



# Valorization of the Pn-Pozzolana to the Synthesis of Fe-pn-Pozzolana Study - Application to the Synthesis of the Fe-Pn-SiO<sub>2</sub>

Andry Tahina Rabeharitsara<sup>\*</sup>, Ando Princia Randriamalala<sup>\*</sup>, Nambinina Richard Randriana, Baholy Robijaona, Marie Hanitriniaina Ratsimba

Chemical Process Engineering Department (Ecole Supérieure Polytechnique Antananarivo – E.S.P.A), Antananarivo University, Antananarivo, Madagascar

## Email address:

rabeharitsara\_andrytahina@yahoo.fr (A. T. Rabeharitsara), andoprinciarandriamalala@gmail.com (A. P. Randriamalala), richardrandriana@gmail.com (N. R. Randriana), holyroby@gmail.com (B. Robijaona), ratsimbamarieh@gmail.com (M. H. Ratsimba)

<sup>\*</sup>Corresponding author

## To cite this article:

Andry Tahina Rabeharitsara, Ando Princia Randriamalala, Nambinina Richard Randriana, Baholy Robijaona, Marie Hanitriniaina Ratsimba. Valorization of the Pn-Pozzolana to the Synthesis of Fe-pn-Pozzolana Study - Application to the Synthesis of the Fe-Pn-SiO<sub>2</sub>. *American Journal of Polymer Science and Technology*. Vol. 8, No. 2, 2022, pp. 28-37. doi: 10.11648/j.ajpst.20220802.12

Received: July 12, 2022; Accepted: July 27, 2022; Published: August 5, 2022

**Abstract:** The valorization of pozzolana into pn-pozzolana used as water softening was studied. This article treated particularly the valorization of the pn-pozzolana and pn-SiO<sub>2</sub> by adding iron-Fe atoms to give the Fe-pn-pozzolana and Fe-pn-SiO<sub>2</sub>. Two synthesis procedures were used with the ironIIethoxide Fe(OEt)<sub>2</sub> as precursor material of the iron-Fe atoms deposits on the pn-pozzolana: first there was the solid-solid synthesis where the pn-pozzolana and the Fe(OEt)<sub>2</sub> are both in solid phase; then there was the solid-liquid synthesis where the Fe(OEt)<sub>2</sub> was a liquid phase solution and pn-pozzolana still in solid phase. It was found that the conversion of the Fe(OEt)<sub>2</sub> deposited on the pn-pozzolana depended very significantly on its amount in relation to the pn of the pn-pozzolana. Thus, as the amount of the Fe(OEt)<sub>2</sub> increased, so its conversion and thus the deposit of the iron-Fe atoms on the pn-pozzolana was better. The ratio noted: "7×n"; where n was the moles numbers of the Fe(OEt)<sub>2</sub> on each monomer unit composing the pn; allowed to parameterize each tests. Thus, seeing that one mole of pn contains 7 moles of pn, hence the total number of the Fe(OEt)<sub>2</sub> deposited in an n-pn trial was "7×n". Consequently, it was shown that the radical mechanism of the iron-Fe atoms depositions on the pn-pozzolana or the pn-SiO<sub>2</sub> by the intermediate of the Fe(OEt)<sub>2</sub> passed initially by the formation of an intermediate by dismutation of the neighboring molecules of the Fe(OEt)<sub>2</sub> with iron-Fe atoms depositions followed by the formation of a by-product "diethyl-peroxide" with other iron-Fe atoms depositions by which the reactions progress had been followed. This mechanism allowed to understand and explain the excellence of the iron-Fe atoms depositions on pn-pozzolana or pn-SiO<sub>2</sub>. Thus, a kinetic study of this Fe(OEt)<sub>2</sub> on the pn-pozzolana followed by the iron-Fe atoms depositions had been carried out at 55°C with the optimum ratio "7×4" and allowed to evaluate and calculate the value of its rate constant of the order of 0.6841 [mol×l<sup>-1</sup>×s<sup>-1</sup>] with 2nd partial order in relation to the Fe(OEt)<sub>2</sub>. Finally, some Fe-pn-pozzolana and Fe-pn-SiO<sub>2</sub> materials were synthesized followed by their characterizations in particular by xrf-spectrophotometer which made it possible to confirm the pn's role of the pn-pozzolana as support promoting the excellent iron-Fe atoms depositions on the pn-pozzolana or the pn-SiO<sub>2</sub> by the intermediate of the ironIIethoxide Fe(OEt)<sub>2</sub> with weight dispersion and alkene rate in the order respectively of 5.11% à 23.02% and 5.59E-4 [mol×g<sup>-1</sup>] to 8.91E-4 [mol×g<sup>-1</sup>].

**Keywords:** Pn, Pozzolana, Pn-Pozzolana, Fe-pn-Pozzolana, Fe-Pn-SiO<sub>2</sub>, IronIIethoxide-Fe(OEt)<sub>2</sub>

## 1. Introduction

This manuscript treated the valorization of pozzolana and silica as materials that could be used as catalyst supports.

This pozzolana came from Iavoko and Tritriva sites in the district of Betafo located in Vakinankaratra, a region of Madagascar. The physico-chemical characteristics of this pozzolana were determined at the OMNIS (Office des Mines

Nationales et des Industries Stratégiques) of Madagascar and at the chemical process engineering department of ESPA - Antananarivo university Madagascar. These materials composed of pn-oxide materials, pn-pozzolana and pn-silica ( $\text{SiO}_2$ ) as supports and synthesized according to procedures established on bibliographies [1, 2], were noted respectively Fe-pn-pozzolana and Fe-pn-Si because they contained also pn, the black citric acid polymer [1-5] and Fe from  $\text{Fe}(\text{OEt})_2$  [6, 7]. Many applications could use these materials for catalysts such as polymerization reactions, reduction reactions like the reduction of  $\text{NO}_x$  (azote monoxide NO and azote dioxide  $\text{NO}_2$ ), toxic gaseous formed during the carburant combustion [8]. Thus, the first part of this publication treated the mechanism of the Fe depositions on the pn-oxide material, pn-pozzolana, synthesized according to a procedure established on bibliographies [1, 2], by the  $\text{Fe}(\text{OEt})_2$  molecules. Experimentations and titration procedures were carried-out and established on the Fe-pn-pozzolana to demonstrate this mechanism supported on pn-oxide materials. In the second part of this publication could be seen the kinetic study of the Fe-pn-pozzolana synthesis such as the  $\text{Fe}(\text{OEt})_2$  as reactant used to put down on the pn-oxide materials pn-pozzolana the Fe. Finally, Fe-pn-pozzolana and Fe-Pn- $\text{SiO}_2$  from pn-oxide materials pn-pozzolana, pn- $\text{SiO}_2$  and  $\text{Fe}(\text{OEt})_2$  [1, 2, 6, 7] were synthesized and characterized. Materials and chemicals used during experimentations were KERN precision scale, XRF spectroscopy, refractometer, magnetic stirrer, magnetic bar, beaker-250ml, graduated burette, test tube, separating funnel, pipette, mortar, oven, citric acid, sulfuric acid 98%, pn-black citric acid polymer, pozzolana, silica, distilled water, HF-0.0026N, NaOH-0.05N,  $\text{Fe}(\text{OEt})_2$ , helianthine, thymol blue, bromophenol blue, hexane.

## 2. Synthesis of the Fe-pn-Pozzolana

Two procedure modes were used during the Fe-pn-pozzolana synthesis: the procedure solid-solid (cf. §2.1) and

the procedure solid-liquid (cf. §2.2). The following table 1 showed the characteristics of pozzolana used during syntheses such as the lavoko pozzolana and Tritriva pozzolana. From these characteristics and the pn-equivalent quantities of the synthesized pn [3, 4, 9, 10] (figure 1), the synthesis of the pn-pozzolana was carried out firstly according to the procedure described in the bibliography [1, 2]. Then, to deposit the ferrous-Fe on the pn-pozzolana, the IronIIethoxide- $\text{Fe}(\text{OEt})_2$  [6, 7] was used knowing that these molecules  $\text{Fe}(\text{OEt})_2$  could deposit in an orderly fashion by hydrogen bond on the pn-black citric acid polymer. For example, in figure 2, three IronIIethoxide- $\text{Fe}(\text{OEt})_2$  molecules were deposited on the one monomer unity of the pn-black citric acid; thus in this case the total moles of the IronIIethoxide- $\text{Fe}(\text{OEt})_2$  was equal to  $(7 \times 3) = 21$  twice the total moles of the pn-black citric acid. Throughout the rest of the manuscript, this notation  $(7 \times n)$  was used to indicate the n moles of IronIIethoxide- $\text{Fe}(\text{OEt})_2$  deposited on the monomer unity of the pn-black citric acid and the total moles of IronIIethoxide- $\text{Fe}(\text{OEt})_2$  per one pn-black citric acid. From this disposition between the IronIIethoxide- $\text{Fe}(\text{OEt})_2$  on the pn-black citric acid was deduced the radical mechanisms for the formation of Fe-atoms deposited. Thus, according to the electronic configuration of the iron, either each IronIIethoxide- $\text{Fe}(\text{OEt})_2$  molecule was broken by a radical mechanism with the formation of diethyl peroxide and depositions of the iron-atom (figure 3), or it's also possible that for two IronIIethoxide- $\text{Fe}(\text{OEt})_2$  molecules disposed side by side the two single electrons of the first IronIIethoxide- $\text{Fe}(\text{OEt})_2$  could activate the radical mechanism which broke the O-Fe-O linked of the second IronIIethoxide- $\text{Fe}(\text{OEt})_2$  to form an iron-atom and the product (a), it's only after that this product (a) suffered the broken radical mechanism to form the other iron-atom with the formation of two diethylperoxide molecules (figure 4). Because of this activation, this second mechanism (figure 4) seemed more probable at low temperature whereas the first mechanism (figure 3) was possible at high temperature.

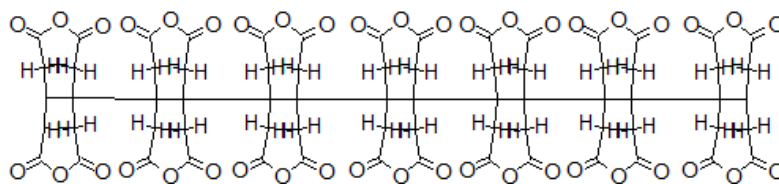


Figure 1. Pn-black citric acid polymer.

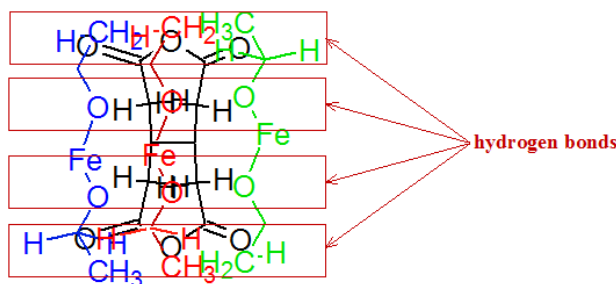
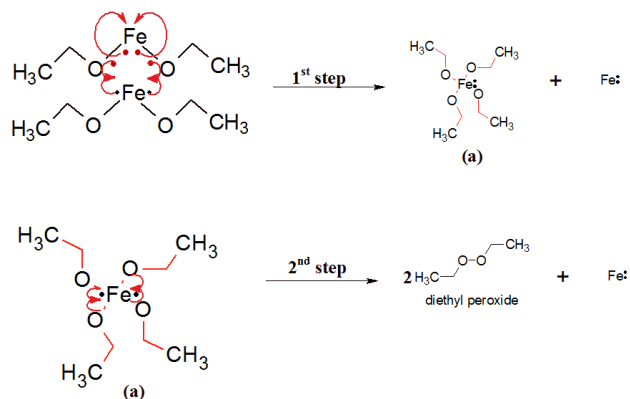


Figure 2. Structure of the monomer unity for  $(7 \times 3)$ -(IronIIethoxide- $\text{Fe}(\text{OEt})_2$ ) / pn-black citric acid polymer) molar ratio 1303.

**Table 1.** Characteristics of Tritriva and Iavoko pozzolana used during experimentations.

[%]	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	Density [g/cm <sup>3</sup> ]	Specific diameter [mm]	Calculated external surface [Å <sup>2</sup> ]	Calculated specific surface [cm <sup>2</sup> /g]
Iavoko pozzolana	14.3532	10.7052	40.9900	8.9210	7.0537	2.5467	0.1920	11.6×10 <sup>12</sup>	122.81
Tritriva pozzolana	12.7020	6.4880	31.9100	8.9210	9.6187	1.7440	0.0790	2×10 <sup>12</sup>	434.37

**Figure 3.** First proposed mechanism for Iron deposition.**Figure 4.** Second proposed mechanism for the Iron deposition.

### 2.1. Solid - Solid Phase Synthesis Procedure of the Fe-pn-Pozzolana Materials

Take the solid raw materials pn-pozzolana and Fe(OEt)<sub>2</sub> and grind them thinly with a mortar. Then put the powders in a glass container and mix them under agitation (manual or magnetic stirrer) to finally have a homogeneous mixture. Then place the whole without a cover in an oven at a stable temperature of 200°C for an hour or more depending on the amount of sample mixture. When the synthesis time is over, remove the product from the oven and cover it with a tightly fitting cover before cooling it at room temperature and away from light. The synthesized product is ready to be characterized.

### 2.2. Solid – Liquid Phase Synthesis Procedure of the Fe-pn-Pozzolana Materials

Take the pn-pozzolana necessary for the synthesis and grind it thinly with mortar. Then, take the volume of the other raw material Fe(OEt)<sub>2</sub> liquid form necessary for the synthesis corresponding to the moles' quantity of raw materials useful for this synthesis. Then mix the two raw materials solution and solid in a glass container without a cover. Stir for at least 3 hours until the ethanol solvent is evaporated and a viscous mixture is obtained. Then, subject this mixture to a heat treatment such as: putting it into an oven at room temperature and programmed to 80°C under a speed 3°C/mn. Leave the product at this temperature for 15 minutes to 45 minutes (depending on the quantity to be treated) in order to evaporate completely the ethanol molecules. Then, raise the oven temperature to 200°C and

leave the product in the oven for an hour or more depending on the quantity to be treated. When the synthesis time is over, remove the product from the oven and cover it with a tightly fitting cover before cooling it at room temperature and away from light. The synthesized product is ready to be characterized. It was found that Fe-pn-pozzolana synthesized by the solid-liquid procedure was more powdery than that by the solid-solid procedure.

## 3. Study of the Fe Mechanism Deposition on the Pn-Pozzolana Materials from Fe(OEt)<sub>2</sub>

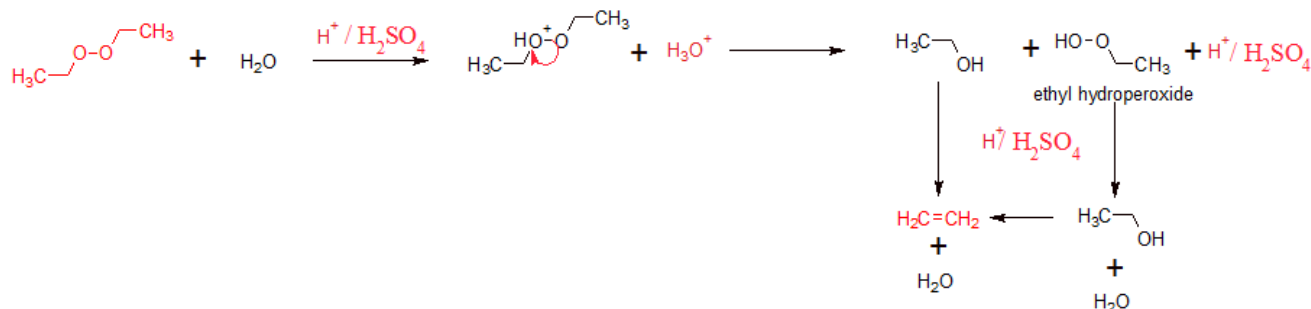
Four parameters had been considered to verify then to determine the mechanism described in the previous paragraph. Thus, the evolution of the transformation of Fe(OEt)<sub>2</sub> molecules into Iron deposited on the pn-pozzolana during the synthesis had been followed and quantified. The first parameter taken into account was the temperature of the experimental follow-up tests. Seeing that the boiling temperature of the by-product to be monitored, diethylperoxide (figure 4) by the indirect titration is 65°C, the temperature of the experimental monitoring tests was reduced to 55°C for 2h and undercover to contain eventual leaks. The second monitoring parameter is the quantification of diethylperoxide molecules deposited on the synthesized pn-pozzolana catalyst at 55°C by HF-0.0026N titration and whose procedure will be elaborated later. The third monitoring parameter was the refractive index of the formed diethylperoxide solution treated with sulfuric acid. The details of this treatment will be seen later in the development of the indirect titration. The fourth parameter was the monitoring of the Fe(OEt)<sub>2</sub> molecules transformed into iron atoms deposited on pn-pozzolana by direct titration of their remains molecules on the synthesized catalyst Fe-pn-pozzolana according to the titration procedure described in the bibliography [6, 7].

### 3.1. Description of the Indirect Titration by HF-0.0026N Procedure

A sample of the synthesized Fe-pn-pozzolana was taken. Then add 35ml of distilled water and mix under magnetic stirring for 1 to 2 minutes to extract the Fe(OEt)<sub>2</sub> and diethylperoxide formed. Filter the obtained solution to retain the remains of the sample's pn-pozzolana solids and record the total volume of the recovered filtrate while determining its refractive index using a refractometer. Then add a drop of sulfuric acid 98% in order to hydrolyze the molecules of diethylperoxide into ethylhydroperoxide and ethanol then to dehydrate these last ones into ethylene according to the

mechanism described in the following figure 5. Add also immediately 5ml to 15ml of hexane and stir the mixture under a magnetic stirrer for a few minutes (15mn to 35mn) then take the refractive index of this solution to see its evolution. Allow setting this solution for 15 minutes. in a separating funnel and then recover the organic phase and its volume which was finally titrated with HF-0.0026N [11, 12]. Thus, the organic phase was composed mainly of ethylene, and eventually few left-over ethanol and ethylhydroperoxide

(figure 5) according to the weight of the sample and its diethylethoxide quantities. So, during the titration, the hydrofluoric acid-HF could react not only with ethylene but also with these few left-over of ethanol and ethylhydroperoxide molecules according to figure 6 and figure 7. Indeed, it was noticed during certain titrations the formation of dark yellow of possible soluble  $\text{CH}_3\text{CH}_2\text{-F}$  salts with ethanol- $\text{H}_2\text{O}$  and  $\text{HO-OH}$  on the bottom and a very light yellow solution on top.



**Figure 5.** Diethylperoxide hydration followed by ethanol dehydration catalyzed by the sulfuric acid protonic acid- $\text{H}^+$ .



**Figure 6.** Reaction between ethanol and fluorhydric acid.



**Figure 7.** Reaction between ethylhydroperoxide and fluorhydric acid.

It was found that by following the synthesis procedure described above (§ 2) where the temperature was at  $200^\circ\text{C}$

with a synthesis-duration of 1h for a rather small quantity without cover, there was almost no more  $\text{Fe}(\text{OEt})_2$  nor diethylperoxide on the Fe-pn-pozzolana material. While at  $55^\circ\text{C}$  with cover for 2h, these different molecules were present, titrated and found either on the surface or certainly trapped in the possible porosities of the Fe-pn-pozzolana material. Thus, two series of results had been obtained while varying the initial quantities of  $\text{Fe}(\text{OEt})_2$  in comparison with pn quantities according to the molar ratios ( $7 \times n$ ) (§ 2.).

**Table 2.** Evolutions of the refractive index of the solutions to be titrated with HF-0.0026N recovered according to the indirect titration procedure (§ 3.1.1) after filtration and after adding 1 drop of sulfuric acid (98%) in comparison with the molar ratios ( $7 \times n$ ) evolutions (Tritriva pozzolana).

(7×n) evolutions (Tritriva pozzolana)		(7×2)	(7×2)	(7×3)	(7×4)	(7×5)
Synthesis procedure		solide-solide	solide-liquide	solide-solide	solide-solide	solide-solide
$I_R$ (after filtration)	$55^\circ\text{C} - 2\text{h}$	1317	-	1317	1328	1314
	$200^\circ\text{C} - 1\text{h}$	1326	1325	1317	-	-
$I_R$ (after adding Sulphuric acid)	$55^\circ\text{C} - 2\text{h}$	1321	-	1321	1324	1360
	$200^\circ\text{C} - 1\text{h}$	1323	1324	1322	-	-

During the synthesis at a high temperature of  $200^\circ\text{C}$ , for the solid-solid synthesis procedure, the recorded refractive indexes after filtration and after adding  $\text{H}_2\text{SO}_4$  decreased when the quantities of the  $\text{Fe}(\text{OEt})_2$  per pn increased from (7×2) to (7×3). These results announced that when the initial quantities of the raw material  $\text{Fe}(\text{OEt})_2$  increased, their transformation into the deposited iron-Fe (figure 3, figure 4) was more important accompanied by the diminution of the by-products such as the diethylperoxide (figure 5) which confirmed and explained the diminution of the refractive index value. And, it was noticed also that, in general from (7×3) to (7×5), the refractive indexes recorded after adding sulfuric acid were higher than the refractive indexes recorded after filtration which could show not only the existence of the

by-product diethylperoxide trapped and retained on the pn-pozzolana but also above all their transformation into ethylene (figure 5) catalyzed by the sulfuric acid protonic acid- $\text{H}^+$ . The diminution of the refractive indexes from 1328- (7×4) to 1314- (7×5) could be explained by the effect of molecules  $\text{Fe}(\text{OEt})_2$  arrangement on the pn-pozzolana for their transformation into the by-product diethylperoxide according to the mechanism described on §2-figure 4. Indeed, at the high values of ( $7 \times n$ ) like (7×5), there were  $\text{Fe}(\text{OEt})_2$  - molecules bulky and disorders on the pn-pozzolana unfavorable to their transformations into the by-products diethylperoxide and ethylene.

Seeing that the sample weight was enough slight, it could be assumed that all diethylethoxide molecules were

transformed into ethylene which were held back by the hexane. Thus, the following table 3 showed the evolution of the ethylene quantities titrated by HF-0.0026N at 55°C for two hours of reaction and different values of the ratio (7×n).

In short, this indirect titration procedure by HF-0.0026N allowed to extract and titrated the diethylethoxide molecules disposed and/or trapped on the pn-Fe-pozzolana materials (figure 5, figure 6, figure 7). Thus, the mechanism proposed

on figure 4 was demonstrated by these experimentations at a low temperature of 55°C. Thus, the results in table 3 showed clearly that as the ratio (7×n) i.e. the quantity of the raw material Fe(OEt)<sub>2</sub> increased, also the quantity of ethylene titrated increased, which confirmed the increase of the diethylethoxide formed through the mechanism on figure 4; and the weight concentration of Fe deposited and the Iron-Fe deposited on the sample rate evaluated by hydrofluoric titration increased also with the ratio (7×n) (table 3).

**Table 3.** Evolutions of ethylene and iron quantities deduced by HF-0.0026N titration at 55°C for different values of the ratio (7×n).

(7×n) evolutions (Tritriva pozzolana)	(7×3)	(7×4)	(7×5)
Sample weight [g]	9.3E-3	8.3E-3	10.3E-3
Initial weight concentration of Fe	3.549E-3	4.732E-3	5.915E-3
Ethylene [moles]	2.62E-6	2.34E-6	7.8E-6
Weight concentration of ethylene [μmolC <sup>≡</sup> /g]	279.57	281.93	757.28
Weight concentration of Fe deposited [μmol/g]	139.785	140.965	378.64
% deposited Fe evaluated by hydrofluoric titration	3.94	2.98	6.40
Iron-Fe deposited [moles]	1.3E-6	1.17E-06	3.90E-06
Iron-Fe deposited weight [g]	7.26E-5	6.53E-05	2.18E-04
Weight % Iron-Fe deposited on the sample evaluated by hydrofluoric titration	0.78	0.79	2.11

### 3.2. Description of the Fe(OEt)<sub>2</sub> Direct Titration Procedure

A sample mass of the synthesized Fe-pn-pozzolana material was taken. Then add 35 of distilled water and stir the mixture for one to two minutes to extract the leftover of Fe(OEt)<sub>2</sub> and the diethylperoxide formed during the synthesis. The solution was then filtered to retain the solid pn. The filtrate volume is measured and then it could be submitted to the refractometer

before the direct determination of its remains of Fe(OEt)<sub>2</sub> whose procedure was quoted in the bibliographies [6, 7]. The following table 4 showed the results concerning the evolutions of the molar conversion in comparison to the (7×n) Fe(OEt)/pn molar ratios and confirmed that the iron-Fe deposited rate increased with this ratio until there were Fe(OEt)<sub>2</sub> – molecules bulky and disorders on the pn-pozzolana at high ratio (7×5) and the % Iron-Fe deposited decreased drastically.

**Table 4.** Evolutions of Fe(OEt)<sub>2</sub> at 55°C for different values of the ratio (7×n).

(7×n) evolutions (Tritriva pozzolana)	(7×2)	(7×3)	(7×4)	(7×5)
Sample weight [g]	3.5E-3	7.3E-3	12.3E-3	2.5E-3
Initial moles of Fe(OEt) <sub>2</sub> [moles]	8.28E-6	2.59E-5	5.82E-5	1.48E-5
Titrated moles of Fe(OEt) <sub>2</sub> [moles]	2.50E-6	5.00E-6	7.5E-6	1.25E-5
Fe(OEt) <sub>2</sub> molar conversion [%]	69.81	80.70	87.11	73.99
Refractive index after filtration	1317	1317	1328	1360
Iron-Fe deposited [moles]	5.78E-6	2.09E-5	5.07E-5	2.29E-6
Iron-Fe deposited weight [g]	3.23E-4	1.17E-3	2.83E-3	1.28E-4
Weight % Iron-Fe deposited	9.22	15.99	23.02	5.11

## 4. Kinetics Study of the Fe Deposits on the Pn-Pozzolana Materials at 55°C with (7×4) Molar Ratio

The kinetic of the general reaction according to the general mechanism, where Fe(OEt)<sub>2</sub> molecules was transformed immediately to Fe, was done by following the weight concentration of the remainder of these Fe(OEt)<sub>2</sub> by titration with NaOH-0.05N for the (7×4) Fe(OEt)<sub>2</sub>/pn molar ratio. Thus, the following table 5 showed the results.

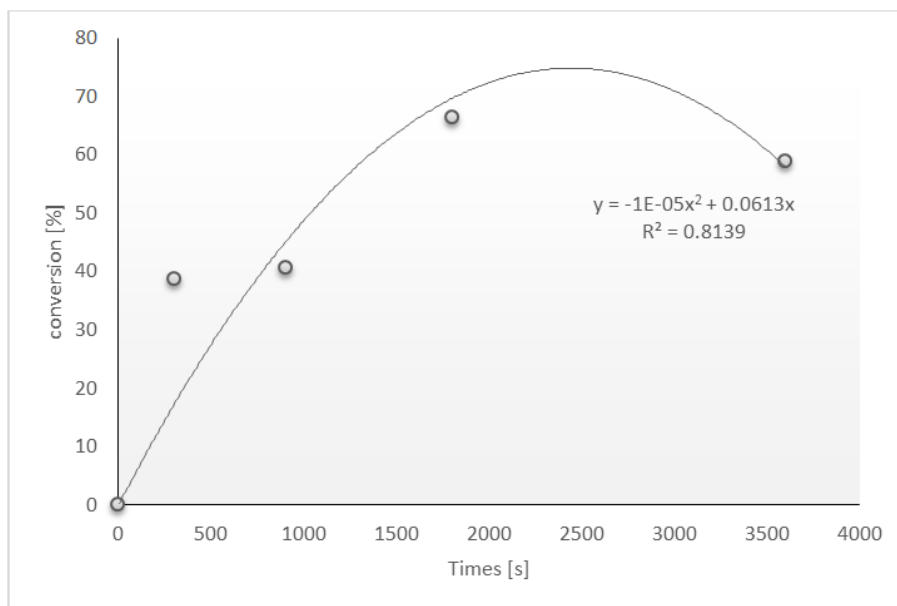
**Table 5.** Evolutions of Fe(OEt)<sub>2</sub> at 55°C for different values of times reaction for the ratio (7×4).

(7×4) Time evolutions [s] (Tritriva pozzolana)	0	300	900	1800	3600
Sample weight [g]	-	2.8E-3	2.6E-3	5.6E-3	4.6E-3
Initial moles of Fe(OEt) <sub>2</sub> [moles]	-	4.08E-6	3.79E-6	8.16E-6	6.70E-6
Titrated remainder moles of Fe(OEt) <sub>2</sub> [moles]	-	2.50E-6	2.25E-6	2.75E-6	2.75E-6
Fe(OEt) <sub>2</sub> Molar conversion [%]	-	38.75	40.63	66.31	58.95
Weight concentration of the [Fe(OEt) <sub>2</sub> ] <sub>weight remainder</sub>	1.46E-3	8.93E-4	8.65E-4	4.91E-4t	5.98E-4
Fe(OEt) <sub>2</sub> weight remainder	6.86E+2	1.12E+3	1.16E+3	2.04E+3	1.67E+3

First, it was noticed in the following figure 8 that the conversion increased with a non-negligible initial conversion

and from approximately 2500s time reaction at approximately 75% conversion, it decreased probably caused

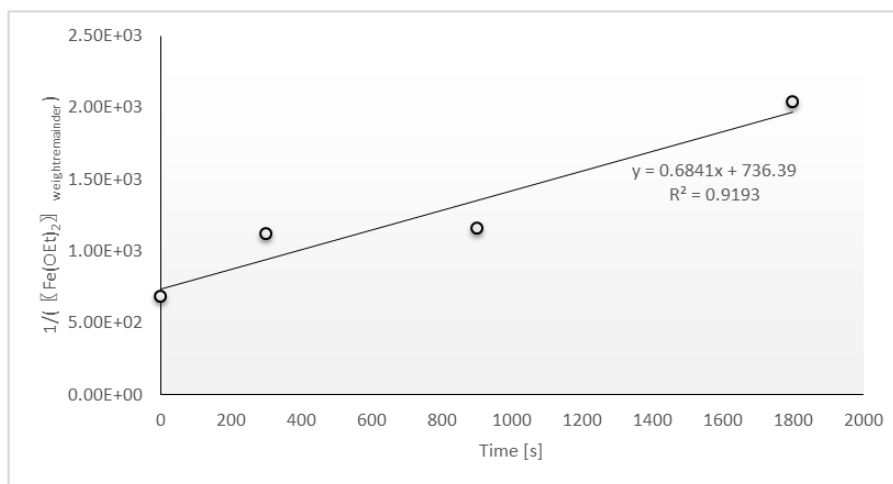
by the decrease of the side by side  $\text{Fe}(\text{OEt})_2$  molecules in the profit of deposited iron-Fe atoms.



**Figure 8.** Evolutions of  $\text{Fe}(\text{OEt})_2$  conversion at 55°C for different values of times reaction and for the ratio (7×4).

Secondly, it was noticed in the following figure 9 that the evolutions of the  $\frac{1}{\text{Fe}(\text{OEt})_2 \text{ weight remainder}}$  with reaction time was a straight line. This result announced that the global reaction of the  $\text{Fe}(\text{OEt})_2$  transformations into deposited iron-

Fe was second order such as the global speed of this reaction was equal to  $v = k \times [\text{FeO}(\text{Eth})_2]^2$  where k the speed constant was equal to  $0.6841 [\text{mol} \times \text{l}^{-1} \times \text{s}^{-1}]$ .



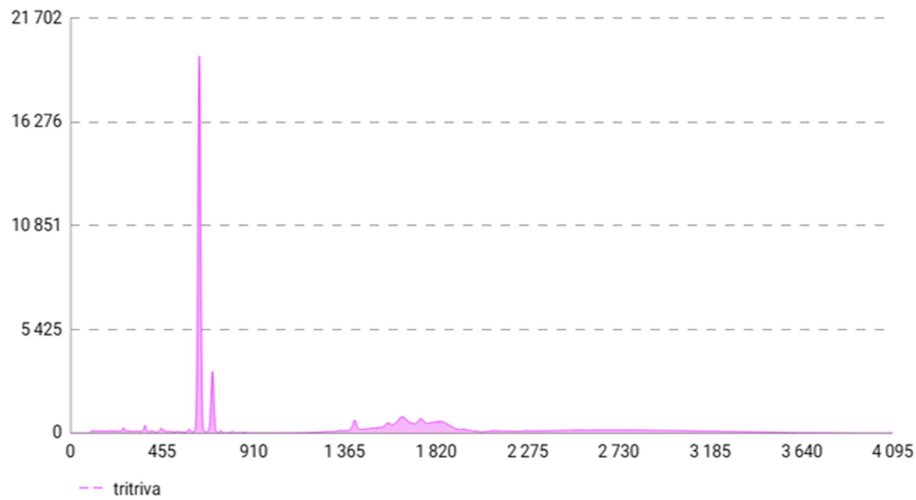
**Figure 9.** Evolutions of  $\frac{1}{\text{Fe}(\text{OEt})_2 \text{ weight remainder}}$  at 55°C for different values of times reaction and for the ratio (7×4).

## 5. Synthesis and Characterizations of Different Fe-pn-Pozzolana and Fe-Pn-SiO<sub>2</sub> Synthesized

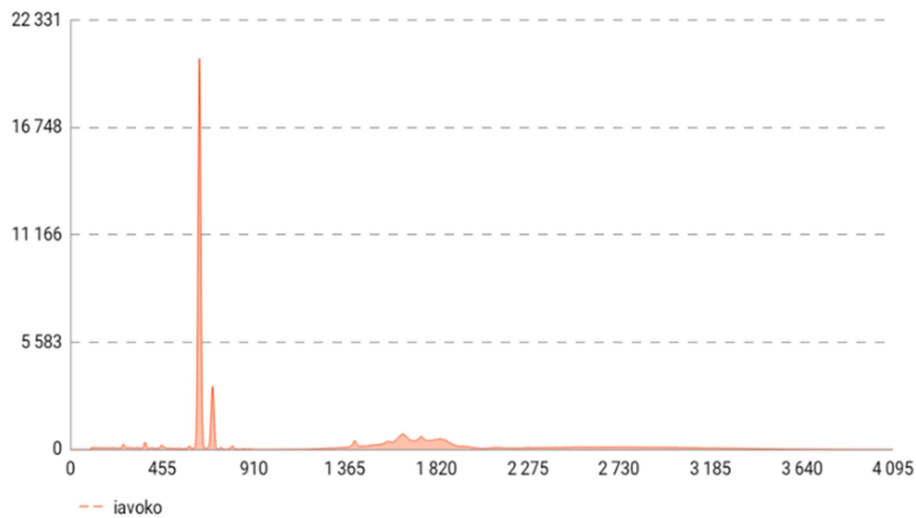
Fe-pn-pozzolana and Fe-pn-SiO<sub>2</sub> was synthesized

according to the procedures described on §-2 and analyzed with the XRF technics. Thus, the following figure 10, figure 11 and figure 12 showed the XRF analysis results of respectively Fe-pn-pozzolana Tritriva, Fe-pn-pozzolana Iavoko and Fe-Pn-SiO<sub>2</sub> such as the purity of the SiO<sub>2</sub> powder was 95%.

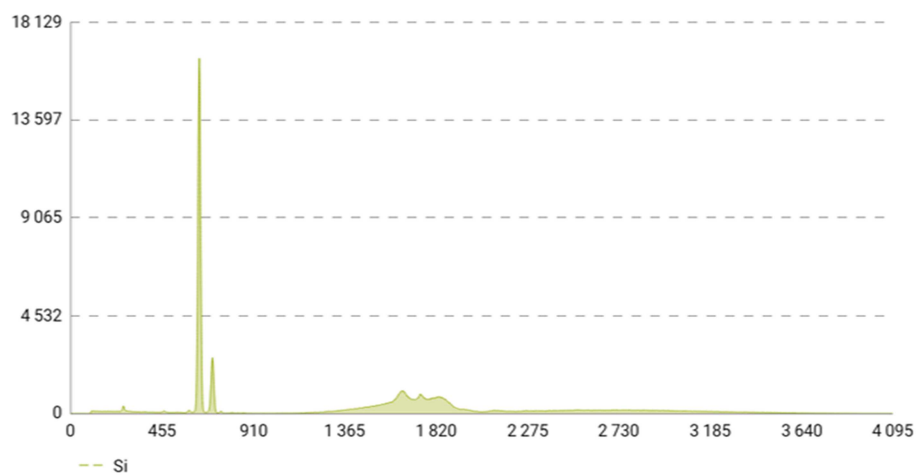




**Figure 10.** Recorded spectra by XRF of Fe-pn-pozzolana Tritriva sample.



**Figure 11.** Recorded spectra by XRF of Fe-pn-pozzolana Iavoko sample.



**Figure 12.** Recorded spectra by XRF of Fe-pn-SiO<sub>2</sub> sample.

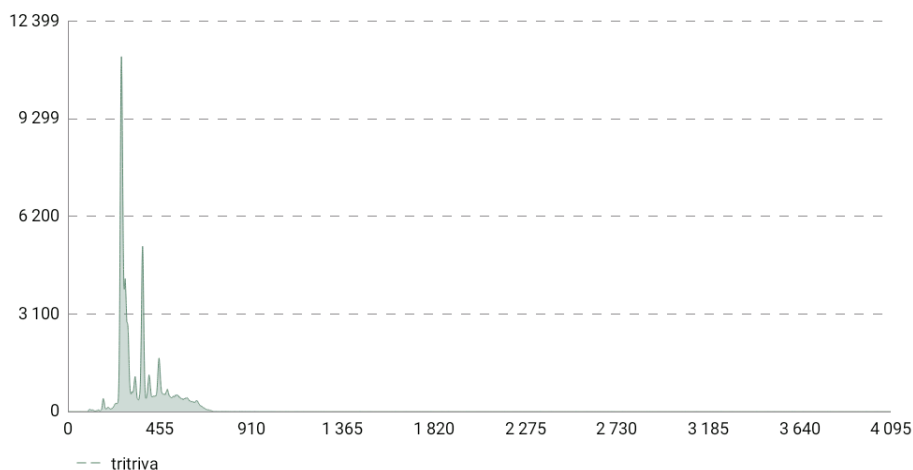
Firstly, it was noticed on every recorded spectrum by XRF two principal pics which was constituted with the deposited Iron-Fe on the surface (The greater pics) and Fe<sub>2</sub>O<sub>3</sub> (The

small pics just beside).

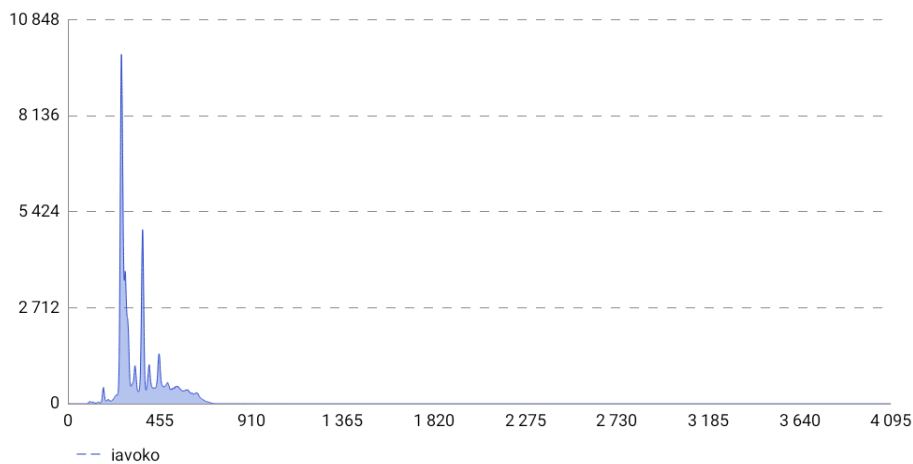
Secondly, it was also noticed, on every recorded spectrum by XRF, pics-sliding-moving particularly for the

deposited Iron-Fe and  $\text{Fe}_2\text{O}_3$  as shown in the following figure 13 to figure 15 in comparison to the previous pics in figure 10 to the figure 12. These pics-sliding-moving were due to the sample matrix effects. Indeed, all samples contained pn-citric acid black polymers disposed on the pozzolana and the  $\text{SiO}_2$  which absorbed their oxides

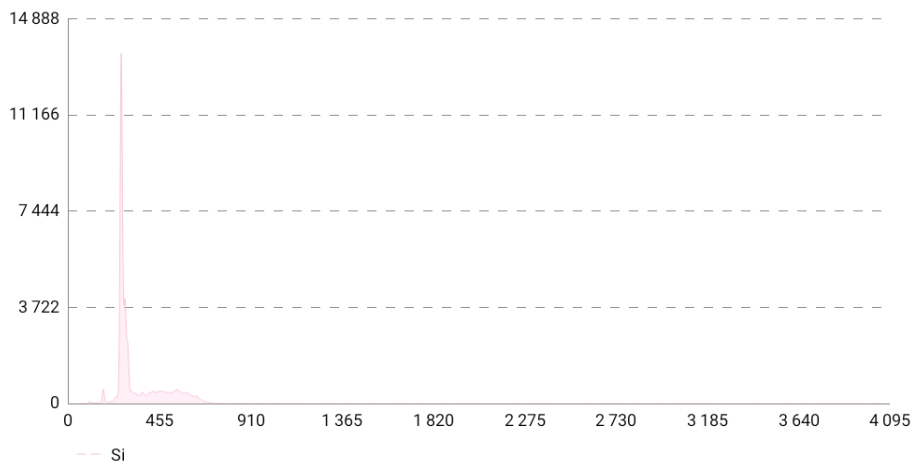
components spectra. In other words, the pics of the iron-Fe deposited were very great and better because they were dispersed well efficacy on the pn-pozzolana /  $\text{SiO}_2$  supports; but the pics of the other oxides were absorbed and very larges. Thus, in the following table 6 were the characteristics of the synthesized materials.



**Figure 13.** Recorded pics sliding-moving spectra by XRF of Fe-pn-pozzolana Tritriva sample.



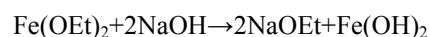
**Figure 14.** Recorded pics sliding-moving spectra by XRF of Fe-pn-pozzolana Iavoko sample.



**Figure 15.** Recorded pics sliding-moving spectra by XRF of Fe-pn-  $\text{SiO}_2$  sample.



To quantify the black polymers fixed in each synthesized product their titrations were necessary according to the following procedure. First, take and weigh the sample, diluted it in a beaker with 15ml of distilled water then add three drops of helianthine. Then, start the titration with 0.05N NaOH. It was found that after a few milliliters, the titrated solution in the beaker becomes light yellow; the equivalent titrant volume was denoted  $V_1$  and this first observation indicated the presence of Fe in the product which was the first to react with the NaOH such as



Indeed the iron arises on the surface of the black polymer which is proven by the first reaction with NaOH. By continuing the dosage, the solution turns completely to orange-yellow which is the indicative color noted  $V_2$  corresponding to the PN-black citric acid polymer titration. The equivalent point for calculating the amount of the PN-black citric acid polymer was the difference between these two volumes. The results of each titration can be seen in table 6 and table 7 below.

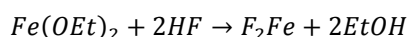
**Table 6.** Equivalent PN of the synthesized Fe-PN-pozzolana/silica samples.

Samples-PN	PN/Iavoko/Fe	PN/Tritriva/Fe	PN/Si/Fe
Mass Sample [g]	0.0068	0.0178	0.0194
nPN equivalent per gram [moles $\times$ g <sup>-1</sup> ]	1.5756E-3	1.8058E-4	4.0501E-4

**Table 7.** Characteristics of the synthesized materials.

Materials/Characteristics	Fe [%]	Fe <sub>2</sub> O <sub>3</sub> [%]	Density [g/cm <sup>3</sup> ]	Specific diameter [mm]	Calculated external surface [Å <sup>2</sup> ]	Calculated specific surface [cm <sup>2</sup> /g]
Fe-pn-pozzolana Tritriva	13.39	2.21	1.744	0.207	0.135	165.93
Fe-pn-pozzolana Iavoko	14.19	2.55	2.5467	0.207	0.135	113.63
Fe-pn-SiO <sub>2</sub>	13.41	2.19	2.4647	0.207	0.135	117.41

For the quantification of the alkene organic function in the synthesized materials, the titration by HF-0.0026N, which was demonstrated to titrate efficiency alkenes organic functions [11, 12], was necessary and followed the following procedure. First, weigh the samples into a beaker, dilute in 30ml of distilled water, stir the solution and add 5 drops of bromophenol blue. Then start the titration with HF 0.0026N. During the titration, two color shifts were observed, the first shift was the color variation of the solutions from blue into very transparent yellow that we denoted  $V_1$ ; this first bend indicated the reaction with HF of Fe(OEt)<sub>2</sub> residues molecules.



The second bend was the color variation of solution from transparent yellow into yellow which indicated the fluorination by the HF [Andry Tahina Rabearitsara, Phandry Nomena Ndjiva Rabearimihaja, betacarotenes assay by hydrofluoric acid solution and validation of this new process by SPC] of (PolyNuclearAromatics-PNA) PNA's alkene in the sample formed during the pn's synthesis [4, 5]. The total HF volume recorded until now was noted  $V_{\text{total}}$ .

Consequently, the alkene weight concentration of the sample (Table 8) was

$$[\text{alkene}] = \frac{(V_{\text{total}} - V_1) \times 10^{-3} \times 0.0026}{m_{\text{ech}}}$$

**Table 8.** The synthesized materials Alkene weight concentration.

Samples-PN	PN/Iavoko/Fe	PN/Tritriva/Fe	PN/Si/Fe
sample weight [g]	0.0140	0.0203	0.0188
Alkene weight concentration [moles $\times$ g <sup>-1</sup> ]	8.91E-4	6.66E-4	5.59E-4

## 6. Conclusion

The “7×n” molar ratio between the amounts of pn in pn-pozzolana and the ironIIethoxide Fe(OEt)<sub>2</sub> amounts was an important parameter for the better synthesis of the Fe-pn-pozzolana and Fe-Pn-SiO<sub>2</sub> materials. This was based on the radical mechanism of neighboring ironIIethoxide Fe(OEt)<sub>2</sub> molecules dismutation guaranteeing a better deposition and dispersion of the iron-Fe atoms on pn-pozzolana and pn-SiO<sub>2</sub> with an optimum ratio at “7×4”. Characterizations of the synthesized materials like with xrf-spectrophotometer was effective and allowed to account the roles of pn and their dispersions on pozzolana and silica as supports of the above

mentioned mechanism. The presence of Fe, pn, alkene functions and porosities in these materials would offer them use and application perspectives like heterogeneous catalysis and polymerisations.

## Acknowledgements

Sincere thanks to the Ecole Supérieure Polytechnique Antananarivo Polytechnics' President. And, sincere respect to Chemical Process Engineering Chief Department (E.S.P.A) as well as Chemical Engineering Laboratory staff and OMNIS- Office of National Mines and Strategic Industries Laboratory for the XRF-analysis.

## References

- [1] Rabemananjara Marie Louise - "Synthèse de PN-pouzzolane et sa valorisation à l'adsorption des polymères marron d'acide citrique et en échangeur cationique PN-pouzzolane-Na" - [Synthesis of PN-pouzzolan and its valorisation for the adsorption of citric acid brown polymers and in PN-pouzzolan-Na cationic exchanger] Mémoire de fin d'étude en vue de l'obtention du diplôme de master titre ingénieur en génie des procédés chimiques et industriels. Ecole Supérieure Polytechnique Antananarivo (E. S. P. A) – Université d'Antananarivo. 2018 - promotion 2018 – Soutenue le 10 Janvier 2020.
- [2] Andry Tahina Rabeharitsara, Nicole Rabemananjara, Nambinina Richard Randriana "Black Citric Acid Polymer (PN) Pozzolana Activated- Na-PN-Pozzolana-CE Material Synthesis Tested As Cationic Exchanger" American Journal of Applied Chemistry; Volume 7, issue 6, December 2019, Pages: 145-160.
- [3] Sammy Eric Andriambola – "Valorisation de l'acide citrique en polymères et en sels de mono- di- et tri-ammonium"- [Valorization of citric acid into polymers and mono-di- and tri-ammonium salts]. Mémoire de fin d'étude en vue de l'obtention du diplôme d'Ingénieur en Génie Chimique. E. S. P. A. Université d'Antananarivo. Promotion 2013.
- [4] Nicole Rabemananjara. "Test d'auto-inflammation du mélange polymère noir d'acide citrique (PN) et du fuel oil (FO) – Etude de la formation de coke" - [Auto-ignition test of black polymer mixture of citric acid (PN) and fuel oil (FO) - Study of coke formation]. Mémoire de fin d'étude en vue de l'obtention du diplôme de Licence en génie des procédés chimiques et industriels. Ecole Supérieure Polytechnique Antananarivo (E. S. P. A) – Université d'Antananarivo. Promotion 2017 – Soutenue le 28 Mars 2017.
- [5] Andry Tahina Rabeharitsara, Nicole Rabemananjara, Nambinina Richard Randriana, Haritiana Jeannelle Rakotonirina, Edouard Andrianarison, André Razafimandefitra, Baholy Robijaona. "Auto-Inflammation Test of Black Citric Acid Polymer (PN) and Fuel Oil (FO) Mixes – Coke Formation". American Journal of Applied Chemistry. Vol. 5, No. 3, June 2017. doi: 10.11648/j.ajac.20170503.11.
- [6] Marson Randrianomenjanahary Avotra – "La synthèse au laboratoire de l'éthanolate de sodium, du citrate tri-sodium, de l'éthanolate de fer-II et du chlorure de fer-II avec de l'éthanol 90°" - [Laboratory Synthesis of Sodium Ethanolate, Tri-Sodium Citrate, Iron II Ethanolate and Iron II Chloride With 90° Ethanol]. Mémoire de fin d'étude en vue de l'obtention du diplôme de Licence en génie des procédés chimiques et industriels. Ecole Supérieure Polytechnique Antananarivo (E. S. P. A) – Université d'Antananarivo - Promotion 2020 – Soutenu le 4 Août 2021.
- [7] Andry Tahina Rabeharitsara, Avotra Marson Randrianomenjanahary, Nambinina Richard Randriana, "Laboratory Synthesis and Titrations of IronIIchloride-FeCl<sub>2</sub> and IronII Ethoxide-Fe(OEt)<sub>2</sub> Using Ethanol-90°" - Hexane and Sodium Ethoxide-Na (OEt)" American Journal of Applied Chemistry. Vol. 9, No. 5, August 2021, pp. 123-130. doi: 10.11648/j.ajac.20210905.11.
- [8] Aurélien Flura – "Réduction Sélective Catalytique Des Nox Par Des Composes Oxygénés" - [Selective Catalytic Reduction Of Nox By Oxygenated Compounds]. Thèse pour l'obtention du Grade de Docteur De L'Université De Poitiers. Soutenue le 01 Juillet 2011.
- [9] Behevitra Rovatahianjanahary - « Synthèse de catalyseurs homogènes B<sub>x</sub>H<sup>+</sup> supportés sur les alcènes des aromatiques et des polynucléaires aromatiques oxygénés composant le bois du pin par traitement à l'acide sulfurique – Application dans la synthèse des polymères noirs d'acide citrique » - [Synthesis of homogeneous B<sub>x</sub>H<sup>+</sup> catalysts supported on the alkenes of the aromatics and oxygenated aromatic polynuclei composing pine wood by treatment with sulfuric acid - Application in the synthesis of black polymers of citric acid]. Mémoire de fin d'étude en vue de l'obtention du diplôme de Licence en génie des procédés chimiques et industriels. Ecole Supérieure Polytechnique Antananarivo (E. S. P. A) – Université d'Antananarivo. Promotion 2018 – Soutenue le 26 Juillet 2018.
- [10] Andry Tahina Rabeharitsara, Behevitra Rovatahianjanahary, Nambinina Richard Randriana – «Pine Wood Powder Treatment To B<sub>x</sub>H<sup>+</sup> Homogeneous Catalyst (H<sup>+</sup>/H<sub>2</sub>SO<sub>4</sub>) Supported On Its Aromatics And PNA – Application In Black Citric Acid Polymer Synthesis». American Journal of Polymer Science and Technology. Vol. 4, No. 1, May 2018, pp. 1-27. doi: 10.11648/j.ajpst.20180401.11.
- [11] Andry Tahina Rabeharitsara, Phandry Nomena Ndjiva Rabearimihaja, – "Betacarotenes Dosage by Hydrofluoric Acid Solution and Validation of This New Process by SPC". American Journal of Applied Chemistry. Vol. 4, No. 3, 2016, pp. 91-96. doi: 10.11648/j.ajac.20160403.14. Received: April 11, 2016; Accepted: April 20, 2016; Published: May 13, 2016.
- [12] Rabearimihaja Phandry Taryh Nomena Ndjiva - «Valorisation Du Betacarotene Extrait De L'huile De Palme Brute Par De L'acide Acétique Pour La Détermination Des Teneurs En Eau De Produits Pétroliers (Gazole /Fuel-Oil) Et Dosage Des Teneurs En Betacarotene Par De L'acide Fluorhydrique» - [Valorization of Betacarotene Extracted from Crude Palm Oil by Acetic Acid for the Determination of Water Content of Petroleum Products (Diesel/Fuel Oil) and Determination of Betacarotene Content by Hydrofluoric Acid]. Mémoire de fin d'Etudes en vue de l'obtention du Diplôme de Master Titre Ingénieur en Génie des Procédés chimiques et Industriels - Ecole Supérieure Polytechnique Antananarivo. Université d'Antananarivo – Promotion 2015 – Soutenue le 06 Mai 2016.