

Research/Technical Note

Black Citric Acid Polymer (PN) Capacity as Raw Material for Cationic Exchanger Realization

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Abstract: The molecular structure of black citric acid polymer (PN) and their hydracids acids functions allowed without doubt their capacities to be potential raw materials for realizing a cationic exchanger. So, the objective of this publication was to study this capacity after activation with sodium hydroxide (NaOH) solution. Two black citric acid polymers PN-2-crispy and PN-3-soft were synthesized whose PN equivalent contents and acidity were evaluated by NaOH-0.05N measuring-out and by Boehm titration. After NaOH-activation which efficacy depends on the PN-size after sieving, two activated-PN were obtained such as PN-2-Na and PN-3-Na whose Na^+ contents were determined by HCl-0.049N titration. Then, exchange cationic tests with CaCO_3 solution were carried out on these activated-PN and the Ca^{2+} contents of treated solution and Ca^{2+} on used PN-2-Na, PN-3-Na was followed by EDTA-complexometric titration. Also, Na^+ and Ca^{2+} on used activated-PN were measuring-out by HCl titration. Results showed clearly that PN once activated with NaOH could carried out cationic exchange and the PN-3-Na was largely active all the time than the PN-2-Na. A global mechanism evolution of these PN-cationic exchange was proposed and also its global kinetic study was done by following-up the $[\text{Ca}^{2+}]$ concentration of treated solution. Results showed that these PN-cationic exchange was second order related with $[\text{Ca}^{2+}]$ concentration of treated solution and the speed constant of PN-2-Na was inferior to the speed constant of PN-3-Na confirming its Ca^{2+} retention capacity.

Keywords: Black Citric Acid Polymer (PN), Sodium Hydroxide, PN-Activation, Chloride Acid, Calcium Carbonate, Cationic Exchange, Complexometric-EDTA, Kinetics

1. Introduction

Black citric acid polymer (PN) was synthesized and their water capacity adsorption were noticed. Then, they were characterized by Boehm titration and NaOH-0.05N titration and finally activated with NaOH to obtain activated black citric acid PN-Na which were characterized by HCl-0.049N to quantify Na's PN. To test the PN-Na's capacities to be a potential cationic exchange raw materials, cationic exchanger tests with a calcium carbonate solution were done and followed-up by complexometric-EDTA titration. Ca^{2+} ions were retained and measuring-out on used PN-Na, also, evolutions of Ca^{2+} concentration on salvage solution allowed to propose a global PN-cationic exchange evolution and its

global kinetic.

2. Citric Acid Black Polymer (PN)

2.1. Generalities

Black citric acid polymer (PN) (Figure 1) is the last polymer obtained by citric acid molecules polymerization catalyzed by acid sites like Brönsted acids H^+ from sulfuric acid or Lewis acids from iron. The first step of this polymerization was citric acid molecules dehydration to form the white monomers which combined together and dehydrated to form the yellow monomers. Then, yellow monomers reacted together with carbon dioxide emission to form red brick polymer, brown polymer and lastly black polymer [1-3].

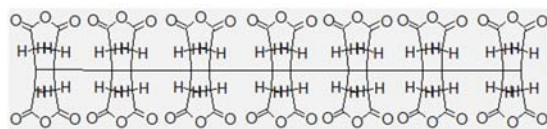


Figure 1. Black citric acid polymer (PN).

2.2. Citric acid black polymer synthesis

Citric acid black polymer synthesis was done according to the procedure cited in the publication concerning its capacity as fuel oil additives [4-5]. But, exceptionally two black polymers were synthesized: for the first, the synthesis was stopped when visually large quantity of black polymer was formed, so we obtained a soft black polymer that we named PN-3 and for the second we didn't stop the reaction if only we obtained a large quantity of crisp black polymer that we named PN-2.

2.3. Citric Acid Black Polymers – Products of Synthesis PN-2 and PN-3 Characterizations

To differentiate PN-2 and PN-3, Boehm titration and NaOH-0.05N measuring out were done to the synthesis.

2.3.1. Citric Acid Black Polymers Equivalent Content Determination of Synthesis Product by NaOH-0.05N Measuring Out

To determine the PN's citric acid black polymers equivalent content, we attacked each PN's oxygen bridge of hydracids-acids functions by NaOH-0,05N. Thus, we obtained Na-carboxylic salts and regenerations of PN's carboxylic acids (Figure 2). For this, take respectively 0.0215[g] and 0.0132[g] of PN-2 and PN-3. Dilute each sample in 15[ml] of distilled water. Then, add two or three drops of helianthine indicator. The equivalent point, which indicated most approximately the transformation of all oxygen bridge; were reached when the solution's color just begin to change with orange-yellow color apparition. As a result, citric acid black polymers equivalent moles content of sample was NaOH's moles divided by 14. Results of citric acid black polymers equivalent content of synthesis titration were showed in the following table 1.

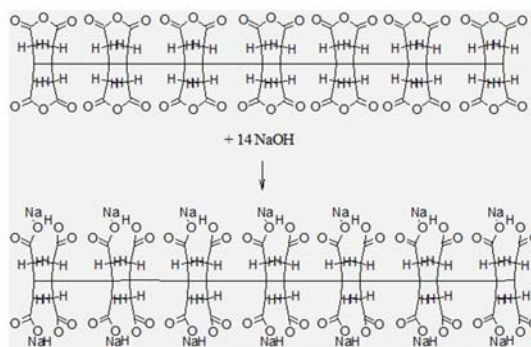


Figure 2. Black citric acid's bridge hydracids-acids functions reaction with NaOH.

Table 1. PN equivalent content of samples PN-2 and PN-3.

Samples	PN-2	PN-3
Sample [g]	0.0215	0.0132
n_{PN} equivalent [moles]	8.3929E-6	7.1429E-6
m_{PN} equivalent [g]	1.3181E-2	1.1218E-2
n_{PN} equivalent per gramme [moles.g ⁻¹]	3.9037E-4	5.4113E-4
PN equivalent content of samples [wt.%]	61.3066	84.9833

After measuring out by NaOH-0.05N, the PN equivalent content of PN-2-the crisp black polymer and PN-3-the soft black polymer were respectively 61.31[%] and 84.98[%]; that is to say the synthesis mode influences the PN equivalent content of black polymer synthesized.

2.3.2. Carboxylic, Phenolic and Lactonic Equivalent Content of Citric Acid Black Polymer Determination by Boehm Titration

PN's surface oxygen functional groups quantification (In the majority carboxyl function) based on the Boehm's titration method [6] was carried out. Thus, respectively, 0.0306 [g] and 0.0305 [g] of PN-2 and PN-3 were shaken in 6.04[ml] of NaOH 0.05N [7-9] during one hour. We obtained a brown mixture solution. Then, the excess of NaOH was titrated (using helianthine indicator) by HCl 0,1N. The equivalent point was reached when in the mixed solution appears red vivid color. Results of Boehm titration were showed in the following table 2.

Table 2. Acidity-directNaOH and Acidity Boehm of samples PN-2 and PN-3.

Samples	PN-2	PN-3
Sample [g]	0.0306	0.0305
PN equivalent content of samples [%]	61.3066	84.9833
n_{PN} equivalent [moles]	1.194E-5	1.6497E-5
n_{PN} equivalent per gramme [moles.g ⁻¹]	3.9020E-4	5.4089E-4
n_{NaOH} [moles]	3.02E-4	3.02E-4
n_{NaOH}/n_{PN} equivalent	25.29	18.31
$M_{samples}$ after titration [g]	0.0009	0.0009
Basic NaOH-Neutralisation rate [%]	97.06	97.05
Acidity total-functional groups by Boehm titration [mmoles.g ⁻¹]	3.5529	4.7528
Acidity total-functional groups by direct NaOH-0.05N titration [mmoles.g ⁻¹]	5.4651	7.5758
Acidity-directNaOH/AcidityBoehm	1.5382	1.5940
Acidity-directNaOH/ n_{PN} equivalent per gramme	14005.89	14006.18

According to the results in table 2, relationship between acidity given by direct NaOH-0.05N titration and acidity given by Boehm-titration is constant equals to 1.6 showing that all

methods give acceptable acidity results. But, seeing that PN samples contains in majority black polymer with carboxylic acid functions and also Acidity-direct NaOH per

$N_{\text{PNequivalentpergramme}}$ values are constant equals to 14,006, the acidity value given by direct NaOH measuring out was more appropriate for the PN-Citric acid Black polymer samples. This didn't rule out the presence of other organic functions in the PN-samples mostly for the PN-2 crisp black polymer [4-5].

3. Citric Acid Black Polymer – Product of Synthesis Water Molecules Retention Capacity

PN's surface chemistry, characterized by Boehm titration and NaOH-0.05N as shown in the table 2, significantly influences the wettability, adsorptive, electrical, electrochemical, catalytic, acide-base, redox, hydrophilic-hydrophobic, and other properties [7]. It was shown that, in particular, oxygen which constitutes 42.77 (%w/w) of citric acid black polymer (PN), influenced its auto-inflammation and improve the auto-inflammation of PN-Fueloil mixes [4-5]. In this case, at ambient air also it was noticed that citric acid black polymer product of synthesis PN-2 and PN-3 adsorbed significantly water. It was followed-up by their weights evolutions.

3.1. Water Molecules Weight Evolution Within the Time

As shown in the following figure 3, at ambient air and in

Table 3. PN-2 and PN-3 water molecules retention capacity.

Samples	PN-2	PN-3
Ambient air exposition duration [h]	336	408
Water moles retained [moles]	0,0311351	0,0678657
Water moles retained per hour [moles/h]	9,26642E-05	1,66E-04
Water moles retained per hour per acidity total NaOH-0.05 [moles/h/mmol.g ⁻¹]	1,69556E-05	2,20E-05

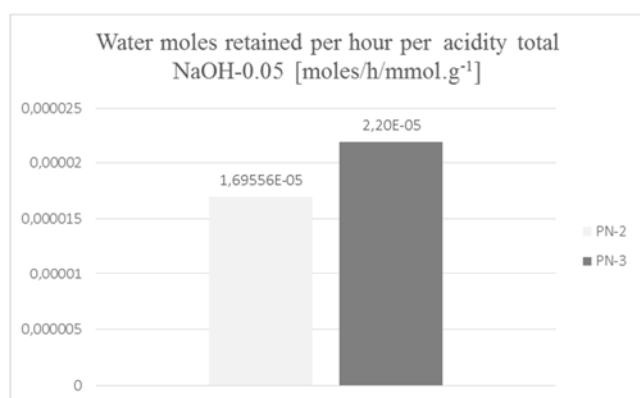


Figure 4. PN-2 and PN-3 water moles retained per hour per acidity total NaOH-0.05.

The presence of important quantity of equivalent PN in PN-3 per sample weight, 1.39 times more than the PN-2 (Table 1), explained the high quantities of acidity total on PN-3 and its high capacity to retain water molecules than PN-2 (Table 3).

Now, it's interesting to view their capacity to be a raw material for polymer cationic exchanger after sieving and activation by NaOH.

general, PN's water adsorption increase proportionately in time. This result is interesting because it confirmed the capacity of PNs synthesized to be easily activated, then to be a potential cationic resin exchanger raw materials.

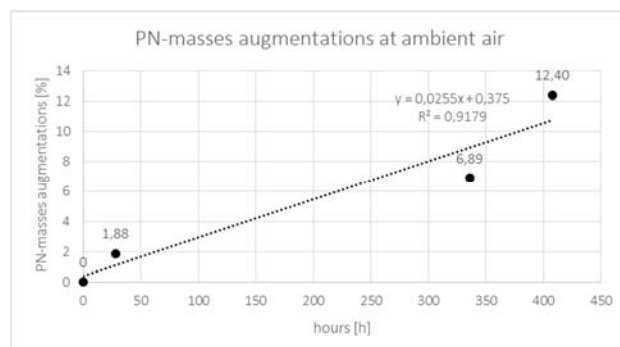


Figure 3. PN weights augmentations in terms of hour at ambient air.

3.2. Water Molecules Evolution Within the Citric Acid Black Polymer – Product of Synthesis Characteristics

To confirm each PN's water retention capacity and to show the acidity total contributions on this water retention, the following table 3 and figure 4 compared the PN-2 and PN-3 water molecules retention according to each acidity content measuring out by NaOH-0.05.

4. Resin and Polymer Cationic Exchanger Principles and Definitions

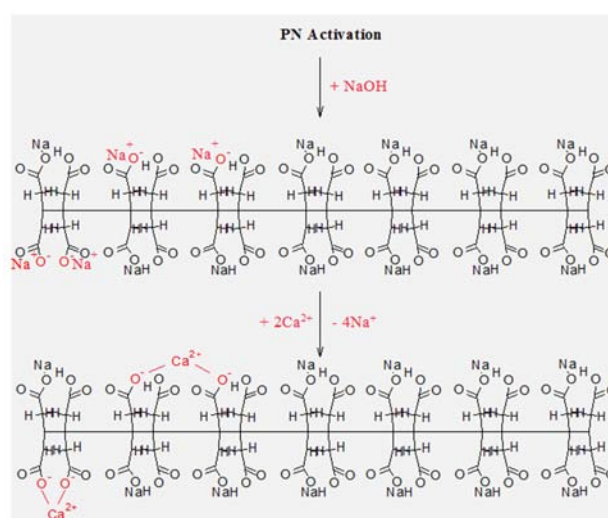


Figure 5. PN Activation with NaOH followed by Ca²⁺ cationic exchange mechanism.

An ion-exchange resin or ion-exchange polymer is an

insoluble matrix or support structure that acts as a medium for ion exchange [10]. Their molecular structure include acids or basics radicals apt to permutate with other ions in the same sign which are in solution with them. This permutation named “ion exchange” presume modification of the solution ionic composition to be treated without modification of the total charge present in solution before exchange [11-12]. According to these ionic exchanger generalities, black citric acid polymer-PN and other citric acid polymers (like brown citric acid polymers) which were water insoluble materials but may be carrying in small quantity by water molecules by hydrogen-bond link could be a potential raw material for the water softening which consist to the reduction/removal of calcium and magnesium ions, principal cause of hardness in water. That is the subject of this manuscript, studying the black citric acid polymer – PN synthesized capacity to be a potential raw material for water softening. Thus, it's necessary to sieve the PN-synthesized for facilitating the NaOH-activation after which PN-Na material was able to play the cationic-exchange polymer according to the following figure 5.

4.1. Sieving System of Citric Acid Black Polymers – Products of Synthesis – Results and Characteristics

The sifting is the action to separate and retain the coarse parts of flour, ashes or chemical powder product through a sieve [13]. Professor Terence Allen characterizes sieving as “The aperture of a sieve may be regarded as a series of gauges

which reject or pass particles as they are presented to the aperture” [14]. Many properties can be influenced by the particle of materials size such as:

- Their strength
- Their taste
- Their dissolution properties
- Their surface activity

Also, it was said in the literature that to limit the pressure losses of the water filtration or purification columns, the balls ion exchanger diameters must be ranging between 0.3[mm] and 1.2[mm] [2-3-15].

Seeing that, the black polymer product of synthesis PN-3 was soft, their sieving was practically impossible but we have agglomerated these materials to obtain PN-3ball whose diameters are ranging between T_i : the lower sieve 0.8[mm] to 2[mm], T_s : the superior sieve. However, the black polymer product of synthesis PN-2 was crisp and after a slight crushing mortar porseleinen we sieved using a vibrating sieve machine with simultaneously two sieves; T_s : the superior sieve and T_i : the lower sieve; whose meshes diameters was respectively 0.8[mm] and 0.25[mm] [2-3]. We obtained the refusals indicating the part of PN retained by the lower sieves. The refusal sizes that we obtained during this sieving procedure was very important because it's one of the responsible of the well diffusion and well reactions of NaOH during the PN-activation step (Figure 5).

Results and characteristics of PN-2 and PN-3 is shown in the following table 4.

Table 4. PN-2 and PN-3 refusals characteristics.

Refusal Characteristics (RC)	Formulas	PN-2RC values	PN-3RC values
Coefficient of uniformity (c.u)	$c.u = \frac{T_s}{T_i}$	3.2	2.5
Specific diameter (ϕ_s) [mm]	$\phi_s = T_i \times (1 + 2 \log c.u)$	0.503	1.437
Fifty diameter (d_{50}) [mm]	$d_{50} = T_i \times c.u^{0.834}$	0.660	1.718
External surface by ϕ_s [mm ²]	$S_{\phi_s} = \pi \times \phi_s^2$	0.794	6.485
Specific volume unit [cm ³]	$V_s = \frac{4}{3} \times \pi \times (\frac{\phi_s}{2})^3$	6.65E-5	0.001553
PN unit mass [g]*	m^*	1.875E-4	0.0437
PN – Volumetric mass [g.ml ⁻¹]	$\rho = \frac{m^*}{V_s}$	2.82	28.17
Specific surface [m ² .g ⁻¹]	$S_s = 3/(\frac{\rho \times \phi_s}{2})$	4232,046	148,276

* m^* PN-unit masses were calculated by weight of a fixed number of sieving PN divided to its number

4.2. Citric Acid Black Polymer – Product of Synthesis Activations by NaOH Procedure

Weigh the crisp and soft black citric acid polymer – product of synthesis respectively PN-2 and PN-3 to be activated. Then, calculate the moles quantity of PN equivalent with taking account of its content for PN-2 and PN-3 measuring out by NaOH-0.05 (§2.3.1. Table 1). And then, prepare a NaOH solution such as the moles quantities of NaOH (99%) was 28 times more than the sample PN equivalent moles quantities and the distilled water volume was 1.5 times more than the NaOH-weight. Agitate the NaOH-solution until all NaOH are soluble in the distilled water. Now, take a syringe-10[ml] and put inside firstly a thin layer of absorbent cotton and then the PN black citric acid polymer to be activated. Press carefully the

set with the syringe press button. Finally, pour the NaOH solution into the syringe, it was noticed that this flowed uniformly through the PN to be activated. When the NaOH solution reached the cotton, it's necessary to block its syringe orifice leaving by putting the syringe press button, then let the activation process during one hour. NaOH activation characterizations are showed in the following table 5.

Table 5. PN-2 and PN-3 activations characteristics.

	PN-2	PN-3
Weight [g]	1.109	1.0147
n_{PN} [moles]	4.327E-4	5.4884E-4
n_{NaOH} [moles]	1.21E-2	1.54E-2
Distilled water volume [ml]	7.2E-1	9.3E-1
NaOH concentration [mol.l ⁻¹]	16.7824	16.4880
Calculated pH _{NaOH}	15.2249	15.2172

4.3. Citric Acid Black Polymers – Products of Synthesis Cationic Exchanger Na Content Determination by HCl-0.049N

After one hour activation, samples were taken on top and on low of the citric acid black polymers-product of synthesis cationic exchanger (PN-Na) to determine their Na content by HCl-0.049N measuring out.

Table 6. PN-2-Na and PN-3-Na activated PN characteristics.

Activated	PN-2-Na	PN-3-Na
Weight [g]	1.1244	1.0232
nNa-activation	1.21E-2	1.54E-2

	On top	On Low	On top	On Low
Sample titration weight [g]	0.0136	0.014	0.0159	0.0085
nNa content [moles]	1.0286E-4	1.0531E-4	1.7160E-05	1.7668E-5
nNa/sample weight [moles.g ⁻¹]	7.56E-3	7.52E-3	1.08E-3	2.08E-3
nNa/sample weight PN-Na proportionality (On Low/On Top)	0.99		1.93	
nNa/sample weight average [moles.g ⁻¹]	7.5425E-3		1.5783E-3	
nNa Total [moles]	8.48E-03		1.62E-03	
nNaTotal/nNaactivation	0.7009 (70.09%)		0.1049 (10.49%)	
n _{PN} [moles]	4.327E-4 (PN-2)		5.4884E-4 (PN-3)	
nNa Total/ n _{PN}	19.6 (20)		2.94 (3)	

It was confirmed that the PN citric acid black polymer product of synthesis activation lead up to the PN-Na a raw material able to play the cationic-exchange polymer rule. Likewise, it was confirmed that the PN-size obtained after the sieving procedure influenced the activation procedure. The PN-2 had 3 times specific diameter lesser and 29 times specific surface more than the PN-3 (Table 4). Consequently, because of the better contact with PN-2, first, the activation of PN-2 was the best such as 70.09[%] of the initial Na moles was retained by PN-2 versus only 10.49[%] for the PN-3; secondly, the total Na moles retained in PN-2 was 6 times more than those of PN-3. Then, comparing the specific diameter, specific surface (Table 4); the Na total retained and the (nNaTotal/n_{PN}) relationship between PN-2 and PN-3, respectively 2.86 [=1.437(3)/0.503(2)-Table 4], 28.54 [=4232.046(2)/148.276(3)-Table 4], 5.23 [=8.48E-3(2)/1.62E-3(3)-Table 6] and 6.67 [=19.6(2)/2.94(3)-Table 6], the activation reaction during one hour between NaOH and PN citric acid black polymer product of synthesis (Figure 5) was effective and hinged on the sieving characteristics as said the bibliography on the paragraph §4.1; that also explained the low activation rate of the PN-3 (only 10.49[%]) versus 70.09[%] for the PN-2.

Noticed that nNa/sample weight PN-Na proportionality between on low and on top samples was normal for the PN-2 (=0.99 equals to one) but for the PN-3, this value was 1.93; that is to say most of Na⁺ (=1.93 times) located on low. Seeing that the NaOH-solution density was more than one and the contact specific surface was little for the PN-3, on low a part of NaOH was probably in hydrogen bond link with the PN-Na activated (particularly for the PN-3-Na) and lead up to think

Thus, respectively, samples PN-2-Na and PN-3-Na were taken and diluted in 15[ml] of distilled water. We obtained a brown mixture solution. Add helianthine indicator, the orange yellow color appeared in solution. Then, NaOH content was titrated by HCl 0,049N. The equivalent point was reached when in the mixed solution appears red color. Results of this titration were showed in the following table 6.

that a part of NaOH might be in hydrogen bond link with the on low PN-3-Na activated confirming its low activation rate (only 10.49[%]). In the following figure 6 and figure 7 are shown the activated citric acid black polymers – products of synthesis PN-2-Na and PN-3-Na according to the HCl-0.049N measuring out (§4.3. – Table 6).

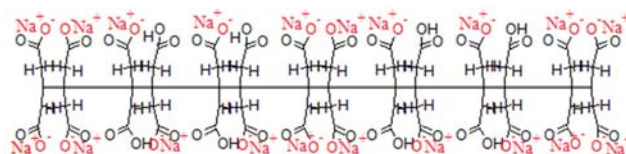


Figure 6. PN-2-Na Activated with NaOH.

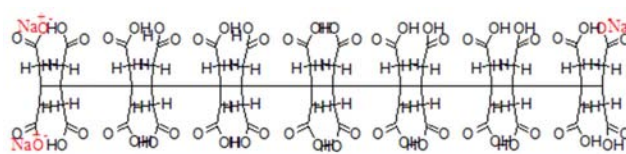


Figure 7. PN-3-Na Activated with NaOH.

5. Exchange Test of Citric Acid Black Polymers – Products of Synthesis Potential Raw Material Cationic Exchanger PN-2-Na and PN-3-Na

5.1. Cationic Exchange Test Principle

The cationic exchange test consist of passing a calcium carbonate (CaCO₃) solution directly through the syringe which contained the activated PN-Na. Salvage the solutions which passed through the PN-Na in beakers continually with paying attention to record the treated-samples solution volume

and the interval time (the duration) related to each treated-samples solution volume. Thus, the flow test rate, the time on stream, the weight hour space velocity (whsv) was deduced. Then, each treated-samples solution Ca^{2+} contents was measured out.

The characteristics of the calcium carbonate solution to be treated is shown in the following table 7.

Table 7. CaCO_3 – solution to be treated characteristics.

CaCO_3 – solution	
CaCO_3 Purity [%]	99
CaCO_3 Solubility - 20°C [g.l ⁻¹]	1.3E-2
CaCO_3 weight [g]	0.001773
Distilled water volume [ml]	150
CaCO_3 – solution concentration [mol.l ⁻¹]	1.16899E-4

Noticed that for the PN-3-Na tests, the treated-samples solution color was enough brown than the PN-2-Na because of a lot of NaOH molecules located underside the PN-3-Na which can sharp the hydrogen bond links between black and brown citric acid polymers. These last were responsible of the brown solution color and the NaOH molecules can reacted not only with their non-activated sites (-COOH) but also with the CaCO_3 to produce another -COONa sites and may be Na_2CO_3 and $\text{Ca}(\text{OH})_2$.

5.2. Ca^{2+} Measuring out of Treated Solution and Used Citric Acid Black Polymers – Products of Synthesis Cationic Exchanger

Once salvaged, each treated-samples solution was titrated with

EDTA. Also, the used PN-Na was titrated with EDTA. The objective was to calculate their Ca^{2+} contents by Ca^{2+} complexometric titration with EDTA [16-17]. Take the samples to be titrated in a beaker. Introduce 20[ml] of pH10 tampon solution. Then, add three drops of NET indicator. The solution color became brown-red. After that, Ca^{2+} content samples was titrated with EDTA and the equivalent point was reached when a light-red color appeared in the solution. Noticed that for the titration, EDTA measuring out concentration improvement was necessary from 0.03N (for PN-2-Na Ca^{2+} measuring out) to 0.002727N (for PN-3-Na Ca^{2+} measuring out) because of the treated-samples solution smallness while the CaCO_3 – treated solution concentration was already small 1.16899E-4[mol.l⁻¹]. It wasn't the case for the used PN-2-Na and PN-3-Na seeing that its Ca^{2+} contents was non negligible. Consequently, in some case EDTA volume equivalent point for treated-sample solution was rectified according to the used PN-2-Na and PN-3-Na total retained Ca^{2+} contents.

6. Exchange Test Results of Citric Acid Black Polymers – Products of Synthesis Cationic Exchanger

6.1. Exchange Test Results in Terms of Retained Ca^{2+} Evolution (Na effect- $\text{Ca}(\text{OH})_2$)

Treated-samples characteristics and operational conditions are show in the following table 8.

Table 8. Treated-samples characteristics and operational conditions.

		PN-2-Na		PN-3-Na	
	N°	Duration [mn]	Volume [ml]	Duration [mn]	Volume [ml]
Treated-samples	1 st	10	1.7	2	1.7
	2 nd	5	1.3	2.5	2
	3 rd	8.5	1.15	7.7	1.8
	4 th	13.5	1.85	12	2.4
	5 th	24.5	2.9	-	-
Cumulated values		62	8.9	24	7.9
Medium flow [ml.mn ⁻¹]		0.16265		0.55845	
CaCO_3 flow [g.h ⁻¹]		1.142E-4		3.920E-4	
whsv [h ⁻¹]		1.054E-4		3.959E-4	
temps de contact T [h]		9487		2526	

Exchange tests results for PN-2-Na and PN-3-Na were shown in the following table 9 according to the treated-samples characteristics and operational conditions.

Table 9. PN-2-Na and PN-3-Na test results.

	N°	PN-2-Na (0.03N-EDTA)		PN-3-Na (0.002727N-EDTA)	
		Ca^{2+} titrated [moles]	Ca^{2+} retained ^[*] [moles]	Ca^{2+} titrated [moles]	Ca^{2+} retained ^[*] [moles]
Treated-samples	1 st	1.5E-7	4.87E-8	1.36E-7	7.44E-8
	2 nd	1.14E-8	1.41E-7	1.36E-7	9.78E-8
	3 rd	1.5E-8	1.19E-7	1.36E-7	<u>7.44E-8</u>
	4 th	0.00 ($\approx 3\text{E}-11$)	2.16E-7	2.73E-7	<u>7.56E-9</u>
	5 th	0.00 ($\approx 3\text{E}-11$)	3.39E-7	-	-
Cumulated values		1.76E-7	8.64E-7	6.82E-7	2.53E-7
Total moles to be treated [moles]		1.04E-6		9.35E-7	
Total moles Ca^{2+} retained on used PN-Na deduced by EDTA titration ^[**] [moles]		8.65E-7		2.54E-7	
Ca^{2+} retained rate [%]		83		27	

N°	PN-2-Na (0.03N-EDTA)		PN-3-Na (0.002727N-EDTA)	
	Ca ²⁺ titrated [moles]	Ca ²⁺ retained ^[*] [moles]	Ca ²⁺ titrated [moles]	Ca ²⁺ retained ^[*] [moles]
nNa total ^[***] [moles]	8.17E-3		1.563E-3	
temps de contact T [h]	9487		2526	

[*] Ca²⁺ retained contents for each treated samples were deduced by subtraction between total moles must be treated corresponding to each treated-samples and their corresponding Ca²⁺ titrated.

[**] Ca²⁺ contents of the used PN-Na was measuring out by complexometric titration with EDTA as said in paragraph §5.2. For this, weight the sample to be titrated, add 10[ml] of distilled water, 20 [ml] of pH10 tampon solution, three drops of NET indicator. The solution color became brown-red. After that, Ca²⁺ content samples was titrated with EDTA and the equivalent point was reached when a light-red color appeared in the solution. Notice that, seeing the total moles to be treated quantities, a weight sample more than 1[g] was judicious and pay attention to the end time otherwise an over-estimation is possible.

[***] Noticed that the nNa total quantities for the exchange tests were slightly inferior to the values in table 6 because of Na quantifications samples.

Na sites importance were confirmed during the exchange test results in table 9 such as more they were more is the Ca²⁺ retained rate. But, their nature play an important role. Logically, more is the contact time and the Na sites of PN-Na more must be the Ca²⁺ retained quantities (moles) versus time. However, the following

figures (Figure 8 – Figure 9 – Figure 10 – Figure 11) showed that the PN-3-Na which has less Na sites than PN-2-Na (Table 6 – Table 9) was all the time more active than the PN-3-Na, even if we plotted the Ca²⁺ retained per Na per contact time evolution versus time (Figure 10 – Figure 11).

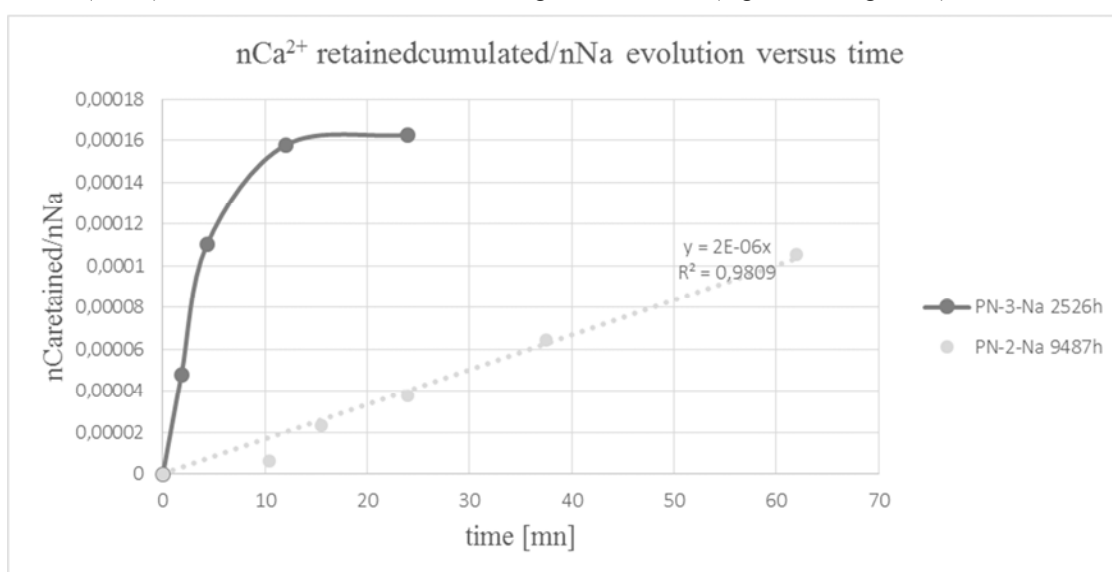


Figure 8. Ca²⁺ moles retained cumulated per Na moles evolution.

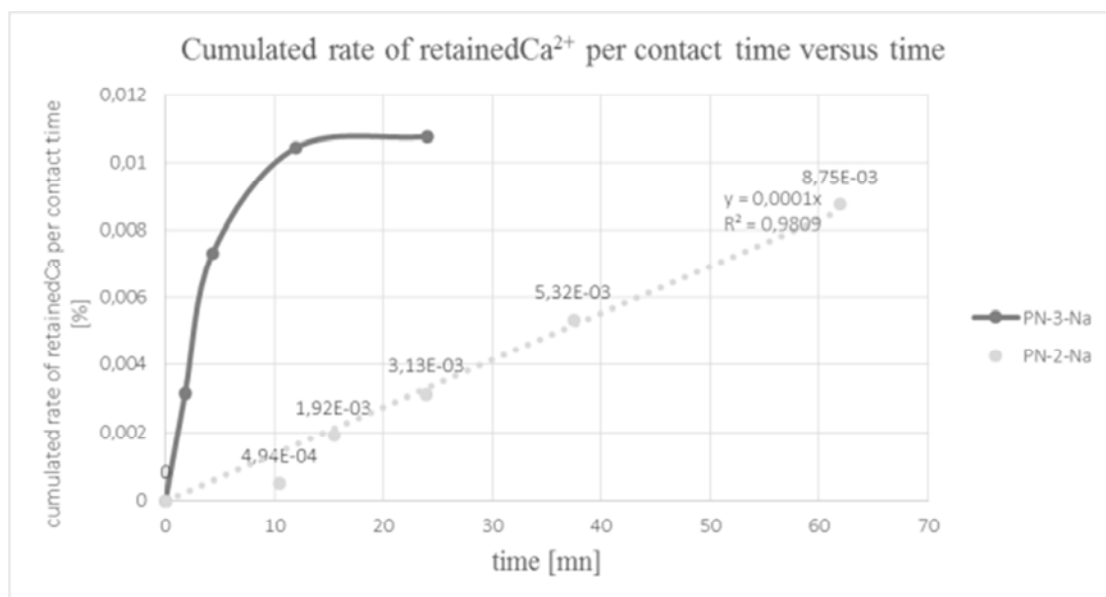


Figure 9. Cumulated rate of retained Ca²⁺ per contact time evolution.

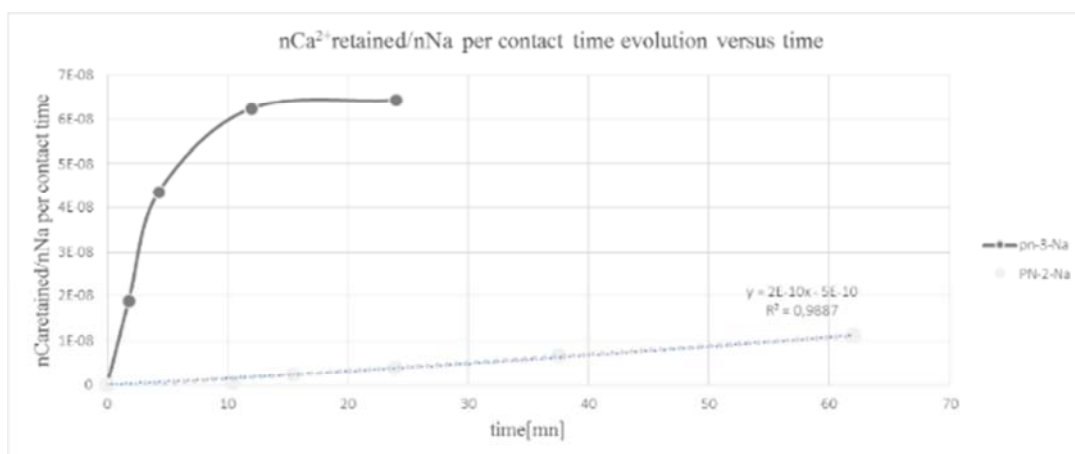


Figure 10. Cumulated Ca^{2+} moles retained per Na moles and per contact time evolution.

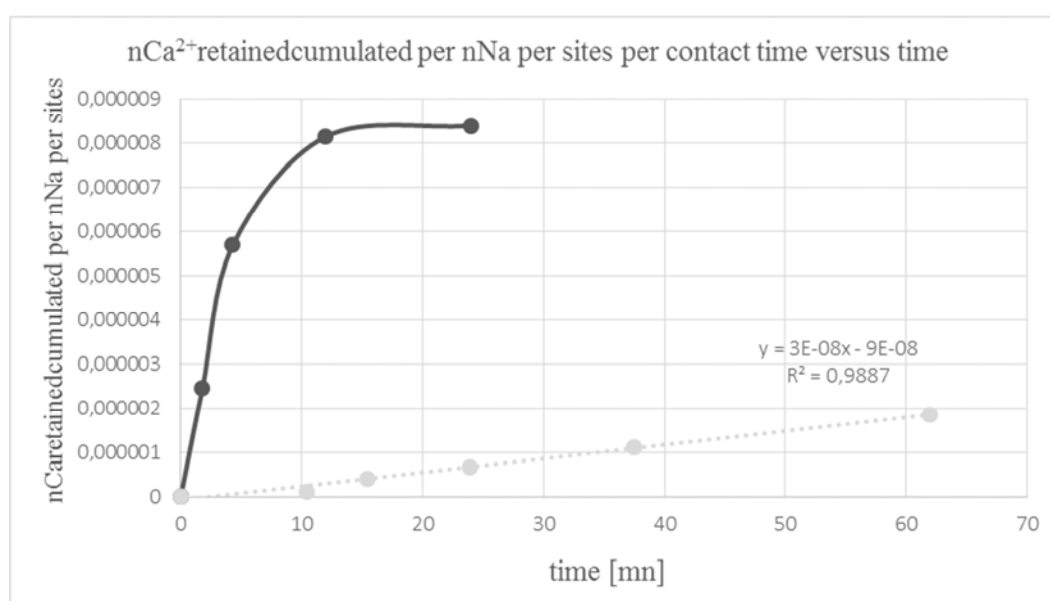


Figure 11. Cumulated Ca^{2+} moles retained per Na moles per sites and per contact time evolution.

These results explained that NaOH sites which are more numerous in PN-3-Na than PN-2-Na (Table 6 - §4.3) and sharpened the hydrogen bond links between black and brown citric acid polymers. These last were responsible of the brown solution color and the NaOH molecules can move through the polymers and reacted not only with their non-activated sites (-COOH) but also with the CaCO_3 to produce another -COONa sites and may be Na_2CO_3 and Ca(OH)_2 . Seeing that the Ca(OH)_2 water solubility ($8.24\text{E-}1[\text{g.l}^{-1}]$) was more important than its CaCO_3 , they move easily and became more retained by exchange mechanism with PN-Na sites. But the Na_2CO_3 were directly transported out with water because of their high solubility ($2.33\text{E+}2[\text{g.l}^{-1}]$). These sites [which are the total quantities

of (-COOH) sites equals to fourteen times the PN-equivalent moles] activities were confirmed on the figure 11; noticed that the sites increase the initial activity of PN-2-Na and PN-3-Na compared with initial activities considering only Na sites. As it happens, Na^+ and Ca^{2+} measuring out by HCl-0.033N and HCl-0.0027N for respectively used PN-2-Na and PN-3-Na were carrying-out. So, weight the used sample PN-Na to be titrated in a beaker, add 15[ml] of distilled water and three drops of Bromophenol Blue BPB indicator, the solution turn to dark red-brown. Begin the titration with HCl and equivalent point is reached when a light red color appeared in solution. The results were shown in the following table 10.

Table 10. Used PN-2-Na and used PN-3-Na Na^+ and Ca^{2+} contents determined by HCl-titration compared with initial Na quantities and Ca^{2+} contents determined by EDTA-complexometric titration.

	Used PN-2-Na	Used PN-3-Na
Samples weight [g]	0.05	0.0256
Ca^{2+} contents by HCl-titration [moles]	$1.05\text{E-}4$	$1.6\text{E-}5$
Na^+ contents by HCl-titration [moles]	$2.11\text{E-}4$	$3.19\text{E-}5$

	Used PN-2-Na	Used PN-3-Na
Initial Na [moles]	8.17E-3 (PN-2-Na)	1.563E-3 (PN-3-Na)
Ca ²⁺ contents by EDTA-titration [moles]	8.64E-7	2.54E-7
ΔCa ²⁺ contents	2.10E-4	3.17E-5
PN[moles]/Δ	2.06	17.32
PN[sites]/Δ	28.87	242.56

Ca²⁺ quantities differences between EDTA-titration and HCl titration were due to the presence of other organic molecules with functions which can reacted with HCl during the HCl-titration. For the crisp PN-2-Na, the functions can be alcohol and or ester with alkene from the citric acid yellow monomers [1-2-3-4-5], and for the soft PN-3-Na, the function majority is alkene from the citric acid yellow monomers. That

why the difference PN/Δ between PN-2-Na and PN-3-Na. However, it's important to say that these functions are negligible in front of PN-Na sites (Table 10).

So, seeing that the Ca²⁺ quantified by EDTA-titration was exact, rectifications of the Na⁺ quantities in used PN-2-Na and PN-3-Na deduced by HCl-titration were done and shown in the following table 11.

Table 11. Used PN-2-Na and used PN-3-Na Na⁺ and Ca²⁺ contents determined by HCl-titration rectifications.

	Used PN-2-Na	Used PN-3-Na
Samples weight [g]	0.05	0.0256
Ca ²⁺ by EDTA-titration [moles]	8.64E-7	2.54E-7
Rectified Ca ²⁺ by HCl-titration [moles]	8.64E-7	2.54E-7
Rectified Na ⁺ by HCl-titration [moles]	4.32E-7	1.27E-7
Initial Na [moles]	8.17E-3 (PN-2-Na)	1.563E-3 (PN-3-Na)

These results on table 10 and table 11 confirmed that during exchange test NaOH molecules can moves through the polymers and reacted not only with their non-activated sites (-COOH) but also with the CaCO₃ to produce another -COONa sites and Na₂CO₃; seeing that Na₂CO₃ high soluble (2.33E+2[g.l⁻¹]) in water, they were directly transported on low out with treated water, that is to say their concentration in the treated solution increases with time. All results conducted to suggest the following exchange PN-Na evolution on figure 12.

[+/-] referred to the less (-) or more (+) quantities of the chemicals according to the citric acid black polymer synthesized PN like PN-2 and PN-3.

Plotting the initial retained Ca²⁺ per PN-equivalent moles quantities (Table 5) and per initial Ca²⁺ concentration versus contact time we obtained the table 12 and figure 13 which confirmed that PN-equivalent quantities and contact time influenced the initial Ca²⁺ retained moles quantities and showed the initial activities of Na sites belonged to PN-2-Na

(19.6 per PN) and PN-3-Na (only 2.94 per PN).

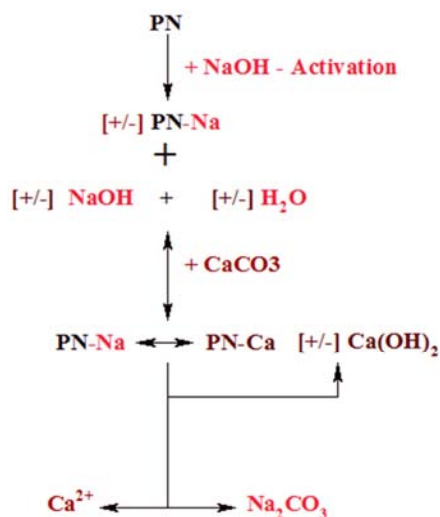


Figure 12. Exchange PN-Na evolution.

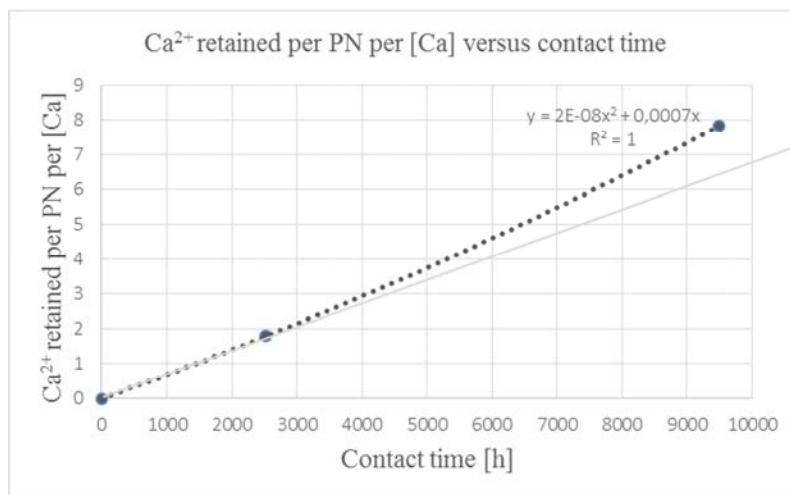


Figure 13. Ca²⁺ moles retained per PN quantities per initial Ca²⁺ concentration versus contact time evolution.

Table 12. Initial retained Ca^{2+} quantities per PN-equivalent moles quantities and per initial Ca^{2+} concentration.

	PN-2-Na	PN-3-Na
Contact time [h]	9487	2526
Initial moles of Ca^{2+} retained per PN moles	1.13E-4	1.36E-4
Initial Ca^{2+} salvage concentration – extrapolation to 1.8[mn] [mol.l^{-1}]	1.44E-5	7.58E-5
n_{PN} [moles]	4.327E-4	5.4884E-4
n_{Na} Total/ n_{PN}	19.6 (20)	2.94 (3)
initial retained Ca^{2+} per PN-equivalent moles quantities and per initial Ca^{2+}	7.82	1.79

Consequently, the initial activity of PN-Na for Ca^{2+} exchange for example equal to $7\text{E-}4$ [molesretained Ca^{2+} per hour [contact time] per $[\text{Ca}]_{\text{concentration}}$] in other words $4.33656\text{E+}20$ [Ca^{2+} entities-retained per hour [contact time] per $[\text{Ca}]_{\text{concentration}}$]

6.2. Exchange test Results in Terms of Treated Water Ca^{2+} and Na^+ Concentration Evolution Versus Time

This paragraph try to study this PN-Na exchange kinetic according to the previous results and exchange PN-Na evolution (Figure 12) with putting conditions operator to make it easy.

First, in general the exchange reaction speed was according

to $[\text{Ca}^{2+}]$ and $[\text{Na}^+]$ concentration evolution such as

$$v = -\frac{d[\text{Ca}^{2+}]}{dt} = -\frac{d[\text{Na}^+]}{dt} = k_{\text{PN}} \times [\text{H}_2\text{O}] \times [\text{Ca}^{2+}]^\alpha \times [\text{Na}^+]^\beta \quad (1)$$

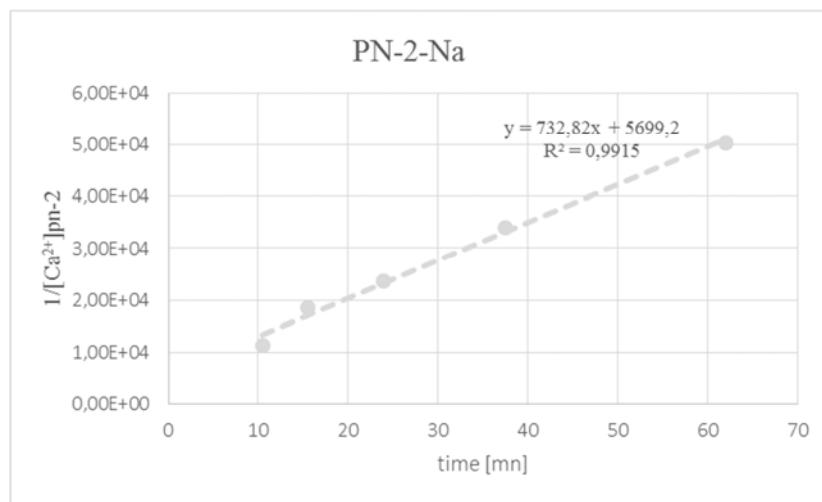
Seeing that on crispy PN-2-Na exchange evolution and soft PN-3-Na exchange evolution, initially all the time the $[\text{Na}^+]$ and $[\text{H}_2\text{O}]$ concentrations were largely superior than the $[\text{Ca}^{2+}]$ concentration, so the above exchange reaction speed became:

$$v = -\frac{d[\text{Ca}^{2+}]}{dt} = -\frac{d[\text{Na}^+]}{dt} = k_{\text{PN,Na+}} \times [\text{Ca}^{2+}]^\alpha \quad (2)$$

These concentrations evolutions were shown in the following table 13.

Table 13. $[\text{Ca}^{2+}]$ concentration evolution for the crispy PN-2-Na and the soft PN-3-Na.

N°	PN-2-Na crispy		PN-3-Nasoft	
	$[\text{Ca}^{2+}]$ [mol.l^{-1}]	$1/[\text{Ca}^{2+}]$	$1/[\text{Ca}^{2+}]$ [mol.l^{-1}]	$1/[\text{Ca}^{2+}]$
1 st	8,82E-05	1,13E+04	7,56E-05	13235,29
2 nd	5,38E-05	1,86E+04	7,16E-05	13970,59
3 rd	4,25E-05	2,35E+04	7,29E-05	13725,49
4 th	2,94E-05	3,40E+04	8,51E-05	1,17E+04
5 th	1,98E-05	5,04E+04	-	-

**Figure 14.** $1/[\text{Ca}^{2+}]$ concentration evolution for the crispy PN-2-Na.

The figure 14 showed clearly that for the PN-2-Na the $1/[\text{Ca}^{2+}]$ increase following the straight line such as $1/[\text{Ca}^{2+}] = +732.82t + 5699.2$. Consequently, second order was the exchange kinetic evolution on the PN-2-Na and secondly its speed constant was

$$k_{\text{PN,Na+}} = +732.82 [\text{mol}^{-1} \times \text{L} \times \text{s}^{-1}]$$

That is to say,

$$v_{\text{PN-2-Na}} = -\frac{d[\text{Ca}^{2+}]}{dt} = -\frac{d[\text{Na}^+]}{dt} = k_{\text{PN,Na+}} \times [\text{Ca}^{2+}]^2 \quad (3)$$

$$v_{\text{PN-2-Na}} = +732.82 \times [\text{Ca}^{2+}]^2$$

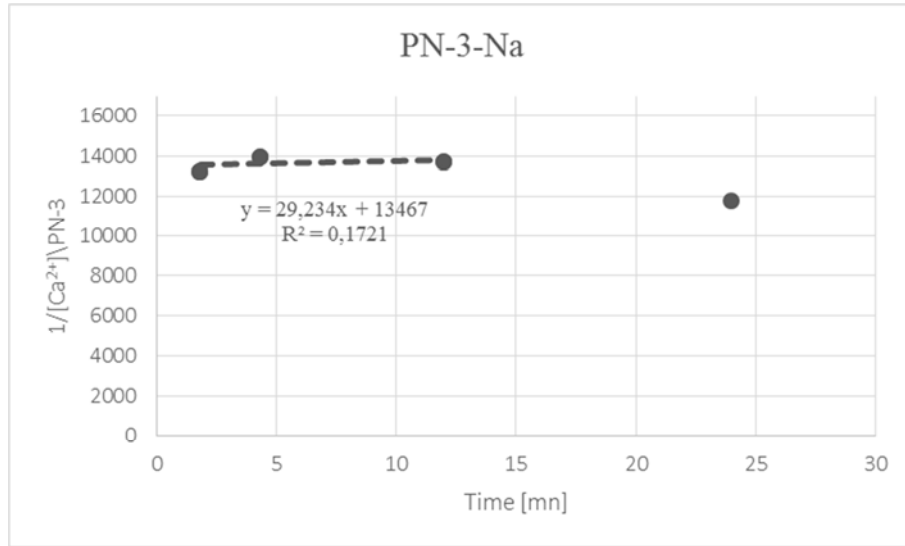


Figure 15. $[Ca^{2+}]$ concentration evolution for the soft PN-3-Na.

The figure 15 showed clearly that initially for the PN-3-Na the $1/[Ca^{2+}]$ increase following the straight line such as $1/[Ca^{2+}] = +29.234t + 13467$. Consequently, second order also was the exchange kinetic evolution on the PN-3-Na and its speed constant was

$$k_{PN,Na+} = +29.234 [mol^{-1} \times L \times s^{-1}]$$

That is to say,

$$v_{PN-3-Na} = -\frac{d[Ca^{2+}]}{dt} = -\frac{d[Na^{+}]}{dt} = k_{PN,Na+} \times [Ca^{2+}]^{\alpha} \quad (4)$$

$$v_{PN-3-Na} = 29.234 \times [Ca^{2+}]^2$$

$k_{PN,Na+}$ values showed large formation of Ca^{2+} in the PN-2-Na treated solution than its PN-3-Na and confirmed the high activity of the PN-3-Na to retain Ca^{2+} compared with PN-2-Na (Figure 8 – Figure 9 – Figure 10 and Figure 11).

These results confirmed also the PN rule as organic structure where ions exchange carried out because first, the PN-3-Na whose PN quantities was 1.39 times more than those PN-2-Na realized all the time important Ca^{2+} retention. Then, secondly noticed that even if low was the PN-3-Na's Na^{+} after activation, it was all the time more active and take to think that activation-exchange-deactivation phenomenon (Figure 12) existed and easier on PN-3-Na.

7. Conclusion

Black citric acid polymer synthesis duration influence the PN's nature especially its equivalent PN content measuring out by NaOH-0.05N. Thus, two black citric acid polymer was synthesized, the PN-2-crispy with equivalent PN content equals to $3.9037E-4$ [moles.g⁻¹] and the PN-3-soft whose synthesis duration was lower and its equivalent PN content was $5.4113E-4$ [moles.g⁻¹] which correspond respectively to 61.31 (wt.%) and 84.98 (wt.%). Also, Boehm titration was done and confirmed the acidity differences between these two samples. However, it was noticed that for the Black citric acid

polymer PN whose structure was composed in the majority of acid functions, the NaOH-0.05N acidity measuring-out is more suitable. Noticed also that PN adsorbed efficiently water on their surfaces and allowed us to study its potentiality as cationic exchanger after NaOH activation. PN particles sizes influenced the activation because the PN-2 crispy whose specific diameter size was 0.503[mm] retained more Na^{+} [(nNa+/nPN-2) = 20] than the PN-3 soft whose specific diameter size was 1.437[mm] with [(nNa+/nPN-2) = 3]. These Na contents were measuring out by 0.049N-HCl. Cationic exchange tests with $CaCO_3$ solution were done with PN-2-Na and PN-3-Na activated PN to show their potentiality to be raw materials for polymer cationic exchanger. So, Ca^{2+} contents of treated solutions was followed-up by EDTA-complexometric titration. Also, Ca^{2+} and Na^{+} of used PN-2-Na and PN-3-Na contents were measuring-out by HCl. Results permitted to suggest a global evolution during the activated PN cationic exchange where PN equivalent and Na^{+} contents were very important. However, it was noticed that the PN-3-Na was all the time more active than the PN-2-Na and the global evolution of retained Ca^{2+} with contact time allowed a parabolic curve. So, the PN's nature and its Na contents at activated status were important for their cationic exchange tests efficacy. The one problem was during the tests NaOH molecules slice the hydrogen-bond link between black citric acid polymer, brown citric acid polymer and other unsaturated functions and allowed to the brown coloration of the treated solution. So, it's a necessity to search solutions to make its color clear using adequate filter. However, it didn't challenge the PN capacity to be a potential raw material for realizing a polymer cationic exchanger not miscible in water after technologic amelioration. Indeed, actually industrialists suggested ions resins formed with a macro-molecular structure which was made up of a substance that allows the resin to be insoluble in water, but also serves as support for functional groups characteristic of resin properties [18-19]. Finally, a global kinetic of those PN-2-Na and PN-3-Na tests cationic exchange was done by following the Ca^{2+}

concentration evolution in solution and showed that the Ca^{2+} speed formation was very important on the PN-2-Na solution than the PN-3-Na solution and confirmed its (PN-3-Na) high capacity to retain Ca^{2+} .

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