

Research/Technical Note

Black Citric Acid Polymer (PN) Pozzolana Activated - Na-PN-Pozzolana-CE Material Synthesis Tested As Cationic Exchanger

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To cite this article:Andry Tahina Rabeharitsara, Marie 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*. Vol. 7, No. 6, 2019, pp. 145-160. doi: 10.11648/j.ajac.20190706.11**Received:** October 1, 2019; **Accepted:** October 22, 2019; **Published:** November 7, 2019

Abstract: It was showed that black citric acid polymer (PN) have capacities to be a potential raw materials for realizing a cationic exchanger seeing that the treated water solution through PN kept a brown color of brown citric acid polymers from PN during its activations with NaOH. So, the objective of this publication was to realize not only materials and process which could clarify the brown color of the PN treated water but also to realize immediately a cationic exchanger materials with at the end a clarified transparent water. Consequently, two raw materials have been selected to do these realizations: pozzolana and black citric acid polymer (PN). The first step was to elaborate a procedure for synthesizing PN-pozzolana material founded upon water as PN's liquid vector, pozzolana/PN weigh relationship, used pozzolana's oxygen total atoms contents, water/pn molar relationship and water/pozzolana molar relationship. Then, PN-pozzolana was characterized by NaOH-0.05N titration enabled to value the on surface PN, the total PN dispersed, the on vacuole PN with maybe pozzolana vacuole porosity recovery rate. Also, the PN-pozzolana material was used to clarify by PN a treated water cationic exchanger according to a procedure using a PN-tubular filter with well-defined experimental conditions leading to good results. The second step was to elaborate a procedure for synthesizing Na-PN-pozzolana-CE cationic exchanger founded upon PN-pozzolana activation with NaOH as described on bibliography followed by thermic treatment. Then, Na-PN-pozzolana-CE cationic exchanger was characterized by HCl-0.049N enabled to value the total Na⁺ dispersed on PN-pozzolana and Na⁺ on surface per total PN moles ratio. Results and discussions of the thermic treatment were done seeing that there were all the time weight diminution of activated Na-PN-pozzolana thermic treated. Finally, exchange cationic tests with CaCO₃ solution were carried-out with different contact time on these Na-PN-pozzolana-CE cationic exchanger and the Ca²⁺ contents of treated water solution was followed by EDTA-complexometric titration. Results showed clearly that not only PN-pozzolana material could clarify the brown treated water but also Na-PN-pozzolana-CE is a good cationic exchanger with a maximal Ca²⁺ retained rate capacity around 93.27 [%].

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

1. Introduction

Firstly, PN-pozzolana materials was synthesized according to a procedure described on the following paragraphs whose principal objective was to disperse PN-molecules efficiently on pozzolana by hydrogen-bond adsorption. Then, they were characterized by NaOH-0.05N titration and used to clarify by PN

a treated water cationic exchanger [1] according to a procedure using a PN-tubular filter with well-defined experimental conditions. Noticed that brown treated water to be clarified pre-treatment was done with citric acid solution to neutralize its possible Na⁺/OH⁻ molecules. Also, a part of PN-pozzolana was activated with NaOH to obtain Na-PN-pozzolana materials which were characterized by HCl-0.049N. Finally, the

Na-PN-pozzolana materials gone through a thermic treatment according to a procedure described on the following paragraphs to obtain a Na-PN-pozzolana-CE cationic exchanger characterized also by HCl-0.049. Discussions and interpretations were done about these first results seeing that thermic treatment improve the activated Na-PN-pozzolana materials characteristics. At the end, cationic exchanger tests at different contact time with a calcium carbonate water solution were done through Na-PN-pozzolana-CE tubular filters and Ca^{2+} ions evolution on treated water solution were followed-up by complexometric-EDTA titration. Also, discussions and interpretations were done about these tests results especially about the pozzolana and PN contributions.

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 [2-4].

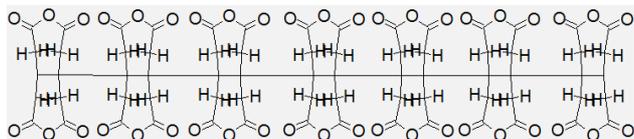


Figure 1. Black citric acid polymer (PN).

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 [5-6]. The following table 1 show the PN characteristics.

Table 1. PN characteristics.

CHARACTERISTICS	UNITY	PN
Molecular formula		$\text{C}_{70}\text{H}_{58}\text{O}_{42}$
Molecular weight	g/mol	1571.492
C weight fraction	%w/w	53.51
H weight fraction	%w/w	3.72
O weight fraction	%w/w	42.77
S weight fraction	%w/w	-
N weight fraction	%w/w	-
H_2O Water	%v/v	-
Asphaltenes weight fraction	%w/w	-
Density	Kg/dm^3	1.0375
Boiling point	$^{\circ}\text{K}$	≈ 573.15
Melting point	$^{\circ}\text{K}$	339.15
Auto-inflammation point	$^{\circ}\text{K}$	643.15
Aspect (room temperature)		crystallized
Odor		neutral
Color		black

2.3. Citric Acid Black Polymers Products of Synthesis Characterized by Its Equivalent PN Content 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 [1]. So, 0.0132 [g] sample was taken and diluted 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 [1]. 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 2.

Table 2. PN equivalent content of used PN.

Samples	PN
Sample [g]	0.0132
$n_{\text{PN}}^{\text{Equivalent}}$ [moles]	5.3571E-6
$m_{\text{PN}}^{\text{Equivalent}}$ [g]	8.4134E-2
$n_{\text{PN}}^{\text{Equivalent per gramme}}$ [moles.g ⁻¹]	4.05844E-4
$\text{PN}^{\text{Equivalent content of samples}}$ [wt.%]	63.7375

3. Pozzolana

3.1. Generalities

Pozzolana (Figure 2) are volcanic natural materials, pyroclastic formed with magma fragments which was thrown up and cooled down in atmosphere during a volcanic. Its color is generally black or red according to the iron oxidation and pozzolana are mainly composed of volcanic glass (SiO_2 amorphous material non-crystallized) [7]. Pozzolana are also composed of silica, aluminum, iron, lime, magnesium, sodium, titanium, potassium, phosphorous, manganese oxides and other trace element [7-9].



Figure 2. Pozzolana (PN).

3.2. Pozzolana Characteristics

Pozzolana is a very vacuole porous materials. Its closed porosity more than $100\mu\text{m}$ and density vary volumetrically from 30% to 60% according to its sieving characteristics [7, 8, 9]. So, Pozzolana has high smell and a water adsorption capacity. Pozzolana pH is neutral and its medium chemical composition is 45% of SiO_2 , 15% of Al_2O_3 and 15% of Fe_2O_3

[8]. Pozzolana used in the following synthesis was crushed and sieved using a vibrating sieve machine with simultaneously two sieves; TS: the superior sieve and Ti: the lower sieve; whose meshes diameters was respectively 0.8 [mm] and 0.25 [mm] [3-4]. We obtained the refusals indicating the part of pozzolana 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-pozzolana synthesis and activation steps. Results and characteristics of pozzolana is shown in the following table 3.

Table 3. Pozzolana refusals characteristics.

Refusal Characteristics (RC)	Formulas	Pozzolana
Coefficient of uniformity (c.u)	$c.u = \frac{T_s}{T_i}$	3.2
Specific diameter (ϕ_s) [mm]	$\phi_s = T_i \times (1 + 2 \log c.u)$	0.503
Fifty diameter (d_{50}) [mm]	$d_{50} = T_i \times c.u^{0.834}$	0.660
External surface by ϕ_s [mm ²]	$S_{\phi_s} = \pi \times \phi_s^2$	0.794
Specific volume unit [cm ³]	$V_s = \frac{4}{3} \times \pi \times (\frac{\phi_s}{2})^3$	6.65E-4
Pozzolana unit mass [g]*	m^*	7.2E-3
Pozzolana- Volumetric mass [g.ml ⁻¹]	$\rho = \frac{m^*}{V_s}$	108.32
Pozzolana Specific surface [m ² .g ⁻¹]	$S_s = 3 / (\frac{\rho \times \phi_s}{2})$	110,21

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

4. PN-pozzolana Synthesis

4.1. Introduction and Generalities

Black citric acid polymer (PN) have capacity as a raw material for cationic exchanger realization after activation with NaOH at pH around 15 [1]. So, 83% of water's Ca^{2+} was retained with PN-2-Na because of Na^+ dispersion on PN but the treated solution color turned to brown showing the presence of brown citric acid polymers [1]. Two solutions may be taken to clear and/or to decrease their concentrations in the treated solution, either put an adequate clarification-filter at the cationic exchanger PN-Na filter exit or synthesize a PN-Na cationic exchanger supported on a porous materials which can retain not only the water- Ca^{2+} but also the water-brown citric acid polymers. It was noticed that pozzolana has capacity to discolor solution [10] and also PN's structure has capacity to retain the brown citric acid polymers (Figure 3) by hydrogen bond and/or absorption.

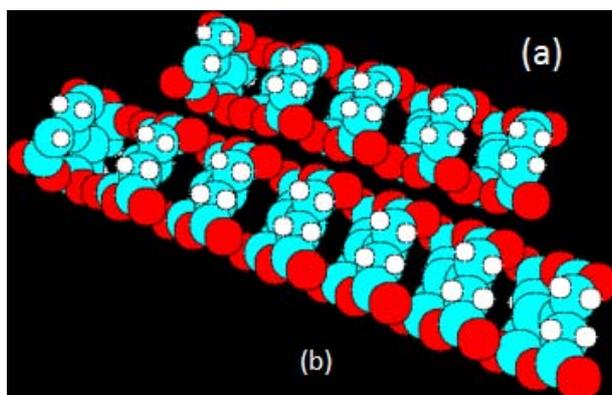


Figure 3. Brown citric acid polymer-structure (a) and PN-structure (b) by ACD/ChemSketch.

So, a project was done [1] to clarify the brown-treated water with PN-glass arrayed one after another in a tubular filter and PN dispersed on glass by mixing in a tubular filter whose

experimental conditions were the flow rate, pressure drop on the tubular filter and crossing number of solution to be clarified through the tubular filter. The prerequisite citric acid neutralization of NaOH-treated solution before clarification procedure was also done considering the NaOH existence according to the previous experimentation mechanism [1]. Thus, results were conclusive because not only, PN's dispersed size increase showing that there were retained brown citric acid polymers (Figure 4), but also globally the refractory index of treated water decreased from 1.6335 to 1.6290 and to 1.3200 for the procedure with prerequisite citric acid neutralization of NaOH-treated solution before clarification procedure.



Figure 4. PN dispersed on glasses after brown-treated water clarification.

But, the color of the clarified water could be improved so other solutions was to synthesize PN-pozzolana as water clarification (§5.) and squarely synthesizing PN-pozzolana-Na cationic exchanger (§6.).

4.2. PN-pozzolana Synthesis Procedure

The objective was to disperse efficiently PN molecules on the pozzolana. Seeing that pozzolana contains oxygen atoms where the PN'S hydrogen atoms could adsorb by hydrogen bond, the PN moles to be dispersed were in terms of pozzolana moles quantity such as 100 [g] of pozzolana there were 45 [g] of SiO_2 (60.08 [g.mol⁻¹]), 15 [g] of Al_2O_3 (101.96 [g.mol⁻¹]) and 15 [g] of Fe_2O_3 (159.69 [g.mol⁻¹]) on average. That is to say, on 100 [g] of pozzolana there were 1,5-Oxygen moles

atom-SiO₂, 0,44-Oxygen moles atom-Al₂O₃ and 0,28-Oxygen moles atom- Fe₂O₃; in other words there were 2.22 Oxygen-moles atoms on 100 [g] of pozzolana. So to receive by adsorption- 58 PN's hydrogen atoms it need approximatively 2600 [g] of pozzolana. That is to say, the weight relationship between pozzolana and PN was 1.66 ($W_{\text{pozzolana}}/W_{\text{PN}}$). Also, seeing that not only pozzolana has high capacity to adsorb water but also PN's density was more than one, it was judicious to use water as liquid vector to carry the PN's molecule towards the pozzolana porosity before the dispersion. The following table 4 show the reactants and liquid vector quantities for the PN-pozzolana synthesis.

Table 4. First PN-Pozzolana reactants and liquid vector quantities.

PN-pozzolana reactants and liquid vector quantities	
PN weight [g]	0.4639
Weight relationship ($W_{\text{pozzolana}}/W_{\text{PN}}$)	1.66
Pozzolana weight [g]	0.7695
Oxygen pozzolana atoms	0.0177778
Molar relationship ($M_{\text{water}}/M_{\text{pozzolana}}$)	20
Molar relationship ($M_{\text{water}}/M_{\text{PN}}$)	1203.71
Water [moles]	0.3555568
Water volume [ml]	6.4

Finally, considering that pozzolana was a hydroxylated material its structure contains naturally water molecules [11, 12, 13] which must be eliminated before the PN adsorption. So, the

following figure 5 show the PN-pozzolana synthesis procedure. The first step consist on pozzolana heat treatment to remove water molecules on pozzolana structure at 523.15 [°K]. So, put the sieved pozzolana (table 3) in a porcelain crucible, and all is taken in an oven programmed from ambient temperature to 523.15 [°K] with 276.15 [°K.mn⁻¹] speed. When temperature is stabilized at 523.15 [°K], count two hours for the heat-treatment. In the same time, put the sieved PN to be dispersed on the pozzolana in a beaker 250 [ml] such as the weight relationship between pozzolana and PN was $W_{\text{pozzolana}}/W_{\text{PN}} = 1.66$ (Table 4) with the water equivalent quantity such as the molar relationship between water and PN was $M_{\text{water}}/M_{\text{PN}} = 1203.71$ (Table 4). Thus, all is taken in a 400 [ml] baker bain-marie at 318.15 [°K] such as the baker-250 [ml] was seated 3 [cm] from the bottom of this baker and the water height was 3 [cm] maximum. Then, when the pozzolana heat-treatment time was past, heat an electric cooktop, put on the water-PN-baker 250 [ml] and add in the same time the pretreated pozzolana just gone out of the oven. Heat and mix the mixture slowly and carefully with glass spatula until water exhaustion and PN-pozzolana synthesized was dry and crisp. Pay attention not to burn the mixture. Finally, characterize the material PN-pozzolana by NaOH-0.05N measuring out [1] which could give the PN total dispersed on the pozzolana, the PN on surface and therefore the PN dispersed in the pozzolana vacuoles porosity (Figure 5).

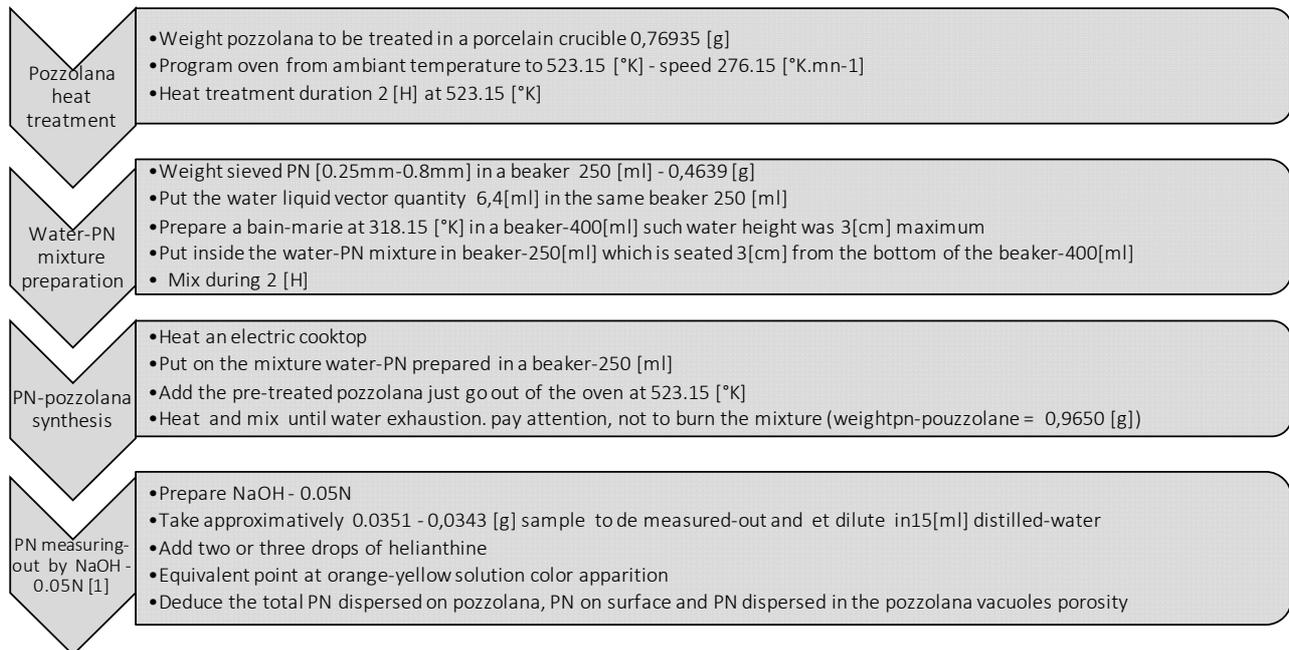


Figure 5. PN-pozzolana synthesis procedure.

4.3. First PN-pozzolana Synthesized Characterizations

Once synthesis finished, took the dry PN-pozzolana synthesized in an over beaker to be weigh. In this case, the weight of PN-pozzolana synthesized was 0.9650 [g]. Notice that there were a rest of PN stucked on the first beaker 250 [ml] (where the synthesis was done) which must be also weighed, and in this case it was 0.138 [g]. Seeing that the initial PN

weigh for the synthesis was 0.4639, so the total weight of PN on surface and in the vacuole porous of PN-pozzolana material synthesized was (0.4639 – 0.138) [g] equals to 0.2809 [g]. The on surface PN was quantified by NaOH-0.05N measuring out [1], consequently the PN in vacuoles porous of PN-pozzolana material was deduced by the total PN quantity minus the on surface PN quantity. The following table 5 show the results.

Table 5. First PN-Pozzolana synthesized characteristics.

PN-pozzolana synthesized characteristics	
PN-pozzolana synthesized weight [g]	0.9650
PN-pozzolana sample weight for measuring-out [g]	0.0343
NaOH-0.05N volume at equivalence point [ml]	0.5
NaOH moles at equivalent point [moles]	2.5E-5
On surface PN-equivalent moles for the sample [moles]	1.7857E-6
On surface PN-equivalent moles per PN-pozzolana weight [moles _{PN-equivalent} / g _{PN-pozzolana}]	5.21E-5
Total on surface PN-equivalent weight for PN-pozzolana synthesized [g] (1)	0.0789 (1)
Initial PN weight [g] (2)	0.4639 (2)
Beaker PN weight [g] (3)	0.1830 (3)
Total PN on PN-pozzolana [g] (4) = (2) - (3)	0.2809 (4)
PN Vacuole porous of pozzolana weight [g] (5) = (4) - (1)	0.202 (5)
PN percentage on PN-pozzolana [%] (6) = [(4)/(2)]*100	60.55 (6)
On surface PN of PN-pozzolana percentage versus initial PN weight [%] (7) = [(1)/(2)]*100	17.01 (7)
On surface PN of PN-pozzolana percentage [%] (8) = [(1)/(4)]*100	28.09 (8)
PN Vacuole porous of PN-pozzolana percentage [%] (9) = [(5)/(4)]*100	71.91 (9)
Pozzolana vacuole porosity recovery rate [%] (10) = [(5)/pozzolana weight (0.7695 [g])]*100	26.25 (10)
Specific surface PN-pozzolana [m ² /g]	661.26

The first PN-pozzolana synthesized characteristics (Table 5) showed that 60.55 [%] of initial PN was putted on the pozzolana structure such as 28.09 [%] of these PN was on surface of the PN-pozzolana and 71.91 [%] of these PN was dispersed in the pozzolana vacuole porous. Also, bibliography said that the pozzolana porosity was approximatively 70% in volume and the dry apparent density of pozzolana that sieves are between 0 [mm] to 3 [mm] is 1 [g/ml] [7]. Seeing that 26.25 [%] (10) of the pozzolana vacuole porosity weight was covered with PN, approximatively there was at the most 43.75 [%] free vacuole porous space on this PN-pozzolana synthesized. Then, noticed that the PN-pozzolana synthesized weight (0.9650 [g]) was less than the pozzolana weight (0.7695 [g]) plus the PN weight (0.4639 [g]) equals to 1.2334 [g]. The 0.2684 [g] weight difference showed that not only the PN-pozzolana heat treatment in the synthesis-process (Figure 5) was efficient to get rid of some water molecules on the pozzolana structure but also a possible PN-equivalent polymerization occurred on the PN-pozzolana during the PN-pozzolana synthesis (Figure 5) accompanied with CO₂ and/or H₂O molecules elimination. So, it is possible to increase the value of this PN-pozzolana material synthesized as monomer-support for polymerization reactions between citric acid polymers [2-4] and/or other monomers. Finally, noticed that the PN-pozzolana synthesized specific surface (661.26 [m²/g]) became less than PN specific surface (2224.23 [m²/g]) but more than pozzolana specific surface (110.21 [m²/g]). This PN-pozzolana specific surface diminution around (1563.04 [m²/g]) confirmed the PN-equivalent polymerization (certainly brown citric acid polymers) during the PN-pozzolana synthesis previously cited.

5. PN-pozzolana Synthesized Used as Brown Treated Water Clarification Products

5.1. Introduction and Generalities

As said on §4, Black citric acid polymer (PN) have capacity

as a raw material for cationic exchanger realization after activation with NaOH at pH around 15 [1]. So, 83% of water's Ca²⁺ was retained with PN-2-Na because of Na⁺ dispersion on PN but the treated solution color turned to brown showing the presence of brown citric acid polymers [1]. The first solution to clarify the treated water was to create an adequate clarification-filter at the cationic exchanger PN-Na filter exit. That is the reason to synthesize the PN-pozzolana (on §4.3) to be used as water clarification retaining organic compound as brown citric acid polymers in a tubular filter whose its composition was clarified in the following paragraph §5.2.

5.2. Brown Treated Water Clarification Procedure and Experimental Conditions

As shown in the figure 6, take 0.5 [ml] of brown treated water to be clarified which had 1.6335 in a beaker 250 [ml]. Then, add the citric acid solution to neutralize the possible little remainder of NaOH molecules in brown treated water to be clarified. Move and mix the mixture slowly. Remind that after exchange test the majority of Na⁺ was transformed to PN-Na and Na₂CO₃ which was high soluble in water and directly transported on low out with treated water according experimental conditions [1]. Conceive the tubular filter by putting into the syringe-5 [ml] (Ø=12E-3 [m] and height H=4.3E-2 [m]) successively a cotton fine layer non pressed (on the bottom), a glass powder sieving between 0.25 [mm] and 0.8 [mm] just above the cotton, the PN-pozzolana sieving between 0.25 [mm] and 0.8 [mm] on the middle and a powder of citric acid on the top. Finally, inject gradually and continually the neutralized brown water to be clarified into the tubular filter. Note the total water to be clarified crossing number through the tubular filter, in this case this number was seven. Note also the flow speed rate of brown water to be clarified through the tubular filter and measure the clarified refractive index of water at the end of the clarification process. Deduce the brown treated water clarification experimental conditions such as the fluid dynamic pressure, the Reynolds number (Re), the liquid flow characteristic and the singular pressure drop. The following table 6 show the

experimental conditions and results for this brown treated water clarification.

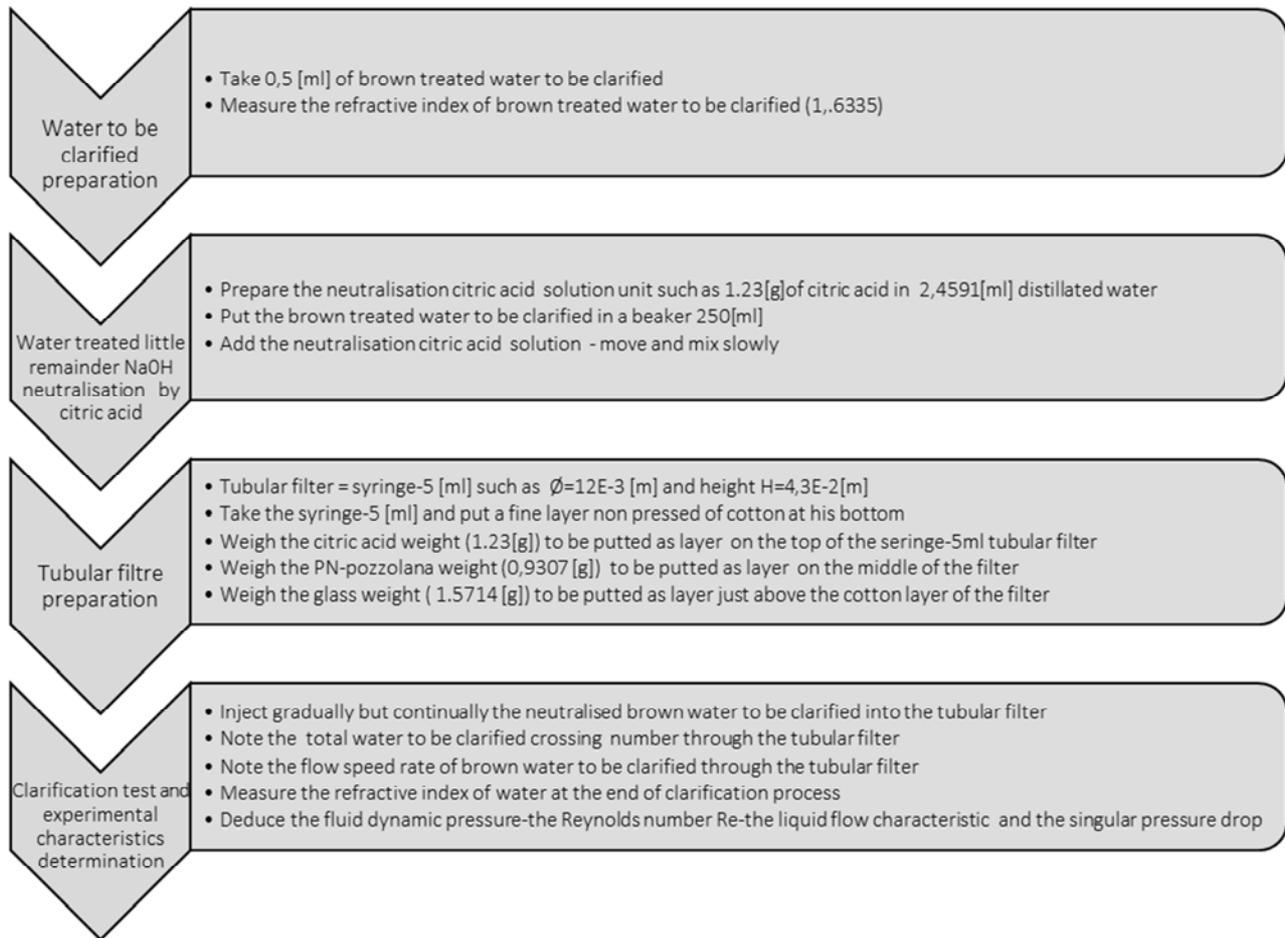


Figure 6. Brown treated water clarification procedure and experimental conditions.

Table 6. Experimental conditions and results for this brown treated water clarification.

Calculated citric acid neutralization solution pH	1.2915
Citric acid layer weight [g]	1.23
PN-pozzolana weight [g]	0.9307
Glass sieved weight [g]	1.5714
Crossing number	7
Brown treated water density [kg/m^3] (1)	1033 (1)
Brown water covered distance [m] (2)	$8.8E-3$ (2)
Covered distance time equivalent [s] (3)	10.7 (3)
Flow speed rate [m/s] (4) (4)=[(2)/(3)]	$8.2243E-4$ (4)
Fluid dynamic pressure [$N.m^{-2}$] (5) (5)=[$0.5 \times (1) \times (4)^2$]	$3.3963E-4$ (5)
Reynolds number (Re) (6) (6)=[$1000 \times (4) \times \varnothing_{syringe} \times (1) / [E6 \times \mu^*]$]	8.8651 (6)
Liquid flow characteristic	Laminar
pressure drop coefficient [Pa] (7) (7)= $64/(6)$	7.2193 (7)
Singular pressure drop [Pa] (8) (8)=[$(7) \times H \times (4)^2 / [\varnothing_{syringe} \times 2 \times g^*]$]	$8.9183E-7$ (8)
Water clarified refractive index	1.3225
¹ Initial brown citric acid moles [moles]	$3.29E-10$
¹ Retained brown citric acid moles [moles]	$1.47E-10$
¹ PN-pozzolana filter retention rate [%]	44.71

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2. μ^* was water viscosity dynamic $1.15E-3$ [Pa.s] seeing that the brow citric acid polymers was completely miscible with water

3. $g^* = 9.81$ [$m.s^{-2}$]

5.3. PN-pozzolana Water Clarification Results and Discussions

As shown in the previous table 6, there was a meaningful

decrease of the treated water refractive index from 1.6335 to 1.3225 and its color was from dark-brown (Figure 7(a)) to light-brown (Figure 7(b)) because of the fall in the brown

citric acid polymers and its derivate concentration in the water clarified (Figure 7(b)) according to the experimental conditions (Table 6); that's why the evaluation of the PN-pozzolana filter rate was about 44.71 [%] [1].



Figure 7. Brown treated water (a) and light-brown clarified water (b) by PN-pozzolana.

It was also important to noticed that for the PN-filter-test [1] done in the same process as PN-pozzolana filter-test but the filter size so the experimental conditions were different [(4)=7.5758 – (5)=2.96E-8 – (6)=0.0408 laminar – (7)=1.1463E-7 – just one crossing], the refractive index decrease slowly from 1.6335 to 1.6325. But, an initial phenomenon of definitely separation of brown citric acid

$$pH = -\log \left[\sqrt{\frac{((K_{a1} \times n_{Ac}) / (3 \times V)) + ((K_{a2} \times n_{Ac}) / (3 \times V)) + ((K_{a3} \times n_{Ac}) / (3 \times V)) + ((K_{PB} \times 10 * n_{PB}) / V) + K_e}{}} \right]$$

Taking that the pKa of the brown citric acid polymers (pKa (BP)) was at maximum equals to the PN pKa ($\approx +13$) and seeing that the initial moles of brown citric acid polymer was very small ($3.29E-10$) than citric acid moles, we obtained the calculated experimental pH of separation equals to 0.3435. At this pH, all citric acid's acid functions (which have respectively pKa1=3.14 – pKa2=4.77 and pKa3=6.39) are in non-separable acid forms $-COOH_i$ $i = \overline{1,3}$ which are favorable to hold by hydrogen bond the brown citric acid polymer and/or its Na-salts forms obtained during the PN activation by NaOH [1]. However, gradually a trickle of brown citric acid polymer salts could reacted with H^+ of citric acid in its vicinity to form citric acid Na-salts and acid form of brown citric acid polymer. In

brief, a strong acidity obtained with citric acid molecules was necessary to carry out a better brown citric acid polymers and its by-product separation.



Figure 8. Clearly separation of brown citric acid polymers above the citric acid layer.

The calculated pH of the above layer solution unit composed with brown citric acid polymers 0.5 [ml], citric acid sieved powder (1.23 [g]) and citric acid solution composed with 1.23 [g] of citric acid and 2.4591 [ml] distilled water was

brief, a strong acidity obtained with citric acid molecules was necessary to carry out a better brown citric acid polymers and its by-product separation.

6. PN-pozzolana-Na Cationic Exchanger Synthesis

6.1. Second PN-pozzolana Synthesized Characterizations

A second PN-pozzolana material was synthesized to be used directly after NaOH-activation as PN-pozzolana-Na cationic exchanger. The following table 7 gave the PN-pozzolana experimental conditions synthesis.

Table 7. Second PN-Pozzolana reactants and liquid vector quantities.

PN-pozzolana reactants and liquid vector quantities	
PN weight [g]	1.5143
Weight relationship ($w_{\text{pozzolana}}/w_{\text{PN}}$)	1.66
Pozzolana weight [g]	2.4877
Oxygen pozzolana atoms	0.057473599
Molar (M) relationship ($M_{\text{water}}/M_{\text{pozzolana}}$)	20
Molar relationship ($M_{\text{water}}/M_{\text{PN}}$)	1192.13
Water [moles]	1.149471971
Water volume [ml]	20.69

The following table 8 gave the characteristics of this second PN-pozzolana material.

Table 8. Second PN-Pozzolana synthesized characteristics.

PN-pozzolana synthesized characteristics	
PN-pozzolana synthesized weight [g] (0)	3.4171 (0)
PN-pozzolana sample weight for measuring-out [g]	0.0341
NaOH-0.05N volume at equivalence point [ml]	0.20
NaOH moles at equivalent point [moles]	1.00E-5
On surface PN-equivalent moles for the sample [moles]	7,1429E-07
On surface PN-equivalent moles per PN-pozzolana weight [moles _{PN-equivalent} / g _{PN-pozzolana}]	2.0947E-5
Total on surface PN-equivalent weight for PN-pozzolana synthesized [g] (1)	0.112 (1)
Initial PN weight [g] (2)	1.5143 (2)
Beaker PN weight [g] (3)	0.3366 (3)
Total PN on PN-pozzolana [g] (4) = (2) - (3)	1.1777 (4)
PN Vacuole porous of pozzolana weight [g] (5) = (4) - (1)	1.0657 (5)
PN percentage on PN-pozzolana [%] (6) = [(4)/(2)]*100	77.77 (6)
On surface PN of PN-pozzolana percentage versus initial PN weight [%] (7) = [(1)/(2)]*100	17.01 (7)
On surface PN of PN-pozzolana percentage [%] (8) = [(1)/(4)]*100	09.51 (8)
PN Vacuole porous of PN- pozzolana percentage [%] (9) = [(5)/(4)]*100	90.49 (9)
Pozzolana vacuole porosity recovery rate [%] (10) = [(5)/pozzolana weight (2.4877 [g])]*100	42.82 (10)
PN moles per PN-pozzolana weight ratio (11)=(4)/M _{PN} (0)	2.19E-4 (11)
Specific surface PN-pozzolana [m ² /g]	-

The second PN-pozzolana synthesized characteristics (Table 8) showed that 77.77 [%] of initial PN was putted on the pozzolana structure such as 09.51 [%] of these PN was on surface of the PN-pozzolana and 90.49 [%] of these PN was dispersed in the pozzolana vacuole porous. Also, bibliography said that the pozzolana porosity was approximatively 70% in volume and the dry apparent density of pozzolana that sieves are between 0 [mm] to 3 [mm] is 1 [g/ml] [7]. Seeing that 42.82 [%] (10) of the pozzolana vacuole porosity weight was covered with PN, approximatively there was at the most 27.18 [%] free vacuole porous space on this PN-pozzolana synthesized. Then, noticed that the PN-pozzolana synthesized weight (3.4171 [g]) was less than the pozzolana weight (2.4877 [g]) plus the PN weight (1.5143 [g]) equals to 4.002 [g]. The 0.5849 [g] weight difference showed that not only the PN-pozzolana heat treatment in the synthesis-process (Figure 5) was efficient to get rid of some water molecules on the pozzolana structure but also a possible PN-equivalent polymerization occurred on the PN-pozzolana during the PN-pozzolana synthesis (Figure 5) accompanied with CO₂ and/or H₂O molecules elimination. So, it was confirmed to increase the value of this PN-pozzolana material synthesized as monomer-support for polymerization reactions between citric acid polymers [2-4] and/or other monomers. Noticed also that at almost the same molar relationship between PN and water which is slightly less dense [5-6], the water amount used for the second synthesis was three twice more than the first synthesis confirming the water role not only to the PN transport but also to the PN polymerization leading to the increasing of the Vacuole porous of PN-pozzolana percentage [%] from 71.91 [%] (First synthesis – Table 5) to 90.49 [%] (Second synthesis – Table 7) and also the increasing of the Pozzolana vacuole porosity recovery rate [%] from 26.25 [%] (First synthesis – Table 5) to 42.82 [%] (Second synthesis – Table 7).

Finally, the first and the second PN-pozzolana synthesized characterizations results confirmed that not only the PN-pozzolana synthesis procedure and the NaOH-0.05N measuring-out were efficient but also their results used and interpretations gave important deals (Table 5 – Table 7) like On

surface PN of PN-pozzolana rate, PN Vacuole porous of PN-pozzolana rate and pozzolana vacuole porosity recovery rate.

6.2. PN-pozzolana Activation Procedure with NaOH – Na-PN-pozzolana

The following figure 9 showed the PN-pozzolana activation procedure with NaOH solution with calculated pH=15.22 [1] – (Figure 9). First, put into a syringe-10ml, with a fine layer of non-pressed cotton at its bottom, the PN-pozzolana to be activated. Add continually and gradually the NaOH solution which quantities were chosen such as the NaOH moles per PN moles ratio equals approximatively to 28. Leave all for one hour. After one hour, take out of the syringe the Na treated PN-pozzolana and the cotton, weigh them and put the Na-PN-pozzolana in a porcelain crucible. to suffer a thermic treatment. Weigh a Na-PN-pozzolana sample (Figure 9) and cotton then measure out their NaOH rate with HCl-0.05N and deduce the on surface and on vacuole porous Na⁺ ions of the Na-PN-pozzolana activated. Secondly, carry out the thermic treatment by putting the porcelain-crucible with Na-PN-pozzolana into the oven (at ambient temperature) programmed from ambient temperature to 408.15 [°K] with 276.15 [°K/mn] speed. When 408.15 [°K] was reached count 32 [mn] to 35 [mn], take the sample out of the oven, weigh all and deduce the Na-PN-pozzolana cationic exchanger weight. Thirsty, characterize the Na-PN-pozzolana cationic exchanger by measuring out the final NaOH adsorbed on PN-pozzolana with HCl-0.05N [1] to form the Na-PN-pozzolana cationic exchanger and deduced the on surface and on vacuole porous Na⁺ ions of Na-PN-pozzolana cationic exchanger. Finally, proceed to the exchange tests by treating a CaCO₃ solution through the Na-PN-pozzolana cationic exchanger filter as described on the bibliography with different contact time [1]. Followed the treated water Ca²⁺ concentration by complexometric EDTA-titration, note all treated water color and its refractive index. The following paragraph §6.3 and §7 gave respectively the results of the Na-PN-pozzolana cationic exchanger characterizations and of the exchange tests.

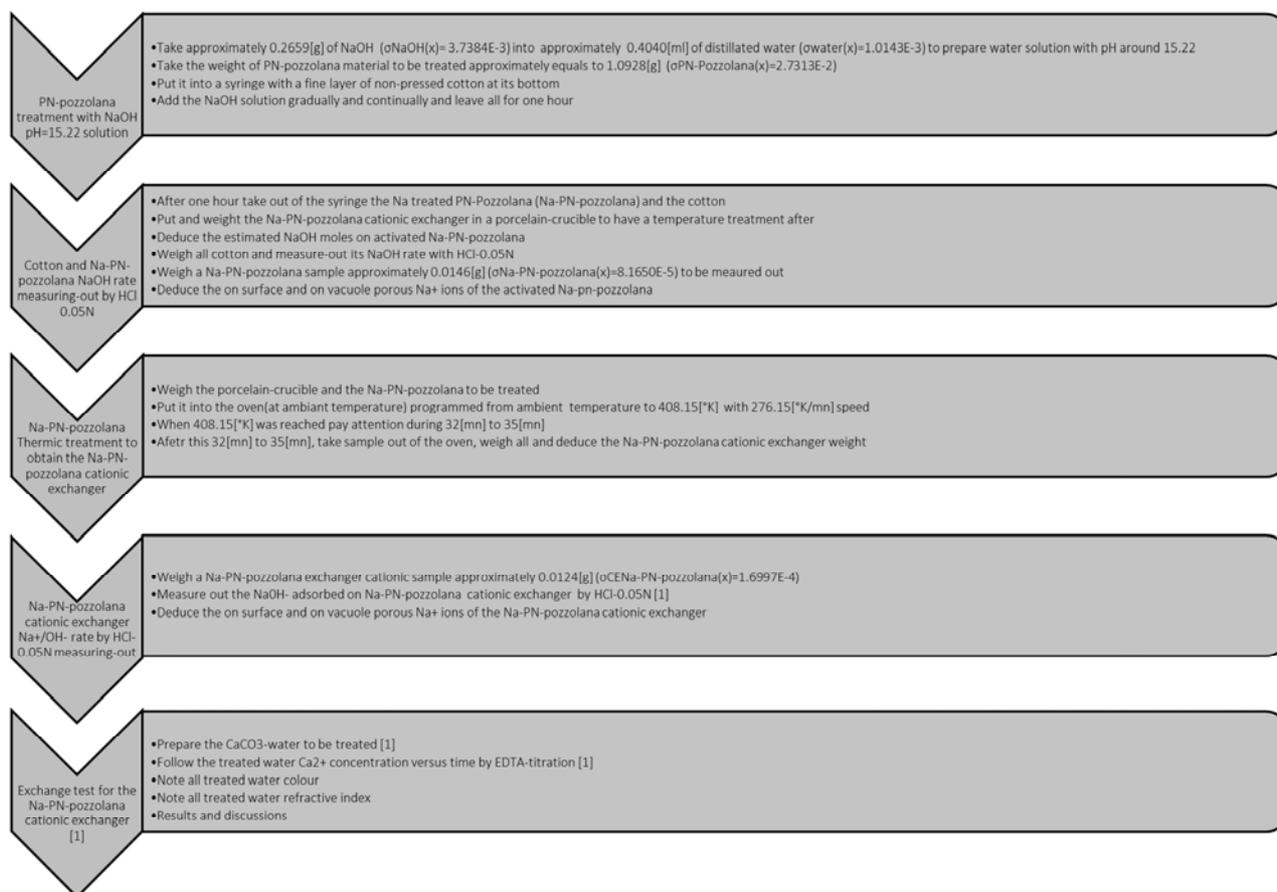


Figure 9. PN-pozzolana activation procedure with NaOH to obtain the Na-PN-pozzolana cationic exchanger.

Three NaOH activations of PN-pozzolana were done to be used after thermic treatment as cationic exchanger on an adsorption-exchange test (Figure 9). The following table 9 showed the results of these NaOH activations.

Table 9. PN-pozzolana activation by NaOH solution results.

	Activation 1	Activation 2	Activation 3
PN-Pozzolana to be activated weight [g] (1)	1.1273 (1)	1.0907 (1)	1.0605 (1)
PN [moles] (2)=(1) \times (11) _{Table8}	2.4739E-4 (2)	2.3936E-4 (2)	2.3273E-4 (2)
NaOH weight [g]	0.2646	0.2703	0.2688
NaOH [moles] (3)	6.64E-3 (3)	6.68E-3 (3)	6.64E-3 (3)
Water volume [ml]	0.4	0.4	0.4
NaOH – concentration [mol.l ⁻¹]	16.4706	16.4707	16.4705
pH (NaOH-solution)	15.2167	15.2167	15.2167
Na moles per PN moles ratio (4)=(3)/(2)	26.84 (4)	27.91 (4)	28.53 (4)
Activation duration [mn]	60	60	60
Na-PN-Pozzolana activated by NaOH weight [g] (5)	1.2712 (5)	1.0946 (5)	1.1963 (5)
Weight NaOH of Na-PN-pozzolana augmentation [g] (6)=(5)-(1)	0.1439 (6)	3.9E-3 (6)	0.1358 (6)
PN-pozzolana weigh augmentation percentage [%] (7)=[(6)/(1)] \times 100]	12.77 (7)	0.36 (7)	12.81 (7)
Estimated Na^+ moles on activated Na-PN-pozzolana (8)=(6)/ M_{NaOH}	3.5978E-3 (8)	9.7507E-5 (8)	3.3952E-3 (8)
Estimated Na^+ deposit rate [%] (9)=[(8)/(3)] \times 100	54.18 (9)	1.46 (9)	51.13 (9)
Estimated Na^+ moles per PN moles ratio (10)=(8)/(2)	14.5430 (10)	0.4 (10)	14.5886 (10)
Estimated Na^+ moles on activated Na-PN-pozzolana per PN-pozzolana weigh ratio (11)=(8)/(1)	3.1915E-3 (11)	8.9399E-5 (11)	3.2015E-3 (11)
Estimated Na^+ moles on activated Na-PN-pozzolana per PN-pozzolana activated weigh ratio (12)=(8)/(5)	2.8302E-3 (12)	8.9080E-5 (12)	2.8381E-3 (12)

In all cases, according to this procedure described on §6.2 Figure 9, the PN-pozzolana weigh increased corresponding to the

NaOH molecules adsorption on PN molecules with an estimated medium ratio equals to 14.5658. Seeing the results on table 9, the

estimated NaOH deposit rate evolve with NaOH concentration.

Then, NaOH really adsorbed on the PN-pozzolana and on cotton was measuring-out by HCl-0.049N according to the procedure described in bibliography [1]. Results of these titrations were shown in the following table 10.

Firstly, noticed that NaOH adsorbed on cotton were few than NaOH adsorbed on PN-pozzolana [Table 10 – (15)-(16)]. Secondly, the HCl-0.049N NaOH measuring-out results interpretations showed that estimated NaOH On vacuole porous of Na-PN-pozzolana activated (6) were all the time approximatively equals to zero if it considered directly only the on surface adsorbed-NaOH. Seeing that the second pozzolana vacuole porosity recovery rate [%] [Table 8 – (10)] was only 42.82 [%], it was really unthinkable that all these pozzolana vacuoles was obstructed at the end of the PN-pozzolana synthesis procedure (figure 5) above all its PN Vacuole porous of PN- pozzolana rate [Table 8 – (9)] were 90.49 [%]. So, it’s suitable to affirm that in this case, the NaOH On surface of Na-PN-pozzolana activated [moles]

titrated by HCl-0.049N [Table 10 – (5)] was similar to the total NaOH adsorbed on the Na-PN-pozzolana during the second PN-pozzolana NaOH-activation. So, in this case it’s rather adequate to have a uniform distribution of NaOH molecules on the Na-PN-pozzolana activated according to the ratio around 16 for all the activated Na-PN-pozzolana [Table 10 – (8)] than on surface with probably multi-PN layer giving the ratio [Table 10 – (11)].

That allow to notice that it’s important to know the PN-pozzolana characteristics by following the PN-pozzolana synthesis procedure described on §4.2 and §4.3 – figure 5 which gave on surface PN, quantified by NaOH-0.05N measuring out [1], consequently the PN in vacuoles porous of PN-pozzolana material was deduced by the total PN quantity minus the on surface PN quantity.

Next, according to the procedure described on §6.2 figure 9, the Na-PN-pozzolana activated by NaOH passed on thermic treatment and the following table 11 gave each activated Na-PN-pozzolana thermic treatment conditions and results.

Table 10. Na-PN-pozzolana activated by NaOH characterizations by HCl-0.049N titration.

Sample weigh [g] (1)	Activation1	Activation2	Activation3
	0.0145 (1)	0.0147 (1)	0.0146 (1)
PN moles per PN-pozzolana weight ratio (2) _{Table8}	2.19E-4 (2)	2.19E-4 (2)	2.19E-4 (2)
Sample PN [moles] (3)=(1)×(2)	3.1755E-6 (3)	3.2193E-6 (3)	3.1974E-6 (3)
Sample PN weigh [g] (4)=(3)×M _{PN}	4.9871E-3 (4)	5.0559E-3 (4)	5.0215E-3 (4)
Estimated Na+ On surface of Na-PN-pozzolana activated [moles] titrated by HCl-0.049N (5)	5E-5 (5)	4.5E-5 (5)	5.75E-5 (5)
Estimated Na+ On vacuole porous of Na-PN-pozzolana activated [moles] (6)=[(11) _{Table9} ×(1)] – (5)	≈ 0 (6)	≈ 0 (6)	≈ 0 (6)
Na+ moles On surface per sample weigh ratio (7)=(5)/(1)	3.4483E-3 (7)	3.0612E-3 (7)	3.9384E-3 (7)
Na+ moles On surface per Total PN moles ratio (8)=(5)/(3)	15.75 (8)	13.97 (8)	17.9834 (8)
Estimated On surface PN-equivalent moles per PN-pozzolana weight [moles _{PN-equivalent} / g _{PN-pozzolana}] (9) (Table 8)	2.0947E-5 (9)		
Estimated On surface PN-equivalent moles PN-pozzolana sample [moles] (10)=(9)×[(1)-(1)×(12) _{Table9}]	3.0287E-7 (10)	3.0789E-7 (10)	3.0496E-7 (10)
Estimated Na moles On surface per On surface PN-equivalent moles ratio (11)=(5)/(10)	165.0863 (11)	146.1561 (11)	188.5493 (11)
PN Vacuole porous of PN- pozzolana percentage [%] (12) (Table 8)	90.49 (12)		
Estimated PN On vacuole porous of PN-pozzolana sample (13)=(12)×0.01×(1)	13.12E-3 (13)	13.30E-3 (13)	13.21E-3 (13)
Estimated Na+ moles On vacuole per On vacuole PN-equivalent moles ratio (14)=(6)/(13)	≈ 0 (14)	≈ 0 (14)	≈ 0 (14)
Cotton Moles Na+ per cotton weigh [moles.g ⁻¹] (15)	6.7583E-5 (15)	8.8986E-5 (15)	1.1405E-4 (15)
Sample Moles Na per sample weigh (16)=(5)/(1)	3.45E-3 (16)	3.06E-3 (16)	3.94E-3 (16)

Noticed that the Na⁺ moles on surface per Total PN moles ratio of Na-PN-pozzolana activated [Table 10 – (8)] values were all the time around and/or slightly superior to 14 which correspond to the hydracids-bound quantities in one PN-molecule (Figure 1). These results confirmed that

initially and generally the PN-molecules which have hydrogen atoms on their structure (Figure 1) were adsorbed by hydrogen-bond on oxygen’s pozzolana [Table 9 – (10)], a posture facilitating their activations with NaOH molecules.

Table 11. Na-PN-pozzolana activated by NaOH thermic treatment results.

Activated Na-PN-pozzolana thermic treatment			
	Activated 1	Activated 2	Activated 3
Na-PN-pozzolana activated weigh [g] (1)	1.2567 (1)	1.0762 (1)	1.1818 (1)
Temperature [°K]	408.15	413.15	413.15
Oven speed [°K/mn]	276.15	276.15	276.15
Thermic treatment duration at 408.15 [°K]-413.15 [°K][mn]	35	32	32
Na-PN-pozzolana activated and thermic treated weigh [g] (2)	1.1609 (2)	1.0298 (2)	1.0402 (2)
Thermic treatment weigh diminution [g] (3)=(1)-(2)	0.0958 (3)	0.0462 (3)	0.1416 (3)
Thermic treatment weigh diminution rate [%] (4)=(3)/(1)	07.62 (4)	04.29 (4)	11.98 (4)
Total Na+ moles per Total PN moles ratio diminutions (5)=(8) _{Table10} -(8) _{Table12}	1.83 (5)	0.8702 (5)	0.866 (5)
Total estimated Na+ moles diminutions (6)=(5) _{Table10} -(5) _{Table12}	1.25E-5 (6)	1E-5 (6)	1E-5 (6)

These light weight diminutions (Table 11) for all activated

Na-PN-pozzolana samples after thermic treatment confirmed

that not only the NaOH molecules were adsorbed efficiently on the PN molecules but also these last were distributed uniformly on the PN-pozzolana even after the thermic treatment. These results confirmed not only that initially and generally the PN-molecules which have hydrogen atoms on their structure (Figure 1) were adsorbed efficiently by hydrogen-bond on oxygen's pozzolana and the the Na^+ moles on surface per Total PN moles ratio of Na-PN-pozzolana activated [Table 10–(8)] stay stable even after thermic treatment [Table 12-(8)] but also they explained these light weight diminutions, so corresponding to water and/or CO_2 eliminations with eventually citric acid monomers polymerization reactions [3-4] as seen on §6.1. At the end, a crisp Na-PN-pozzolana cationic exchanger material were obtained (Figure 10) and characterized by HCl-0.05N titration.



Figure 10. Crisp Na-PN-pozzolana cationic exchanger material.

6.3. Na-PN-pozzolana Cationic Exchanger Synthesized Characterizations by Na Content Determination with HCl-0.049N – Results and Discussions

NaOH adsorbed on the Na-PN-pozzolana cationic exchanger obtained after thermic treatment was quantified by HCl-0.049N measuring-out according to the procedure described in bibliography [1] and compared with the NaOH adsorbed on Na-PN-pozzolana activated. Results of these titrations were shown in the table 12. Once again, the HCl-0.049N NaOH

measuring-out results interpretations showed that estimated NaOH on vacuole porous of Na-PN-pozzolana-CE (6) were all the time approximatively equals to zero if it considered directly only the on surface adsorbed-NaOH. Seeing that the second pozzolana vacuole porosity recovery rate [%] [Table 8 – (10)] was only 42.82 [%], it was really unthinkable that all these pozzolana vacuoles was obstructed at the end of the PN-pozzolana synthesis procedure (figure 5) above all its PN Vacuole porous of PN- pozzolana rate [Table 8 – (9)] were 90.49 [%]. So, it's suitable to affirm that in this case, the NaOH On surface of Na-PN-pozzolana-CE [moles] titrated by HCl-0.049N [Table 10 – (5)] was similar to the total NaOH adsorbed on the Na-PN-pozzolana-CE during the second PN-pozzolana NaOH-activation. So, in this case it's rather adequate to have a uniform distribution of NaOH molecules on the Na-PN-pozzolana-CE according to the ratio around 15 for all the Na-PN-pozzolana-CE [Table 10 – (8)] than on surface with probably multi-PN layer giving the ratio [Table 12 – (11)]. That allow to notice that it's important to know the PN-pozzolana characteristics by following the PN-pozzolana synthesis procedure described on §4.2 and §4.3 – figure 5 which gave on surface PN, quantified by NaOH-0.05N measuring out [1], consequently the PN in vacuoles porous of PN-pozzolana material was deduced by the total PN quantity minus the on surface PN quantity. So, noticed that the estimated total moles NaOH quantities of Na-PN-pozzolana-CE cationic exchanger [Table 10 – Table 12 – (5)] titrated by HCl-0.049N and distributed uniformly on the Na-PN-pozzolana-CE per total PN moles ratio decreased a little all the time [Table 11 – (5)]. It was certainly caused by the thermic treatment of the Na-PN-pozzolana activated. The thermic treatment provoked water and/or CO_2 (by polymerizations) eliminations without disrupting the uniformity of NaOH molecules dispersion on the PN-pozzolana-CE even if a little quantity of NaOH [Table 11 – (6)] was eliminated and/or retained by silicate pozzolana structure as glass network modifiers [14] during the thermic treatment.

Table 12. Na-PN-pozzolana-CE cationic exchanger characterizations by HCl-0.049N titration.

	Activation1	Activation2	Activation3
Sample weigh [g] (1)	0.0123 (1)	0.0122 (1)	0.0126 (1)
PN moles per PN-pozzolana weight ratio (2) _{Table8}	2.19E-4 (2)	2.19E-4 (2)	2.19E-4 (2)
Sample PN [moles] (3)=(1)×(2)	2.6937E-6 (3)	2.6718E-6 (3)	2.7594E-6 (3)
Sample PN weigh [g] (4)=(3)×M _{PN}	4.2304E-3 (4)	4.1960E-3 (4)	4.3336E-3 (4)
Estimated Na ⁺ On surface of Na-PN-pozzolana-CE cationic exchanger [moles] titrated by HCl-0.049N (5)	3.75E-5 (5)	3.5E-5 (5)	4.75E-5 (5)
Estimated Na ⁺ On vacuole porous of Na-PN-pozzolana activated [moles] (6)=[(11) _{Table9} ×(1)] – (5)	1.7555E-6 ≈ 0 (6)	≈ 0 (6)	≈ 0 (6)
Na ⁺ moles On surface per sample weigh ratio (7)=(5)/(1)	3.0488E-3 (7)	2.8689E-3 (7)	3.7698E-3 (7)
Na moles On surface per Total PN moles ratio (8)=(5)/(3)	13.92 (8)	13.0998 (8)	17.2139 (8)
Estimated On surface PN-equivalent moles per PN-pozzolana weight [moles _{PN-equivalent / g_{PN-pozzolana}}] (9)(Table 8)	2.0947E-5 (9)		
Estimated On surface PN-equivalent moles PN-pozzolana cationic exchanger sample [moles] (10)=(9)×[(1)-(1)×(12) _{Table9}]	2.5692E-7 (10)	2.5553E-7 (10)	2.6318E-7 (10)
Estimated Na ⁺ moles On surface per On surface PN-equivalent moles ratio (11)=(5)/(10)	145.9598 (11)	136.9699 (11)	180.4848 (11)
PN Vacuole porous of PN- pozzolana percentage [%] (12) (Table 8)	90.49 (12)		
Estimated PN On vacuole porous of PN-pozzolana sample (13)=(12)×0.01×(1)	11.13E-3 (13)	11.04E-3 (13)	11.40E-3 (13)
Estimated Na ⁺ moles On vacuole per On vacuole PN-equivalent moles ratio (14)=(6)/(13)	1.5773E-4 ≈ 0 (14)	≈ 0 (14)	≈ 0 (14)

7. Exchange Test of Na-PN-pozzolana--CE (Cationic Exchanger) Material

7.1. Exchange Test Principle

As described in the bibliography [1], the cationic exchange test consist of passing a calcium carbonate (CaCO_3) solution directly through a syringe 10 [ml] which contained the Na-PN-pozzolana-CE material as tubular filter. Salvage the solutions which passed through the Na-PN-pozzolana-CE 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. For all tests, 16 [ml] of CaCO_3 -solution must be treated.

The characteristics of the calcium carbonate solution to be treated is shown in the following table 13.

Table 13. 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

Table 14. Treated-samples characteristics and operational conditions.

Na-PN-pozzolana-CE cationic exchanger tests							
		Test-1		Test-2		Test-3	
Treated-samples	N°	Duration [second]	Volume [ml]	Duration [mn]	Volume [ml]	Duration [mn]	Volume [ml]
	1 st	5.7	4	7.3	3.1	34.23	6.5
	2 nd	11.4	8	15.8	6	31.13	5.1
	3 rd	5.7	4	24	3.1	23.47	4.4
Cumulated values		22.8	16	47.1	12.2	88.83	16
Medium flow [ml.mn ⁻¹]		42.11		0.4		0.2	
CaCO ₃ flow [g.h ⁻¹]		2.96E-2		2.81E-4		1.27E-4	
whsv [h ⁻¹]		117.80		1.26		0.57	
Contact time τ [h]		8.49E-3		7.94E-1		1.76	

8.1. Exchange Test Results in Terms of Retained Ca^{2+} Evolution and Treated Ca^{2+} Concentration Evolution Versus Time

Table 15. Na-PN-pozzolana-CE cationic exchanger tests results.

Na-PN-pozzolana-CE cationic exchanger tests							
		Test-1		Test-2		Test-3	
Treated-samples	N°	Ca ²⁺ titrated [moles]	Ca ²⁺ retained [moles]	Ca ²⁺ titrated [moles]	Ca ²⁺ retained [moles]	Ca ²⁺ titrated [moles]	Ca ²⁺ retained [moles]
	1 st	1.36E-7	3.31E-7	6.76E-8	2.95E-7	5.32E-8	7.07E-7
	2 nd	1.31E-7	8.04E-7	1.64E-7	5.38E-7	4.87E-8	5.48E-7
	3 rd	2.18E-8	4.46E-7	4.23E-8	3.20E-7	2.40E-8	4.90E-7
Cumulated values		2.89E-7	1.58E-6	2.74E-7	1.15E-6	1.26E-7	1.75E-6
Total moles Ca ²⁺ to be treated [moles]		1.87E-6		1.43E-6		1.87E-6	
Na-PN-pozzolana-CE weigh used (1) [g]		1.1434 (1)		1.0165 (1)		1.0148 (1)	
nPN total [moles] (2)=(1)×(2) _{Table8}		2.51E-4		2.23E-4		2.23E-4	
nNa ⁺ total [moles] (3)=(2)×(8) _{Table12}		3.49E-3		2.92E-3		3.83E-3	

CaCO ₃ – solution	
Distilled water volume [ml]	150
CaCO ₃ – solution concentration [mol.l ⁻¹]	1.16899E-4
Total CaCO ₃ -solution to be treated [ml]	16

7.2. Ca²⁺ Measuring Out of Treated CaCO₃-solution Water Samples

As described in the bibliography [1], once salvaged, each treated-samples solution was titrated with EDTA. The objective was to calculate their Ca^{2+} contents by Ca^{2+} complexometric titration with EDTA [15-16]. 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. For all titration, the EDTA concentration was 0.002727N.

8. Exchange Test Results of Na-PN-pozzolana-CE Material as Cationic Exchanger

The following table 14 showed the treated-samples characteristics and operational conditions for each tests.

Na-PN-pozzolana-CE cationic exchanger tests							
		Test-1		Test-2		Test-3	
Treated-samples	N°	Ca ²⁺ titrated [moles]	Ca ²⁺ retained [moles]	Ca ²⁺ titrated [moles]	Ca ²⁺ retained [moles]	Ca ²⁺ titrated [moles]	Ca ²⁺ retained [moles]
Ca ²⁺ retained rate (1) [%]		84.55		80.82 (87.55)*		93.27	
Total treated volume [ml]		16		12.2		16	
Contact time τ [h]		8.49E-3		7.94E-1		1.76	

Cationic exchange tests results for the Na-PN-pozzolana-CE were shown in the table 15 according to the treated-samples characteristics and operational conditions on the previous table 14.

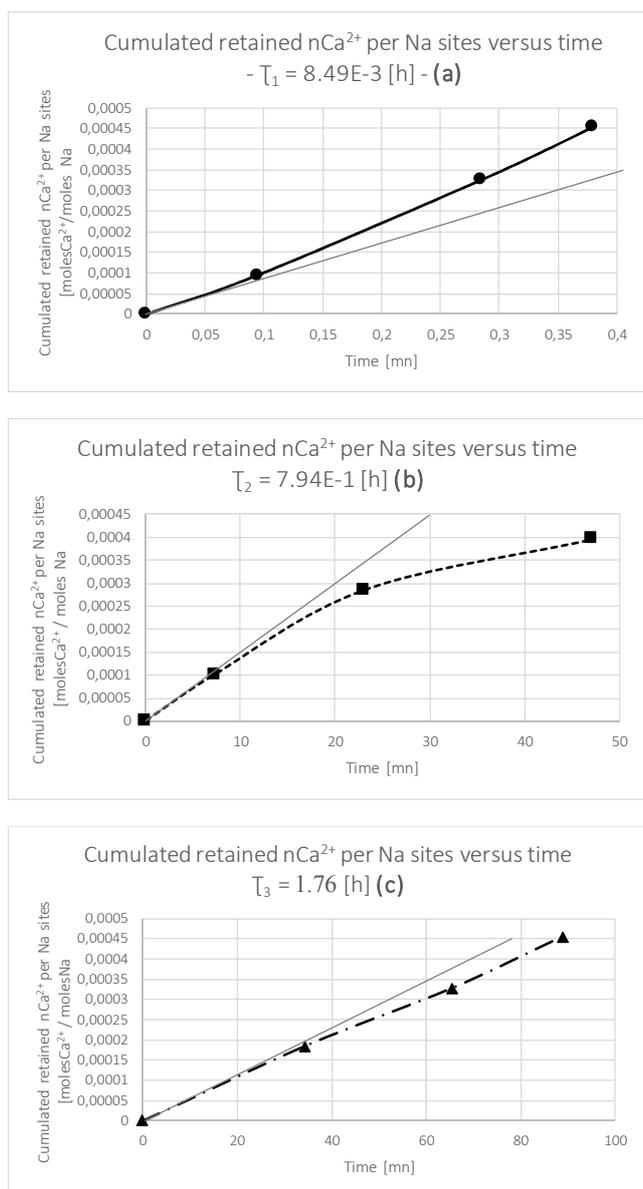


Figure 11. Na-PN-pozzolana-CE cationic exchanger cumulated retained Ca²⁺ per Na sites versus time for different contact time (a) – (b) and (c).

These figures 11 showed that cumulated retained Ca²⁺ quantities per Na sites versus time increased for all contact times but notice was done that the initial speed of cumulated

retained Ca²⁺ moles decreased with contact time such as their values for contact times τ_1 , τ_2 and τ_3 were respectively $8.57E-4$ [moles Ca²⁺ retained per Na per minute], $1.50E-5$ [moles Ca²⁺ retained per Na per minute] and $5.83E-6$ [moles Ca²⁺ retained per Na per minute] as shown the following figure 12.

So, when contact time was low, the speed of the water to be treated and its residence time through the Na-PN-pozzolana-CE tubular filter was high. Consequently, notice that not only initially the Ca²⁺ quantities (around 10^{-7} [moles]) treated through the Na-PN-pozzolana-CE tubular filter were weak than the Na sites quantities (around 10^{-3} [moles]) (Table 15) so initially the [Ca²⁺] concentration were weak than the [Na] sites concentrations, but also seeing that the pozzolana-support make-up principally with SiO₂ and/or Al₂O₃ and MgO whose pH_{pzc} (Isoelectric point) were respectively 2 – 9.1 and 12.4 [17]; these initial operational conditions furthered not only the Ca²⁺ adsorption on Na⁺ sites which were transformed to Na₂CO₃ but also the possible Ca²⁺ adsorption on free pozzolana- SiO₂ and/or Al₂O₃ and MgO sites where neighboring pH were superior to their pH_{pzc} (Isoelectric point). Also, seeing that the pH_{pzc} (Isoelectric point) of Al₂O₃ and MgO free sites were high, when their neighboring pH were inferior, it favored also the adsorption of brown citric acid polymers molecules by hydrogen bound. That explained the obtaining of clean treated water with best refractory index near of those water as shown in the table 16 which confirmed that an active Na-PN-pozzolana-CE was synthesized.

In the same logic, when contact time was high, the speed of the water to be treated and its residence time through the Na-PN-pozzolana-CE tubular filter was low. Consequently, notice that not only initially the Ca²⁺ quantities (around 10^{-6} [moles]) treated through the Na-PN-pozzolana-CE tubular filter increased even if its quantities stayed weak than the Na sites quantities (around 10^{-3} [moles]) (Table 15) so initially the [Ca²⁺] concentration and its residence time increased particularly on vacuoles, but also seeing that the pozzolana-support make-up principally with SiO₂ and/or Al₂O₃ and MgO whose pH_{pzc} (Isoelectric point) were respectively 2 – 9.1 and 12.4 [17]; these initial operational conditions furthered Na₂CO₃ vacuoles retention which balanced with Ca²⁺ retained on vacuoles and finally conducted initially preferentially to CaCO₃ elimination without adsorption and explained the diminution of initial Na-PN-pozzolana-CE activities when the contact time increase (Figure 12). But, noticed that in these initial operational conditions the neighboring pH of free SiO₂ sites increase and the neighboring pH of free Al₂O₃ – MgO sites decrease which favored once more the adsorption of brown citric acid polymers molecules. That explained the obtaining of clean treated water

with best refractory index near of those water as shown in the following table 16 and the figure 13 (Test-1) which confirmed that an active Na-PN-pozzolana-CE cationic exchanger was synthesized.

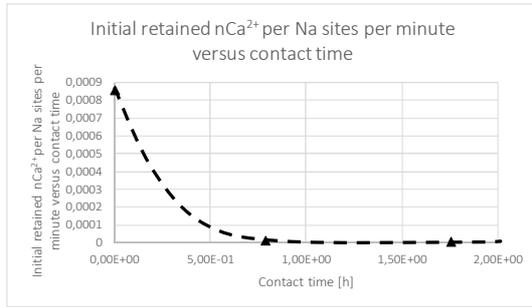


Figure 12. Initial retained nCa^{2+} per Na sites per minute evolution according to the contact time.

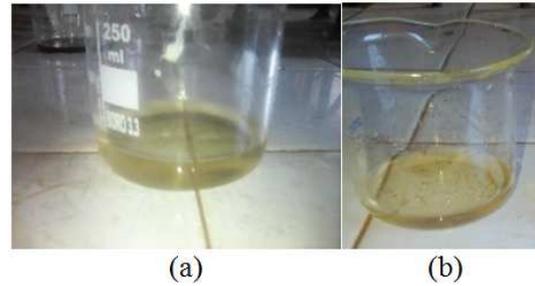


Figure 13. Transparent slightly brown-yellow (a) and transparent slightly yellow (b) treated water solution through the Na-PN-pozzolana cationic exchanger according Test-1 experimental conditions.

Table 16. Na-PN-pozzolana-CE tubular filter treated water characteristics.

Na-PN-pozzolana-CE cationic exchanger tests			
Seringue 10 [ml] – Tubular filter			
	Test-1	Test-2	Test-3
Contact time τ [h]	8.49E-3	7.94E-1	1.76
Medium flow [ml.mn ⁻¹]	42.11	0.4	0.2
CaCO ₃ flow [g.h ⁻¹]	2.96E-2	2.81E-4	1.27E-4
whsv [h ⁻¹]	117.80	1.26	0.57
Ca ²⁺ retained rate (1) [%]	84.55	0.82 (87.55)* *conversion estimated at 16 [ml]	93.27
Refractive Index (After only one crossing through the cationic exchanger)	1.32	1.31	1.3060
Treated water color	Transparent slightly brown-yellow after 5 at 7 crossing-cycles through the cationic exchanger (Figure 11 (a))	Transparent slightly yellow	Transparent slightly yellow

Also, noticed that at the end the total Ca²⁺ retained rate by Na-PN-pozzolana-CE tubular filter increased with contact time as showed the following figure 14. These results confirmed not only the Na-PN-pozzolana-CE efficacy but also the statement that during exchange test on PN-Na material [1], NaOH molecules can moves through the PN-polymers and react not only with their non-activated sites (-COOH) but also with CaCO₃ to produce another -COONa active sites and so on until its deactivation.

8.2. Na-PN-pozzolana--CE (Cationic Exchanger) Exchange Kinetic Simplified at High Contact Time

This paragraph try to study this Na-PN-pozzolana-CE exchange kinetic by following the [Ca²⁺] evolution versus time of the treated water. First, in general the exchange reaction speed was according to [Ca²⁺] and [Na⁺] concentration evolution such as

$$v = -\frac{d[Ca^{2+}]}{dt} = -\frac{d[Na^+]}{dt} = k_{PN} \times [H_2O] \times [Ca^{2+}]^\alpha \quad (1)$$

Seeing that on Na-PN-pozzolana-CE exchange evolution mainly at low contact time (§8.1), initially and all the time the [Na⁺] and [H₂O] concentrations were largely superior than the [Ca²⁺] concentration, so the above exchange reaction speed became:

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

These concentrations evolutions were shown in the following table 17.

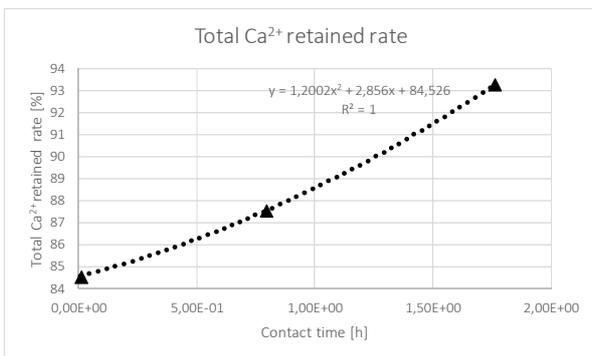


Figure 14. Total retained Ca²⁺ rate evolution with contact time.

Table 17. Treated water Ca²⁺ concentration evolution on Na-PN-pozzolana-CE tubular filter.

Na-PN-pozzolana-CE cationic exchanger tests							
Seringue 10 [ml] – Tubular filter							
		Test-1		Test-2		Test-3	
Contact time τ [h]		8.49E-3		7.94E-1		1.76	
Treated-samples	N ^o	[Ca ²⁺] [mol.l ⁻¹]	1/[Ca ²⁺] [mol.l ⁻¹]	[Ca ²⁺] [mol.l ⁻¹]	1/[Ca ²⁺] [mol.l ⁻¹]	[Ca ²⁺] [mol.l ⁻¹]	1/[Ca ²⁺] [mol.l ⁻¹]
	1 st	3.41E-5	29336.3	2.18E-5	45837.92	8.18E-6	122234.45

Na-PN-pozzolana-CE cationic exchanger tests							
Seringue 10 [ml] – Tubular filter							
	Test-1		Test-2		Test-3		
2 nd	2.23E-5	4.49E+4	2.54E-5	3.94E+4	8.78E-6	1.14E+5	
3 rd	1.81E-5	5.54E+4	2.24E-5	4.46E+4	7.87E-6	1.27E+5	

So, at low contact time the figure 15 showing the $1/[Ca^{2+}]$ Na-PN-pozzolana-CE evolution versus time and notice that it increased with following a straight line such as $1/[Ca^{2+}] = +89,955t + 20411$ with $R^2=0.9941$. Consequently, second order was the exchange kinetic evolution on the Na-PN-pozzolana-CE and its speed constant was

$$k_{PN,Na+} = +89,955 [mol^{-1} \times L \times s^{-1}]$$

That is to say,

$$v_{Na-PN-pozzolana-CE} = k_{PN,Na+} \times [Ca^{2+}]^2$$

$$v_{Na-PN-pozzolana-CE} = +89,955 \times [Ca^{2+}]^2$$

Seeing that $[Ca^{2+}] \ll 1$ this result confirmed that the Ca^{2+} quantities recovered on treated water with Na-PN-pozzolana-CE increased slowly than on PN-Na [1] and confirmed its capacity to an efficient cationic exchanger.

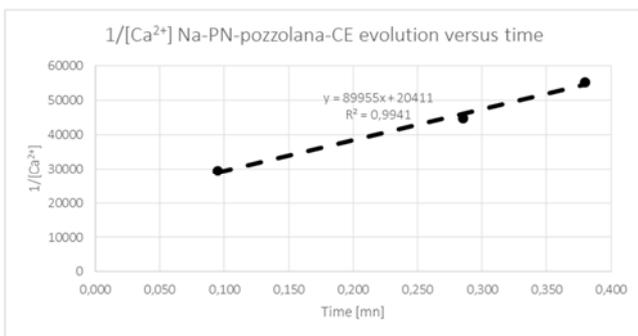


Figure 15. $1/[Ca^{2+}]$ of treated water evolution versus time at $T = 8.49E-3$ [h].

Only, it was important to notice that at high contact time the $1/[Ca^{2+}]$ of treated water evolution versus time reflected the discussions done on §8.1 saying that initially the increasing of residence time of treated water conducted to the increase of Ca^{2+} quantities on the tubular filter and Na_2CO_3 vacuoles retention favoring balanced between Ca^{2+} and Na^+ adsorption retained on vacuoles. So, without considering Na^+ evolution, a less line curve was obtained with low R^2 as shown the figure 16 and figure 17.

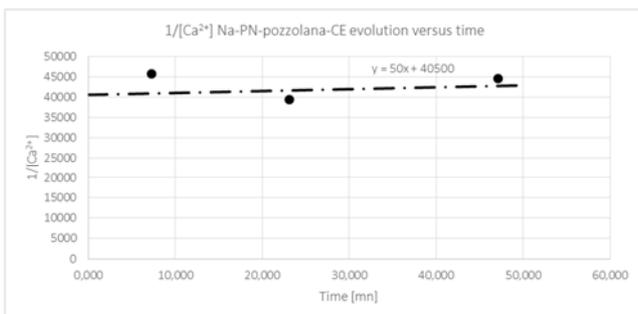


Figure 16. $1/[Ca^{2+}]$ of treated water evolution versus time at $T = 7.94E-1$ [h].

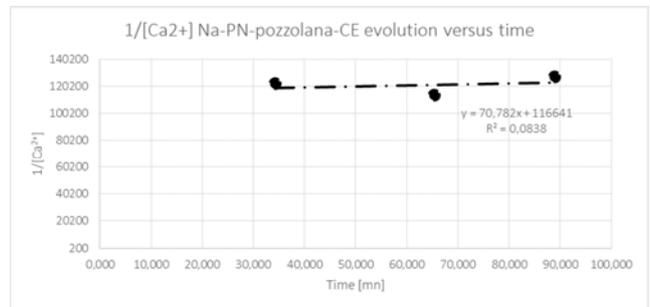


Figure 17. $1/[Ca^{2+}]$ of treated water evolution versus time at $T = 1.76$ [h].

Consequently, second order was the exchange kinetic evolution on the Na-PN-pozzolana-CE and its speed constant was

$$k_{PN,Na+,7.94E-1} \approx +50 [mol^{-1} \times L \times s^{-1}]$$

$$k_{PN,Na+,1.76} \approx +70.78 [mol^{-1} \times L \times s^{-1}]$$

That is to say,

$$v_{Na-PN-pozzolana-CE} = k_{PN,Na+} \times [Ca^{2+}]^2$$

$$v_{Na-PN-pozzolana-CE,7.94E-1} \approx +50 \times [Ca^{2+}]^2$$

$$v_{Na-PN-pozzolana-CE,1.76} \approx +70,78 \times [Ca^{2+}]^2$$

9. Conclusion

Cationic exchange tests with $CaCO_3$ distilled water solution showed that Na-PN-pozzolana-CE is an efficient cationic exchanger. Two procedures-steps were necessary to come to terms of synthesizing the Na-PN-pozzolana-CE cationic exchanger. The first procedure consisted of the PN-pozzolana synthesis using water as PN's liquid vector through the pozzolana structure which allowed to a good dispersion of PN-equivalent molecules not only on pozzolana's surface but also inside the pozzolana's vacuole with a non-negligible free pozzolana's vacuole. The second procedure consisted of firstly, the PN-pozzolana activation with NaOH to obtain an activated Na-PN-pozzolana and secondly its thermic treatment which allowed also to a good dispersion of Na^+ atoms on PN-pozzolana with Na^+/PN moles ratio around the average of 15. Noticed that these thermic treatment of Na-PN-pozzolana activated provoked not only water molecules eliminations but also probably CO_2 molecules eliminations corresponding to PN-equivalent molecules polymerization without disrupting the uniformity of Na^+ dispersion on the Na-PN-pozzolana-CE synthesized against its dispersion on activated Na-PN-pozzolana, probably because of the PN-molecules which have hydrogen atoms on

their structure and were initially and generally adsorbed efficiently by hydrogen-bond on oxygen's pozzolana according to the procedure described previously. Finally, Na-PN-pozzolana-CE cationic exchange kinetic was studied for different contact time and showed that its speed followed second order with $[Ca^{2+}]$ concentration of treated water solution. Notice that, initially speed-constant was important at low contact time certainly due to the residence time favoring cationic exchange to the detriment of balanced between Ca^{2+} and Na^+ . In spite of that, the total Ca^{2+} moles retained at the end of treatment of same treated volume water solution increased with contact time and the maximal Ca^{2+} retained rate capacity around 93.27 [%] for this Na-PN-pozzolana-CE cationic exchanger.

Acknowledgements

Sincere thanks to the E. S. P. A Polytechnics' President. And, sincere gratitude to Chemical Process Engineering Chief Department (E. S. P. A) as well as Chemical Engineering Laboratory staff.

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