloth and a layer of activated carbon, thickness 1 to 3 centimeters, helps retain mineral pollutants toxic from washing water. The second made up with a sieve covered at the bottom of a tissue and iodine-based product layer (consisting of iodized salt 200 mg/g), crushed skeleton of mackerel fish (350 mg/g) and egg shell (450 mg/g) of one thickness of 1 to 3 cm. Contaminated water passing through both sieves is processed to the maximum. After

settling of the process water, it was clarified in a micro-flotation unit which has permit to obtain:
-A colored supernatant liquid;
-A paper slime that is thickened and collected for purification and draining. The quality of the treated water depends on the Suspended Solids (SS), Biologic Oxygen Demand in 5 day (BOD_5), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC).

2-6- Measured calorific value of fuels

The calorific value of a fuel corresponds to the amount of heat released per unit mass during combustion. The heat capacity of the bomb and tank was calculated from a test made with benzoic acid. The warmth of combustion of the sample is measured by combustion of 0.5 g of sample beforehand homogenized (ADEME et al., 2001).

III. RESULTS AND DISCUSSIONS

3-1-Sorting and categorization

During sorting, it was recovered from paper waste- boxes up to 37.74 kg/t of paper. The papers recovered de-ink (newsprint and paper magazine press) about 15.26 kg/t and papers packing box represents 22.48 kg/t. Following the sorting, the majority (98%) A_4 size paper, was chosen for de-inking. These quantities are less than those reported by the European Commission (2011) (50- 100 kg/t paper) for efficient operation recovered papers.

3-2-Soaking and soaking time

i)-Maceration proper

Observations allow us to deduce that 2.416 gr/min at 7.337 gr/min of white paper sheets (like A_4 format) commonly used can be manually macerated. The paper-cardboard packaging is more difficult to macerate (0.045 gr/min).

Table 1: Determination of the paper maceration time

Categories	Unit weight (kg)	Amount of raw material (kg)	Unit contact surface (cm²)	Amount of water (liter)	Soaking Time (Hour)
Printing paper	0.0045	1.0200	625.1850	7.2400	73.8000
Papers, cardboard and similar packaging	1.0800	2.4600	722.2500	1.0800	94.6200

From these data, it emerges that the average maceration of paper and cardboard is 84.21 hours, i.e. 03 days 13 hours. These durations are more longer than those obtained for virgin paper which, submerged in water for a period of 12 hours, facilitates its disintegration during trituration (Pelletier, 1992).

The liquid obtained at the preliminary stage of imbibition tends towards a black color with an average pH of 7.1 and an average conductivity of 170 µS. After removing the papers put in soaking, deposits at the bottom of the container were provided with staples, glue aggregates, sand residues whose masses have been recorded in the following table 2:

Table 2: Quantity of unwanted items from the preliminary stage of cleaning the paper waste

Categories	Amount of raw material (kg)	Amount of staple (g)	Amount of glue aggregate (g)	Amount of sand (g)
Printing, office, newspaper and related paper	5.22	25.90	29.20	25.40
Papers, cardboard and similar packaging	8.48	41.30	23.10	25.90

The addition of hydrogen peroxide made it possible to obtain the release of metals by reacting with previous NaCl solution.

3-3- De-inking of the pulp

3-3-1-) - PHASE 1: Pretreatments with solutions acids

i) -Treatment with sulfuric acid

Mixing the H_2SO_4 solution with the pulp in suspension gave a solution pasty (S_2) at pH 5, in a pulper in the middle acidified with H_2SO_4 including 20gr of cardboard paper were diluted in 100 milliliters of hydrogen peroxide at 45°C. Flotation in an acidic medium (pH = 5) allowed to establish the variation in whiteness between [14-45] in function of the pH, with a maximum pH of 7. These results are like those obtained by Galland

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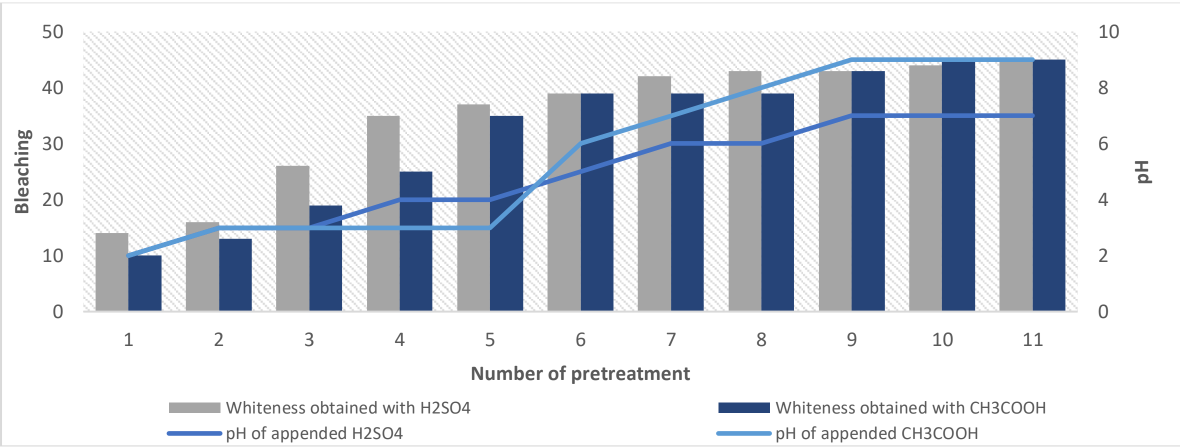
(2001) who obtained a whiteness of 45 by the same process.

ii) -Treatment with acetic acid

The pasty solution (S2) obtained by mixture of 25ml of CH_3COOH (0.5 mole/liter; pH 3) with 20gr of cardboard pulp, has been diluted in 100 milliliters of hydrogen peroxide at 45°C at pH 5. The conductivity (257µS) shows that the solvent obtained is strongly ionized at 60% in CH_3COO^- ions and H^+ (minority). Introducing 02 ml of liquid soap of pH 8.7 in (S2), established the variation in whiteness between [10-45] depending on of pH, with a maximum pH of 7. These results are like those obtained by Galland (2001) who obtained a whiteness of 45 by the same process



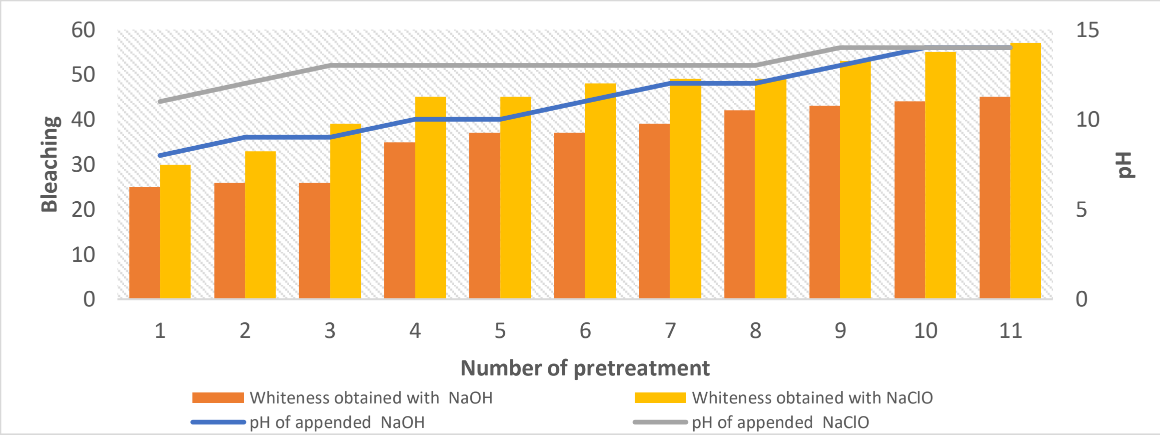
Graphic 1: Bleaching level of pretreated papers and cardboards with acidic solution of CH_3COOH and H_2SO_4

iii) -Treatment with soda (NaOH)

Mixing the solution with the dough by suspension gave a pasty solution (S_2) at pH 8.8 in a pulper in a basic medium with soda at 20g/l of paper-cardboard, diluted in 100 milliliters hydrogen peroxide at 45°C. The 242µS conductivity of the solution shows that the solvent obtained is strongly ionized at 70% NaOH. The new selective flotation, following the introduction of 02 ml of liquid soap, bringing (S_2) to pH 8.7 with a conductivity of 280µS, allowed to drop and eliminate residual inks in the form of foam by making it possible to establish the variation of the whiteness between [25-45] depending on the pH, with a Maximum pH of 7. These results are like those obtained by Galland (2001) who obtained a whiteness of 45 by the same process.

iv) -Treatment with sodium hypochlorite

The basic solution (S_2') at 50°C with addition of sodium hypochlorite (NaClO) and hydrogen peroxide made it possible to vary the mixing volumes as a function of time to obtain the various pH variants of the S_2' solution [11.3-13.8]. Very high conductivity shows that the solvent obtained is strongly ionized at 70% NaClO. 100 mg of the pulp in the pulper were added 50 ml of the solution (pH 8.7 and conductivity 157µS). Then adding H_2O_2 continuously in the mixer (pulper) helped promote ink dropout and subsequent flotation. The measurement of the whiteness made it possible to observe a whiteness variant between [30-49]. The introduction of 2ml of liquid soap with a pH of 8.7 and a conductivity of 280µS at 45°C allowed the mixture to be diluted as well constituted. The dough thus deinked undergoes a new thickening and the whiteness obtained is 57. These variations are like those obtained by Galland (2001) who obtained a whiteness of 45 by same process. The final whiteness of the pasta mechanically bleached does not exceed 80 to 85% because not all C = O bonds are destroyed (Marlin, 2007).



Graphic 2: Bleaching level of pretreated papers and cardboards with alkali solution of NaOH and NaClO

3-3- Quality of contaminated process water
i) - Sludge mineralization

The parameters which have been studied at 20°C are the pH, conductivity, resistivity, mineralization, suspended solid (SS), BOD_5, COD, TOC.

Table 3: pH and conductivity measurement

Parameters	Average
pH	8.80
T°C	20
Conductivity(µS/cm)	230.22
Resistivity(ohm.cm)	4661.33
Mineralization(mg/L)	178.11

The mineralization of the pulp obtained varies between [129.19-260.62]mg/l. These results are similar to those obtained for primary sludge by Primeau, (2014), Thacker, (2006), Bird and Talberth, (2008) and Likon and Trebše, (2012). These authors also noticed the presence of the materials minerals such as calcium carbonate ($CaCO_3$), clay, and titanium dioxide, as well as ash. This sludge therefore contains few elements fertilizers and degrade very slowly (NCASI, 1999a; Olivier, 2007).

-Oxygen demand of the sludge

Suspended solids (SS) obtained by filtration varies between] 1210-2320 [mg/l. These values are higher than those of urban effluents [250 - 600] mg/l (Thomas, 1995; Copp, 2002; Canler et Perret, 2004), but lower than those of the papermaking [1800-4200]mg/l (Gupta, 1997 ; Dutta, 1999; Bajpai, 2000).

Table 4: SS, BOD_5, COD, TOC measurement

Parameters	Average
SS ($mg.\ L^{-1}$)	1737.33
BOD_5($mg.\ L^{-1}$)	368
COD ($mg.\ L^{-1}$)	2073.6
TOC ($mg.\ L^{-1}$)	1721.83

The obtained chemical oxygen demand (COD) is between 1676-2689mg/l. These values are in the range found for pasta manufacturing and between 1200-10000mg/l by Dilek and Gokcay (1994), Bajpai (2000), Rohella, et *al.*, (2001). Determination of biological demand by oxygen in 5 days (BOD_5), [112-630]mg/l, is less than [150-5000]mg/l determined for the pasta making (Dilek and Gokcay., 1994; Bajpai, 2000; Rohella et *al.*, 2001) and less than 690mg/l determined in stationery (Cindy, 2007). However, all the organic carbon is accounted for when determining the TOC (1095-2231mg/l). These values are greater than 200-1200 mg/l obtained for urban effluents (Thomas, 1995; Copp, 2002; Canler and Perret, 2004), but less than 2510mg/l for industries paper mills (Cindy, 2007). They are also more low than those between [1200-10000] determined by Dilek and Gokcay (1994); Bajpai, (2000) and Rohella et *al.* (2001).

ii) - The impact of demand reports in sludge oxygen

The BOD_5/TOC ratio is between 0.09-0.29.It is relatively distant from that of wastewater urban which ranges from 1.0 to 1.6. Likewise, that ofBOD_5/COD between 0.06-0.29, it is lower to that of untreated domestic water which varies from 0.4 to 0.8. These results also indicate that the dough paper in the case of this study is partially biodegradable.

Table5: BOD_5/TOC, BOD_5/COD, COD/TOC, COD/BOD_5 ratio

Parameters	Average
$\frac{BOD5}{COD}$	0.16
$\frac{BOD5}{TOC}$	0.19
$\frac{COD}{BOD5}$	8.95
$\frac{COD}{TOC}$	1.25

The COD/TOC ratio varying between 0.95-1.61 is an indication of the low oxidation rate of organic products because less than 5.33 corresponding to that defined by CREPA, (2007). The COD/BOD_5 ratio varying between [3.39-14.96] is an indication of the presence of a large proportion of material that is not biodegradable as reported by CREPA, (2007).

3-3-4-Measured calorific value of paper-based fuels

The average calorific value measured for combustible briquettes made from non-pretreated is 12.53MJ/Kg, lower than that of fuel briquettes made from cardboard paper pretreated (12.65MJ/Kg). These results are less than 13.15MJ/Kg, obtained by Fick, (2013) for that of coal which varies between 29-35 MJ/Kg. Paper has a lower calorific value which oscillates between 2400KJ/Nm^3 (wet) - 3500KJ/Nm^3 (dry), carton 2300KJ/Nm^3 (wet) - 3800KJ/Nm^3 (dry) and plastic mixed 5500KJ/Nm^3 (wet) -7400KJ/Nm^3 (dry).(Standard INC05-01-04, 2004). Moreover, this power calorific would be attributable to the average weathering of paper and cardboard waste is 65.06 cm per recycling. Overall, the calorific value of fuels varies between [3.20-22.52] MJ/Kg. The lowest calorific values were observed with pretreated paper (95%) - sand (5%) and cardboard (95%) - sand (5%). The highest calorific value high was found for the combustible briquette made from pretreated paper (98%) - plastic (02%) with a calorific value of 22.51 MJ / Kg while the lowest (3.20MJ / Kg) was that of the briquette made from pretreated cardboard (95%) – sand (05%).

IV. CONCLUSION

Pretreatment in the preliminary phase has consisted of pre-cleaning the papers waste, to soften them and allow the release of metals and other coarse pollutants (staple, paperclip, glue, etc.) with salt water. In phase I, deinking with H_2SO_4 allowed to observe the minimum whitening (26) of the pulp at pH of 3, while maximum whitening (45) was observed on the solution brought to pH 7. The deinking with CH_3COOH made it possible to observe minimum bleaching (39) of the pulp at a pH of 6, while the maximum whitening (45) was observed to the pH of the solution brought to 9. In addition to phase I, the thickening of the paste was made at a concentration of 18%. Phase II, the introduction of a alkali solution based on soda (NaOH, 15%), hydrogen peroxide (25%) on the dough deinked with acetic acid (CH_3COOH) allowed the dough to be deinked at a whitening level (45) while processing with acetic acid (CH_3COOH) followed by treatment with NaClO (3%) and hydrogen peroxide (1%) an allowed to obtain a laundering of around 45. The introduction of alkali solution based sodium hypochlorite (bleach (NaClO, 9.6%)) and hydrogen peroxide (25%) on the dough deinked with sulfuric acid (H_2SO_4) allowed de-inked the pulp to a bleach level (45) while the treatment with sulfuric acid (H_2SO_4) followed by treatment with NaClO (3%) and peroxide of hydrogen (1%) made it possible to obtain a laundering of the order of 57. The pre-processing of waste paper and cardboard decreases their power calorific.

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