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Valorization of cashew nut shells as a binder for paint

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ABSTRACT

Actually, manufacturers are committed to developing bio-based products in order to replace fossil-based products with greater environmental impact. The International Associated Laboratory of the University of Antananarivo/University of Lyon1 is developing sustainable chemistry as one of its main research area. One of the examples in this field is the processing of cashew nut shell oil (CNSL) which is the main waste product of cashew nuts.

The extraction of CNSL was realized using butyl acetate as a solvent. Binder synthesis was then carried out from this cashew nut shell liquid (CNSL) using potassium hydroxide and sodium chloroacetate in solution in order to obtain the oxyacetic derivative of CNSL. The latter was used as a binder in our paint and varnishes formulations. The material obtained as stable, free from any organic solvent (100% "water born") and didn't require the use of drying agent or toxic additives. Weather resistance is estimated at over two years.

Keywords: cashew nut shell oil, oxyacetic acid, bio-sourced, binder, paint.

I. Introduction

Consumers increasingly prefer products that respect the environment. Sustainable development is defined as “a mode of development that meets the needs of the present generations without compromising the ability of future generations to meet their own needs” [1]. Consequently, manufacturers are committed to developing products derived from biomass in order to replace products derived from petroleum. Biomass represents organic matter of plant, animal, bacterial or fungal origin that can be used as a source of energy or as raw material for the production of chemical in various industrial sectors. Biomass can be modified by physical, chemical or biological treatments (Standard EN 16575) [2]. Madagascar produces up to 6,072 metric tons of cashew almonds per year [3]. The anacardate is known by the scientific name *Anacardium* western and is classified in the family ANACARDIACEAE. It is native to Brazil. The species is called “Mahabibo” by the Malagasy and grows mainly along the north-west coast, in the regions of Diana and Boeny [4]. Cashew Nut Shell Liquid (CNSL) is a by-product of the cashew nut. It is a cheap and renewable material that replaces alkylphenols with certain advantages [5]. This liquid has various biological activities such as anti-tumor [6], antioxidant [7], gastro-protective [8], antibiotic [9] and industrial applications as biofuel [13] and fuel [14]. In industry, CNSL polymers and resins are used as friction materials, surface coatings and anti-corrosion paints [5]. “Natural” CNSL consists mainly of (45-65%) anacardic acid, (15-31%) cardol, (10-22%) cardanol and traces of methylcardol [10] [11] [12] **Figure 1**. While “technical” CNSL is mainly composed of cardanol (60-95%), 4 to 19% cardol, 1 to 2% anacardic acid, 0.3 to 10% polymer material and 1.2 to 4.1% 2-methylcardol [10] [11].

The objective of this work is to valorize these main components of CNSL by chemical reactions. CNSL had been transformed into amphiphilic molecules that can be used as detergents [15] and as binders for paints [16].

II-Methods

II.1-Materials

The cashew nut shells were collected in the Boeny region in November 2013. These shells are stored in jute bags protected from light and moisture.

Reagents required for the synthesis of binders such as sodium chloroacetate were purchased from Aldrich. The solvents and materials used in the formulation of the paints were provided by local distributors such as Chimidis, SPCI and MCI or generously donated by the company Aurlac (Antananarivo).

II.2-Methods

II.2.1-Extraction of the CNSL

4.5 kg of ground cashew nut shells were weighed and placed in a 50 L steel pilot reactor, then hot macerated at 90°C for 1 h in 6 L of butyl acetate. The mixture was mechanically stirred regularly. This step was repeated three times and the solvent was changed every hour. After filtration, the filtrate was evaporated using a rotary evaporator at a temperature not exceeding 45° C under vacuum. This precaution was taken to avoid any risk of degradation in order to obtain natural CNSL without decarboxylation of anacardic acid

II.2.2-Synthesis of CNSL oxyacetic acid

Ranarijaona et.al described the synthesis of CNSL oxyacetic acid in isopropanol **(Figure 2)** for paint binder applications [16].

293 mmol or 100g of CNSL, 1025.5 mmol or 57 g of potash and 300 mL of isopropanol were mixed in a 2L jacketed reactor. The temperature was raised to 40°C to dissolve the potash. Then 703 mmol or 81 g of sodium chloroacetate was added. The reaction was refluxed at a temperature of 85° C. for 2 hours. The suspension was recovered hot and evaporated to give the oxyacetate salt of CNSL which was dissolved in 300 mL of distilled water. The solution at pH 7 was subjected to liquid/liquid partition with 200 mL of ethyl acetate. The aqueous phase was washed twice with 100 mL of ethyl acetate to eliminate the trace of CNSL in the crude mixture. 55 mL of hydrochloric acid (11N HCl) were added until the pH was equal to 3. This step was followed by liquid/liquid partition with 250 mL of AcOEt. The CNSL diacid was recovered after evaporation of the organic phase.

II.2.3-Paint formulation

Three formulation tests were carried out to compare paint texture and drying time using the same concentration of 0, 9 g/L or 22 mmol/L NaOH solution, CNSL oxyacetic acid, fine dolomite filler and red iron oxide pigment [16].

Test 1: RFH 46

12 g of CNSL oxyacetic acid, 4.8 g of fine dolomite and 3.2 g of iron oxide were mixed. Then, 20 mL of NaOH solution 1.5% in moles relative to the CNSL oxyacetic acid of the, were slowly added to the mixture followed by regular stirring with a mechanical stirrer (700 revolutions / min) at room temperature for 20 to 30 min until a stable emulsion was obtained.

Test 2: RFH 47

12 g of CNSL oxyacetic acid, 4.8 g of fine dolomite, 3.2 g of iron oxide and 512 mg or 5% cobalt octoate were mixed. Then, 20 mL of NaOH solution or 1.5% in mole equivalent of oxyacetic acid of the CNSL, were slowly introduced into the mixture followed by regular stirring with a mechanical stirrer (700 revolutions / min) at room temperature for 20 to 30 min until a stable emulsion was obtained

Test 3: RFH 48

11 g of CNSL diacid, 1g of CNSL, 4.8 g of fine dolomite and 3.2 g of iron oxide were mixed. Then, 20 mL of NaOH solution at 1.5% in moles relative to the oxyacetic acid of the CNSL, were gradually added to the mixture followed by regular stirring with a mechanical stirrer (700 revolutions / min) at room temperature for 20 to 30 min until a stable emulsion was obtained.

III-Results

III.1- CNSL Extraction

From 4.5 kg of cashew nut shells, the first extraction yielded 29% of natural CNSL, the second 9.6% and the third 4.1% **(Figure 3).**

III.2-CNSL oxyacetic acid synthesis

From 100 g of CNSL, 114 g of pure CNSL diacid were obtained (RFH 53 B) 97% (without trace of CNSL) and 10.5 g CNSL mixture and CNSL diacid (RFH 53 A) 14% were recovered from the liquid/liquid partition with AcOEt at pH 7. **(Figure 4 and 5).**

III.3-Paint formulation

Three formulation tests were carried out with CNSL oxyacetic acid and they are summarized in **Table 1**

Test 1 (RFH 46), composed of 30% by mass or 12 g of binder (oxyacetic acid from pure CNSL), 12% by mass or 4.8 g of filler (fine dolomite), 8% or 3.2 g of pigment (red iron oxide) and 50% or 20 mL of NaOH solution or 1.5 % in mole equivalents of binder, gave a good appearance, i.e. a good emulsion, but a slight foaming reaction was observed. The paint obtained has a drying time of 10 hours **(Figure 6a).**

Test 2 (RFH 47), 512 mg or 5% cobalt octoate gave a satisfactory appearance but with some foaming and air bubbles. The paint was stable with a drying time of 8h **(Figure 6b).**

Test 3 (RFH 48), 11 g of pure CNSL oxyacetic acid, 1 g of CNSL, 4.8 g of fine dolomite, 3.2 g of iron oxide and 20 mL of NaOH (1.5% in mole equivalents of binder) gave a paint with a large amount of foam and air bubbles. It had a drying time of 24 h **(Figure 6c).**

IV. Discussion

From 4.5 kg of crushed cashew nut shells, 1.7 kg or 39% of natural CNSL were obtained after pooling the first two extractions, which have the same profile on thin layer chromatography. The third extraction gave 185.7 g or 4.1% of mixture of CNSL and polar products, indicating that two extractions were not sufficient.

The RFH 111 synthesis used 3.4 equivalents of potassium hydroxide and 2.6 equivalents of sodium chloroacetate to give the best yield result of 97% pure CNSL oxyacetic acid and 14% residual CNSL.

Three paint formulation tests were done; test 1, 2 and 3 had 10hours, 8 hours and 24 hours outdoor exposure respectively. Among the three tests, the presence of CNSL in the binder slowed down the drying process (24 hours compare to 10 hours for formulation 1) and conversely cobalt octoate accelerated the drying of the paint formulation (8 hours compare to 10 hours for the formulation 1).

V. Conclusion

Hot extraction with butyl acetate yielded 1.73 kg or 3.9% of cashew nut shell liquid which were used to synthesise a binder for paint.

The binder, a stable film of oxyacetic acid of CNSL, was obtained in a single step of chemical reaction without tedious separation.

The formulation was 100% water-based paint with >90% natural based components, without drying agent or additives and exhibited good stability against various solvents and in tropical conditions.

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Tables

Table 1: Paint formulation

<table>
<tr><th></th><th>Standard conditions</th><th>CNSL Oxyacetic (g)</th><th>Cobalt Octoate (mg)</th><th>CNSL (g)</th><th>Stability</th><th>Drying time (hours)</th></tr>
<tr><td>RFH 46</td><td rowspan="3">-4.8 g of fine dolomite
-3.2 g of iron oxide
-20 mL NaOH 1.5 mol%</td><td>12</td><td></td><td></td><td rowspan="3">Water
Ethanol
Acetone
Hexane</td><td>10</td></tr>
<tr><td>RFH 47</td><td>12</td><td>512 ou 5%</td><td></td><td>8</td></tr>
<tr><td>RFH 48</td><td>11</td><td></td><td>1</td><td>24</td></tr>
</table>

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Figures

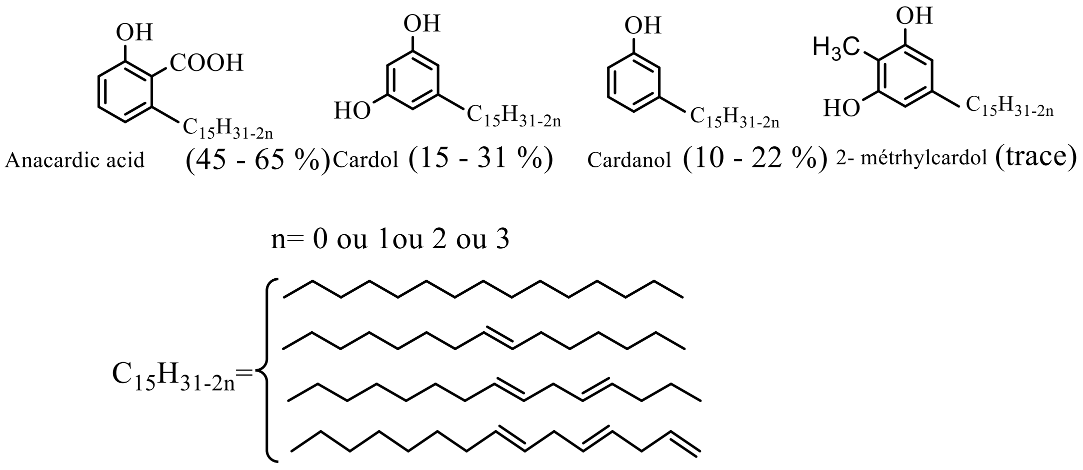

Figure 1: Composition of natural CNSL

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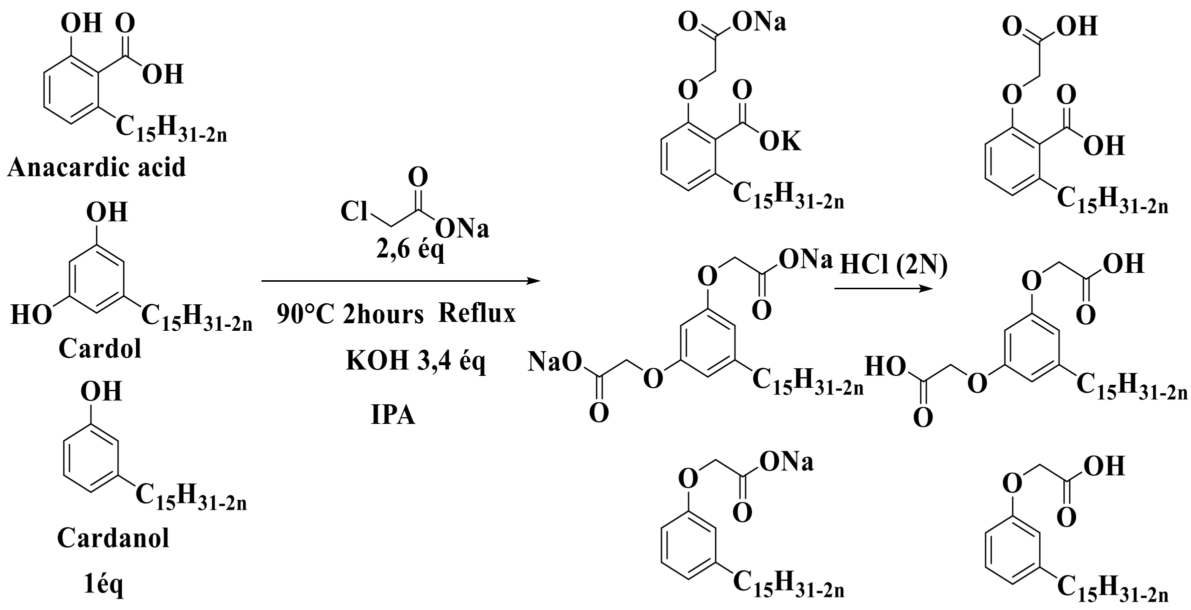

Figure 2: Synthesis of CNSL oxyacetic acid in IPA

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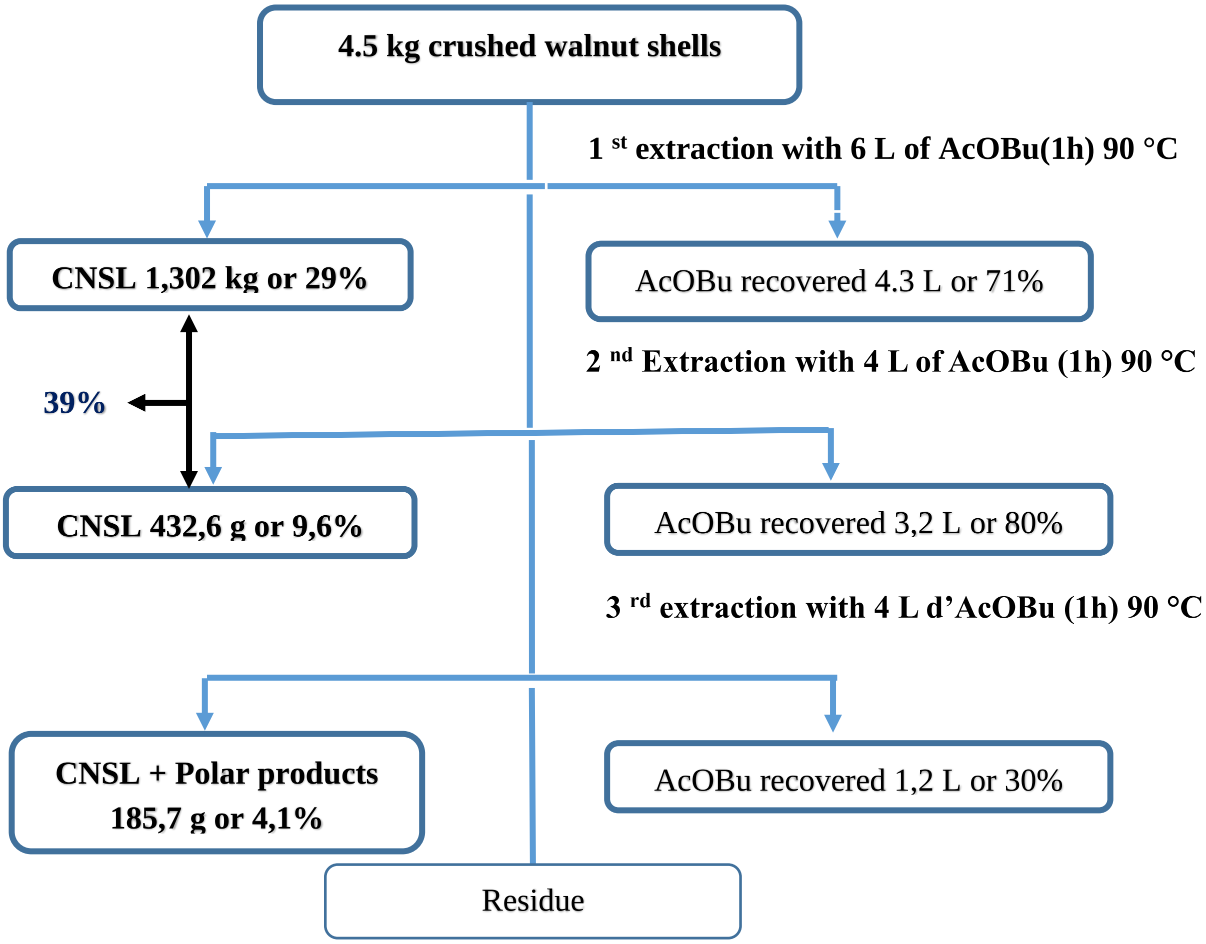

Figure 3: Extraction of CNSL

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100 g ou 293 mmol of CNSL

1-57,4 g ou 1025,5 mmol KOH

2-300 mL Isopropanol

CNSL oxyacetate salt

Isopropanol evaporation 270 mL recovered

CNSL oxyacetate salt without isopropanol

- Addition 300 mL H_20
- Addition 200 mL AcOEt
- Washing (2X) of 100 mLAcOEt

Evaporation of the AcOEt phase

385 mL recovered

CNSL + DIACIDE OF CNSL

RFH 53 A 10,5g or 8,9%

Aqueous phase

Acidification by HCl (11N) 55 ml has pH= 3

Addition of 250 mL AcOEt

Sharing L/L (H_2O/AcOEt

Evaporation of the AcOEt (250 mL recovered)

DIACIDE OF CNSL RFH 53 B

114 g or 97,2%

Figure 4: Result of the synthesis of oxyacetic acid from CNSL

Eluent: AcOEt 100%
Developer: -sulfuric vanillin

Figure 5: CCM of oxyacetic acid from CNSL

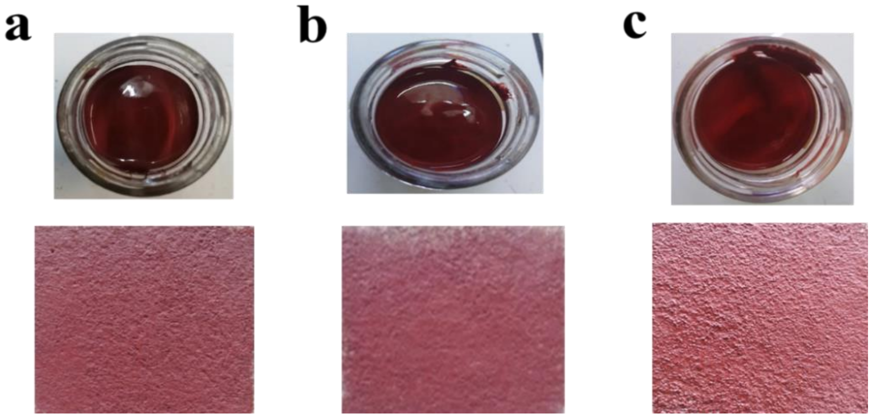

Figure 6: Comparison of paints with pure CNSL oxyacetic acid **(a)**, with pure CNSL oxyacetic acid and cobalt octoate **(b)** and with pure CNSL oxyacetic acid and 1 g of CNSL **(c)**