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MSB - 3-Methyl-3-Sulfanylbutan-1-Ol Extraction Its Esterification with Citric Acid and PPCA Materials Synthesis

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Abstract: The 3-methyl-3-sulfanylbutan-1-ol (MSB) is a thiol molecule which could be used as food additive flavor agent and encountered in the white wine, in the coffee perfume, in the passion fruit and in the cat urine where it's the responsible of its strong odor characteristics. Thus, this manuscript treated first the valorization of the cat-litters by extracting their MSB molecules using the ethanol-90° solvent. The number of the extraction per sample, its duration and the rinse cycle number are three factors influencing the extraction efficiency. In any case, the ethanol-90° extraction of the MSB molecule is interesting and allow to recover an MSB solution which concentration was deduced by the sulfur titration according to a $BaCl_2$ precipitation procedure. Then, the second part of this manuscript treated the study of the esterification-addition reaction between the citric acid molecules and the MSB molecules. A titration procedure was established allowing to follow the sulfur concentration during this esterification-addition reaction. The results of these experimentations permitted not only to establish a kinetic study of this reaction but also to purpose some reactional mechanism where it was discovered that the sulfur atom of the MSB molecule play a fundamental role during this citric acid esterification reaction. Additionally, the kinetic parameters indicated that the protonic acid H^+ concentration, the citric acid concentration and the MSB molecule concentration influenced the speed of this esterification reaction between the citric acid molecules and the MSB molecules. Finally, using the results and experimental conditions of the esterification reaction, the third part of this manuscript was dedicated to the synthesis of a material based on black citric acid polymers (pn), pozzolana and citric acid named PPCA (pn-pozzolana-citric-acid) which could play the role of a cat-litter.

Keywords: PPCA, 3-Methyl-3-Sulfanylbutan-1-ol (MSB), Citric Acid, Esterification, Acid Sites, Basic Sites

1. Introduction

The molecule MSB is used in different fields in consequence its extraction efficiency from the litter or other supports was very important to its valorization. Many methods could be used to its extraction like solvent extraction or esterification with citric acid molecule. Thus, the first part of this manuscript treated the extraction of the MSB molecules from the cat-litter using ethanol-90° as solvent. The second part is devoted to the study of the esterification-addition reaction between the citric acid and the MSB molecules, three mechanism models were particularly taken into account and their correspondent kinetic parameters were determined using the experimental

results. The latest part treated the synthesis procedure and the characterizations of a new materials named PPCA – pn-pozzolana-citric-acid which could be used eventually as a cat-litter and manufactured with citric acid, citric acid black polymers (pn) and pozzolana from the Iavoko-Madagascar pozzolana deposit which characteristics could be seen in the bibliography below [6]. In this part, the PPCA-materials were synthesized according to two different procedures using distilled water and ethanol-90° as solvent; then they were characterized by determining their basic sites and their acid sites using the Boëhm titration methods [1]. Materials and chemicals used during experimentations were KERN precision scale, chronometer, glass spatula, iron spatula, ceramic crucible, refractometer, magnetic stirrer, magnetic bar, flask-250ml, heating mantle-250ml, condenser, beaker-100ml, beaker-250ml, beaker-400ml, graduated burette, test tube, separating funnel, thick ash-free filter paper, glass funnel, pipette, mortar, oven, citric acid, pn-black citric acid polymer, pozzolana, used cat-litter, distilled water, HNO3, HCl-1N, HCl-0,1N, HF-0.0026N, NaOH-0.05N, BaCl2-0,5N, helianthine, bromophenol blue, ethanol-90°.

2. Extraction of MSB from a Cat Litter

2.1. Description of the MSB Molecule Extraction Procedure

5.2066 [g] of used cat litter, smelling well the MSB and with a mass of, was taken and placed in a 100[ml] beaker. Then add 37 [ml] ethanol and cover tightly with a lid. Leave the extraction system on for at least 2 hours, then recover this first extraction and perform a second longer extraction. In this extraction experiment, two times had been taken, 22h38mn and even more 74heures. When each extraction step has been completed, always proceed to the MSB solution extraction step, during which the extraction solution is decanted into a 250[ml] beaker, leaving the litter in the 100[ml] beaker. Finally, an ethanol wash-rinse stage containing at least 4 cycles was carried out on the retained litter to ensure that it was free of all MSB molecules. The refractive index of both the ethanol and the recovered solution is determined using a refractometer. Indeed, from the 4th cycle onwards, the refractive index of the recovered solution is equal to that of the ethanol extraction solution confirming the efficiency of this procedure. Extraction results are presented in the following table 1.

Table 1. Extractions of the cat litter by ethanol-90° results.

N° extraction	1st test	2nd test
Litter weight [g]	5.2066	5.1832
Extractions number	Two (2) extractions	Only one (1) extraction
Ethanol-90° used Volume for each extraction [ml]	37	74
Total rinse-wash volume [ml]	100	50
Total extraction volume [ml]	174	124
Total extraction duration [h]	22h38mn	74
Total wash-rinse stage cycles	4	2
Total volume extracted [ml]	134.5	102
refractive index after 1st extraction	1.3545	1.351
refractive index after 2nd extraction	1.3525	_
Refractive index wash-rinse solvent	1.351	1.350
Refractive index after wash-rinse	1.351	1.350
MSB molecules Mass concentration per total extraction volume [$\mu mol.g^{-1}.ml^{-1}$]	2.1	2.2
MSB molecules Mass concentration per total extraction volume per hour [$\mu mol.g^{-1}.ml^{-1}.h^{-1}$]	9.2784E-2	2.9730E-2

2.2. Discussions of the Extraction Results in the Table 1

The results of this table 1 and the following figure 1 and Figure 2 show that:

1. The refractive index after the first extraction is always higher than the refractive index of the solvent ethanol-90°, confirming the efficiency of the solvent ethanol for the extraction of the cat pee molecule.
2. The single extraction procedure with a longer extraction time is more efficient than the double extraction procedure, since the mass concentration of MSB molecules per total extraction volume with the double extraction is higher - 2.2/2.1 (Table 1). However, with the addition of the time parameter in the determination of the mass concentration, the double extraction procedure is largely more efficient than the single extraction procedure - 9.2784E-2/2.9730E-2, with an estimated mass extraction rate of 24.78%.
3. The wash-rinse step with ethanol-90° is effective because only after two cycles, or a maximum of four cycles, is the litter washed of its MSB molecules.
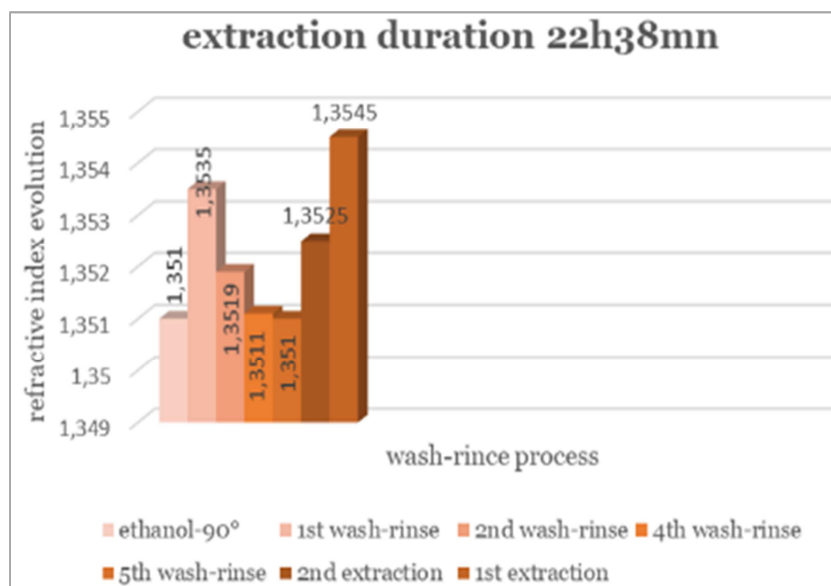
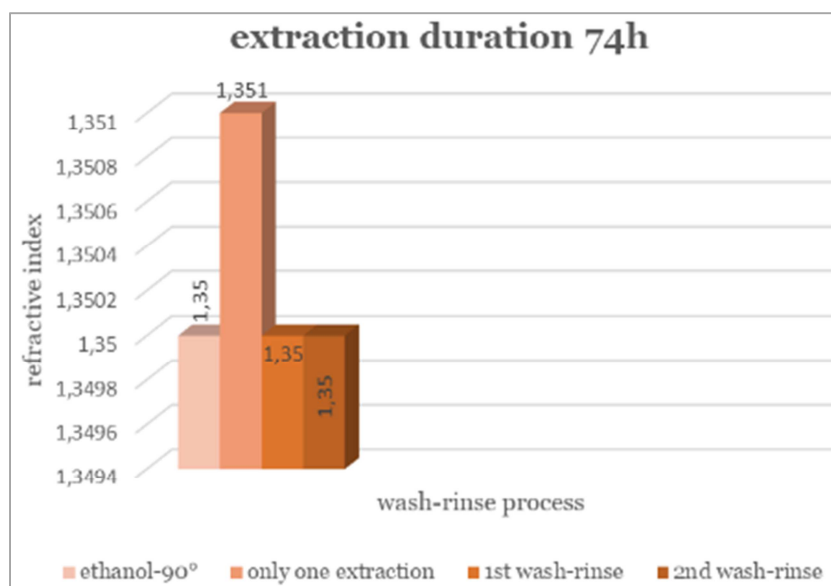**Figure 1.** *Refractive index evolution for the two-2 extractions.*

Figure 2. *Refractive index evolution for the only one-1 extraction.*

3. Determination of the Extracted Solution's MSB Concentration by Gravimetric Method

The MSB molecule content of the extracted solution was directly deduced from its sulfur content [1]. Thus, 5ml of MSB solution was taken as a sample and then attacked hot (50°C to 60°C) in a beaker with 5ml HNO_3, the whole being stirred continuously for at least an hour with a glass spatula. After a few minutes of HNO_3 attack, a clear release of dark-brown nitrogen dioxide – NO_2 appears, confirming the effectiveness of the attack with the formation of H_2SO_4 dissolved in the solution. After one hour, let everything cool down and add 10ml HCl-1N, 30ml distilled water and bring the solution to near boiling point, then add first drop by drop then all at once 20ml $BaCl_2$-0.5N to proceed with the sulfate precipitation. Heat for a few minutes, then cool and rest in a desiccator for 24 hours to complete the precipitation. White sulfate precipitates settled to the bottom of the beaker, then recovered by filtration through thick ash-free filter paper on a glass funnel. Rinse the beaker thoroughly to recover all precipitates. The final step is calcination. Transfer the filter and its contents to a tared ceramic crucible (m_1); dry the assembly at 75°C for a maximum of one hour, then place in an oven programmed to gradually raise the temperature to 900°C, and leave at this temperature for 30 minutes. Let cool gradually and weigh (m_2). Deduce the number of moles of sulfur in the sample-S such as:

$$S = (m_2 - m_1) \times \frac{0,416}{96} \qquad (1)$$

Two extractions had been carried out (cf. §2) on the same litter under the same experimental conditions, but only the second extraction had been carried out 29 days after the first.

As a result, two MSB molecule extracts (cf. §2) were made, and the results of their sulfur content, and consequently their MSB molecule content, are given in the following table 2:

***Table 2.** Extracts MSB concentrations rate results.*

N° extraction	1st test	2nd test
Litter weight [g]	5.2066	5.1832
Total extraction volume during the titration [ml]	134,5	102
Sample volume [ml]	5	5
sample carrier weight [g]	210.3086	210.3558
sample carrier weight and sulfates [g]	210.3253	210.3721
sulfates weight [g]	0.0167	0.0163
Sample sulfates quantities [moles]	7.2367E-5	7.0633E-5
Extracts sulfates quantities [moles]	1.9105E-3	1.4409E-3
Extracts MSB molecules quantities [moles]	1.9105E-3	1.4409E-3
Extracts MSB molecules concentration [moles/l]	14.2045E-3	14.1265E-3
Litter MSB molecules weight concentration [moles/g]	3.6693E-4	2.7799E-4

The weight concentration of MSB molecules showed a difference of 8.894E-5 [mol/g], i.e. a decrease of 24.24%. Seeing as the second extraction was carried out on the same litter but only after 29 days compared to the first extraction, the 24.24% decrease can be explained by the evaporation of MSB molecules and water. Indeed, the water content of the litter was evaluated at 15.45% and it had been noted that the odor of the MSB molecule on the used litter was still very strong in the second extraction.
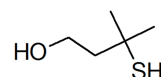
4. Esterification-Addition Reaction Between MSB and Citric Acid Molecules

4.1. Description of These Reactions

The MSB molecule responsible for the characteristic odor of cat urine is a thiol with an alcohol function (Fgure 3).

***Figure 3.** The molecule - 3-methyl-3-sulfanylbutan-1-ol (MSB).*

As a result, an addition reaction can take place not only between the carboxylic acid functions of the citric acid molecule and the sulfur of the MSB molecule, but also between these citric acids' carboxylic acid functions and the alcohol functions of either the MSB or either the reactant citric acid. In all cases, previous studies [2-8] have shown that these addition reactions require H^+ protons as catalysts. In fact, the H^+ proton activates an alcohol function into an oxonium ion intermediate, which is immediately converted into a carbocation after dehydration, a highly reactive carbocation reacting with the basic form of a carboxylic acid function of another citric acid molecule, leading to the formation of an ester and the regeneration of an H^+ proton at the acidic catalytic site (Figure 4).
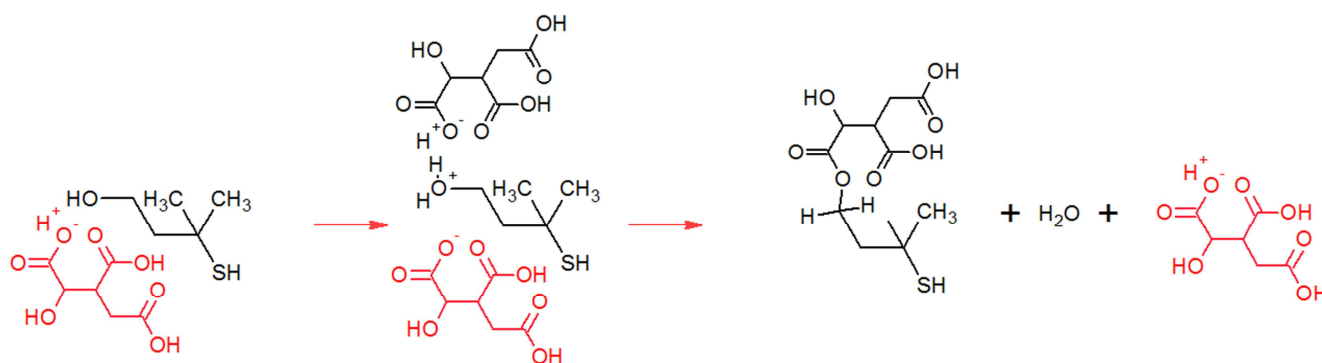
***Figure 4.** The esterification between the MSB alcohol function and the citric acid molecules catalyzed by their own protonic acids.*

On the other hand, the H^+ proton can also activate a hydroxide of a carboxylic acid function of citric acid in its acidic form to form an oxonium ion intermediate which is immediately transformed into a highly reactive carbocation on which not only the basic form of a carboxylic acid

function of another citric acid molecule is added, leading to the formation of an ester and regeneration of an acidic catalytic site H^+ proton, but also the electronic doublets of the sulfur molecules (figure 5).
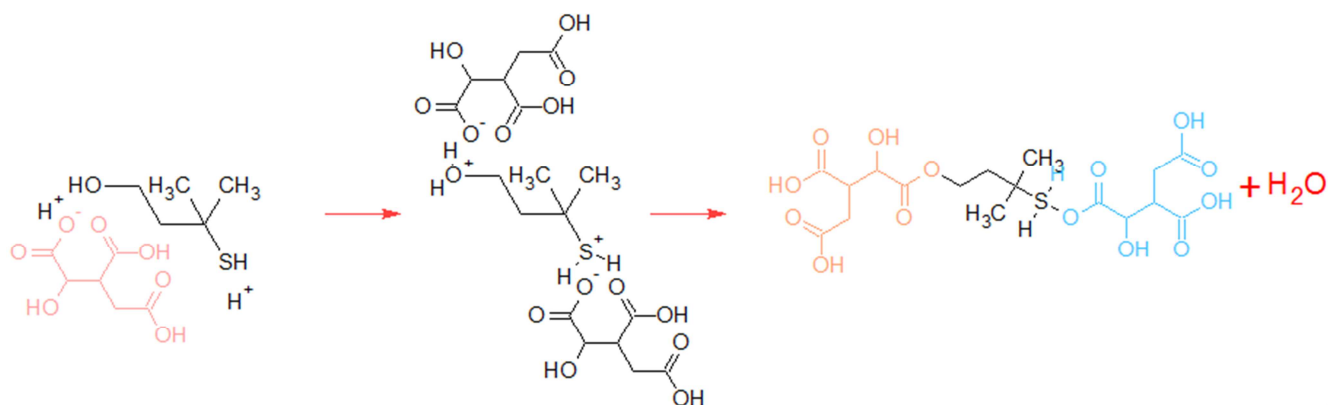
Figure 5. The esterification between the MSB thiol function and the citric acid molecules catalyzed by their own protonic acids.
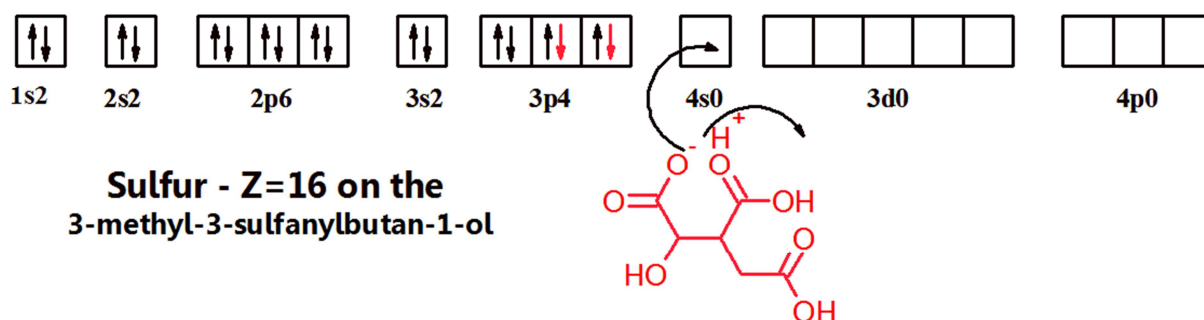

Figure 6. The sulfur vacant cases and their bonds with the citric acid molecules on the 3-methyl-3-sulfanylbutan-1-ol.

Sulfur is a third-period atom in group VIA. So, like oxygen, it has two electron doublets, and after 3spd hybridization, vacant cells are also present in the 3d cells (Lewis acid sites), in which electron doublets from the oxygens of the carboxylic acid in its basic form are added to give citric acid sulfur esters accompanied by regeneration of protons-H^+ (figure 5). This is the case, for example, with deca-di-fluoride (SF10) or tetra-fluoride (SF4). This doesn't exclude the formation of only two bonds (I1) and (I2) towards a stable electronic configuration of neon 10[Ne] and argon 18[Ar]. But this model did not take into account the bond explained in the previous sentence and would be incomplete. This led to the model in the figure 6 and figure 5 which would lead to an extreme model towards a stable configuration of krypton 36[Kr].

4.2. Citric Acid Esterification of the MSB Solution

The citric acid was weighed, and the volume of extracted MSB solution required for the planned reaction was measured with a test tube. Take the MSB solution in a 250ml flask and bring the reaction volume to 200ml by adding the necessary volume of distilled water in which was dissolved in the same time the citric acid. The heating mantle is heated between 141°C and 159°C. When everything is ready and stabilized, including the pipette for taking the 1ml sample, put the flask into the heating mantle and put also the condenser on top of the flask. Start timing and 1ml samples are taken after 1mn, 3mn, 5mn, 10mn, 15mn, 30mn, 60mn of reaction and stored in small hermetically sealed glass containers with lids until their titrations. The following table 3 shows the experimental conditions of this test:

Table 3. Experimental conditions of the MSB esterification with citric acid.

Citric acid weight [g]	0.0856
Citric acid quantities [mol]	4.4555E-4
Citric acid concentration [mol/l]	2.7E-3
Ethanol 90° volume [ml]	31
Distillated water volume [ml]	169
Pure Ethanol volume [ml]	27.9
v/v (water-Ethanol)	6.17
n/n (water-Ethanol)	353.7
n/n (Ethanol-citric acid)	1072.39
n (MSB)	4.4867E-4
n/n (MSB-citric acid)	1.007

4.3. Protocol and Assay Procedure for Quantifying Citric Acid Molecules Non-Reacting with Sulfur

Place 30ml of distilled water into a beaker- 250ml and heat the assembly on a flask heater at temperature between 159°C and 200°C. Add the 1ml sample to be titrated and hydrolyze for 5 min to break the sulfur-free citric acid ester bonds formed. After 5 minutes of hydrolysis, cool the sample to be titrated in the beaker to room temperature, then add 3 drops of helianthine and proceed to the titration with a NaOH-0.05N titrant solution. Thus, during this hydrolysis, citric acid and eventually ethanol esters formed during esterification between citric acid molecules were hydrolyzed. Also, citric acid esters of the MSB alcohol function were the hydrolyzed. However, the hydrolysis of the sulfur esters

formed by addition between the citric acid hydroxide functions and the MSB sulfur would be excluded, due to the dative nature of these bonds with sulfur and their stability in the molecules formed (figure 5, figure 6).

4.4. Experimental Results for the Esterification-Addition Between the MSB and Citric Acid Molecules

Dosing MSB extracts at different reaction times enabled us to draw up the following table 4 and figure 7 showing the evolution of the citric acid content of the reaction medium, and then to deduce the various initial kinetic parameters according to the proposed reaction mechanisms. In all cases, an evaluation of the kinetic parameters based on the expression of the overall rate of this esterification-addition reaction between the MSB molecule and citric acid was made from these experimental results.
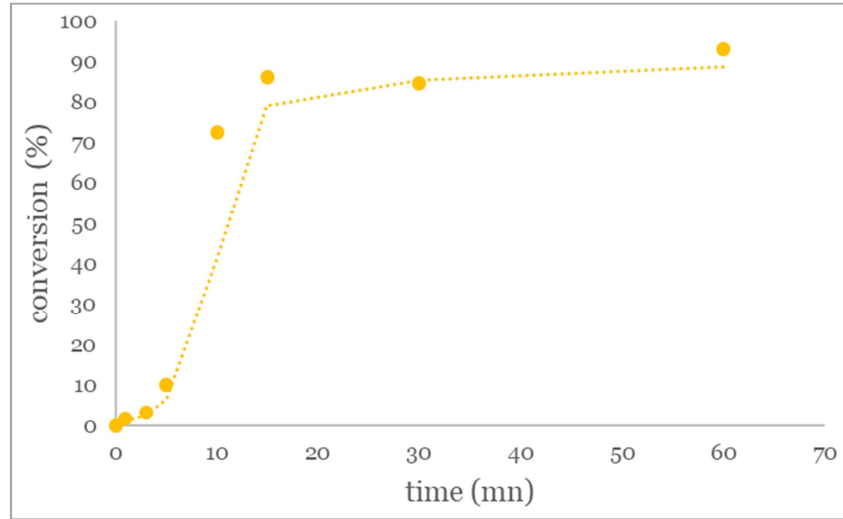

Figure 7. *The evolution of the citric acid conversion with the reaction time.*

Table 4. *Experimental results of the MSB esterification with citric acid.*

Reaction time [mn]	1	3	5	10	15	30	60
nH^+ (moles)	3.55E-6	3.5E-6	3.25E-6	1E-6	5E-7	5E-7	2.5E-7
nAc (moles)	4.3720E-4	4.3105E-4	4.0026E-4	1.2316E-4	6.1578E-5	6.842E-5	3.0789E-5
X-global citric acid conversion (%)	1.87	3.25	10.16	72.36	86.18	84.64	93.09
$[H^+]$ (mol/l)	2.1515E-5	2.1212E-5	1.9697E-5	6.0606E-6	3.0303E-6	3.0303E-6	1.5152E-6

Noted that:
1. During the experimentation under this closed reflux system, the reaction volume is assumed to be constant and equal to 165ml.
2. The reaction speed is equal to

$$v(reaction) = \frac{-1}{(V \times v_i)} \times \frac{d[C_i]}{dt} \tag{2}$$

3. The initial calculated pH is equal to 3.0877 so the initial H^+ concentration is equal to 8.1715×10^{-4} [mol/l].

4.4.1. Evaluation of Overall Kinetic Parameters for a Model Reaction Between Three Moles of Citric Acid and One MSB Mole

The reaction speed is equal to:

$$v(reaction) = \frac{-1}{(V \times v_i)} \times \frac{d[C_i]}{dt} = k \times [ethanol]^a \times [citric\ acid]^\alpha \times [MSB]^\beta \times [H^+]^\omega \tag{3}$$

However, during this manipulation the ethanol content is in excess, so the reaction speed can be written as follows

$$v(reaction) = \frac{-1}{(V \times v_i)} \times \frac{d[C_i]}{dt} = k_{see} \times [citric\ acid]^\alpha \times [MSB]^\beta \times [H^+]^\omega \tag{4}$$

For the evaluation of the speed constants, in this first case it was assumed that three citric acid molecules are attached to the sulfur of the MSB molecule, so as to have the complete model involving the formation of the stable configuration of the noble gas neon from two citric acid molecules plus one citric acid molecule which contributes a dative bond to the vacant sulfur squares. Thus, the overall reaction of this studied reaction can be written:

$$3 citric\ acid + 1 MSB \rightarrow 1 product \tag{5}$$
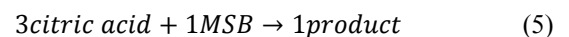
From this reaction, it could be deduced the Table 5 showing the MSB molecule advancement and the corresponding reaction speeds for this overall reaction above.

Table 5. Reaction advancement and speed evolution for this model reaction Equation-(5).

reaction time [mn]	1	3	5	10	15	30	60
n MSB(moles)	3.0294E-4	3.0499E-4	3.1525E-4	4.0762E-4	4.2815E-4	4.2587E-4	4.3841E-4
[MSB] (mol/l)	1.836E-3	1.8484E-3	1.9106E-3	2.4704E-3	2.5948E-3	2.5810E-3	2.6570E-3
[H^+] (mol/l)	2.1515E-5	2.1212E-5	1.9697E-5	6.0606E-6	3.0303E-6	3.0303E-6	1.5152E-6
[citric acid]	2.65E-03	2.61E-03	2.43E-03	7.46E-04	3.73E-04	3.20E-04	1.87E-04
Reaction speed (mol.l^{-4}.s^{-1}]	1.70391E-06	6.2749E-07	3.1415E-06	1.1309E-05	2.5133E-06	1.1894E-07	1.4996E-07

Application of the neperian logarithm function over the equation-(4) and considering the values of the entities' concentrations over the first four instants in Table 5, an equation system with four unknowns is established. Solving this equation system yielded results from which the values of the four kinetic parameters α, β, ω and k_{see} are deduced and evaluated with proportionality. These values are presented in the following table 6.

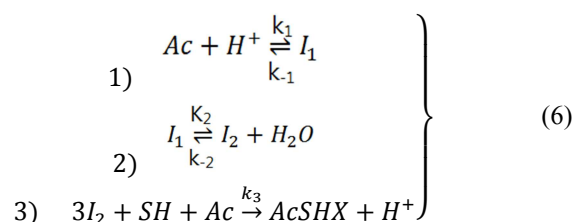*Table 6. Evaluated values of the kinetic parameters for the equation-(4) §.4.4.1.*

α	β	ω	k_{see}
-0.032	+2	+0.539	2.62E+348

4.4.2. Proposed Mechanisms for This Addition-Esterification Reaction between Citric Acid (3 Moles) and the MSB Molecule (one Mole)

Applying quasi-steady-state theory to the reactive intermediates, and considering only the initial points for which the concentrations of I_2 intermediates and reaction products are assumed to be negligible on the mechanism (6), the following equation - (7) is deduced:

$$\left.\begin{array}{l} 1)\quad Ac + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \\[2ex] 2)\quad I_1 \underset{k_{-2}}{\overset{K_2}{\rightleftharpoons}} I_2 + H_2O \\[2ex] 3)\quad 3I_2 + SH + Ac \overset{k_3}{\rightarrow} AcSHX + H^+ \end{array}\right\} \quad (6)$$

$$v = (k_1 \times [Ac]^3 \times [H^+]^3) - k_{-1} \times ([Ac]_0 - [Ac])^3 \quad (7)$$

After linearization, the following equation-(8) is deduced;

$$\frac{v}{([Ac]_0 - [Ac])^3} = k_1 \times \frac{([Ac] \times [H^+])^3}{([Ac]_0 - [Ac])^3} - k_{-1} \quad (8)$$

Based on the above experimental results, the following table 7 and figure 8 are drawn up.

Table 7. Values table of the equation-(8) deduced from experimental results Table 5.

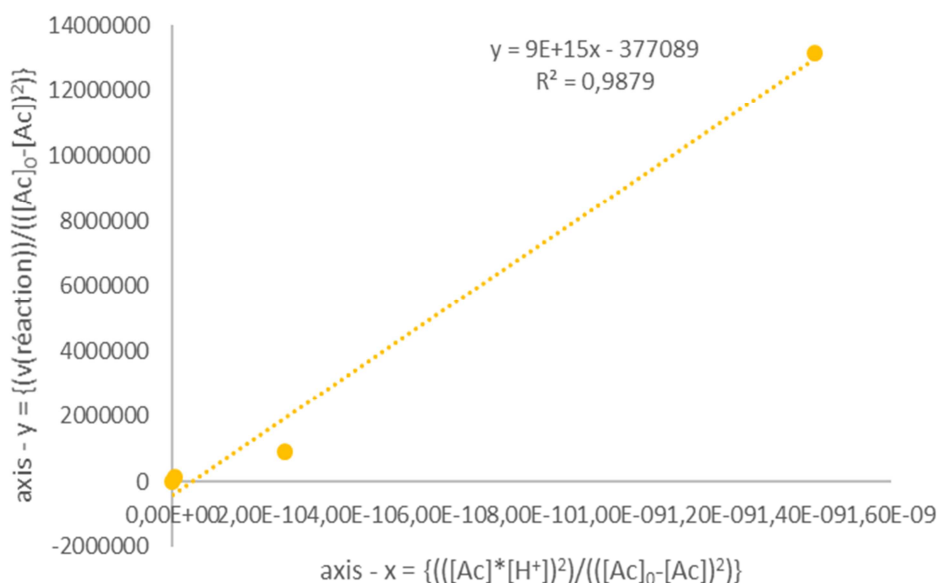| Axis - x $\{(([Ac]*[H^+])^3)/(([Ac]_0-[Ac])^3)\}$	1.4296E-09	2.5074E-10	5.2750E-12	1.2411E-17
Axis - y $\{(v(réaction))/(([Ac]_0-[Ac])^3)\}$	13147357.98	924597.1545	151909.233	1516.11894
k_1	9.00E+15			
k_{-1}	377089			

Figure 8. Curve corresponding to the values on table 7.

4.4.3. Evaluation of Overall Kinetic Parameters for a Model Reaction Between Two Moles of Citric Acid and One MSB Mole (Stable Neon)

In this case, for the evaluation of the rate constants it was assumed that two citric acid molecules are attached to the sulfur of the MSB molecule, to get the complete model involving the formation of the stable configuration of the noble gas neon from two citric acid molecules. Thus, the overall reaction can be written as follows in the equation-(9).

$$2 citric\ acid + 1MSB \rightarrow 1product \qquad (9)$$
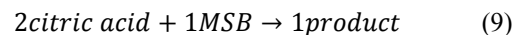
From this reaction, it could be deduced the Table 8 showing the MSB molecule advancement and the corresponding reaction speeds for this overall reaction above.

Table 8. Reaction advancement and speed evolution for this model reaction (Equation-(9).

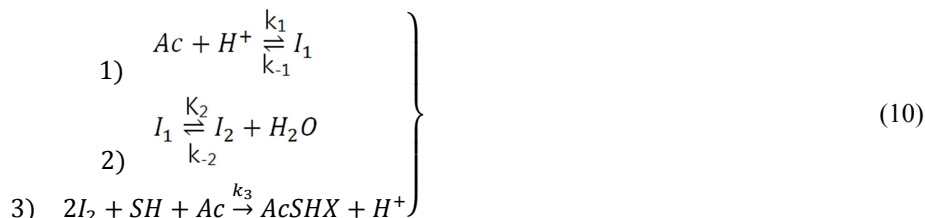| reaction time [mn]	1	3	5	10	15	30	60
n MSB(moles)	2.30E-04	2.33E-04	2.49E-04	3.87E-04	4.18E-04	4.22E-04	4.33E-04
[MSB] (mol/l)	1.39E-03	1.41E-03	1.51E-03	2.35E-03	2.53E-03	2.56E-03	2.63E-03
[H+] (mol/l)	2.1515E-5	2.12E-5	1.97E-5	6.06E-6	3.03E-6	3.03E-6	1.51E-6
[citric acid]	2.65E-03	2.61E-03	2.43E-03	7.46E-04	3.73E-04	3.20E-04	1.87E-04
Reaction speed	2.56E-06	9.41E-07	4.71E-06	1.70E-05	3.77E-06	1.78E-07	2.24E-07

Application of the neperian logarithm function over the equation-(4) and considering the values of the entities' concentrations over the first four instants in Table 8, an equation system with four unknowns is established. Solving this equation system yielded results from which the values of the four kinetic parameters α, β, ω and k_{see} are deduced and evaluated with proportionality. These values are presented in the following table 9.

Table 9. Evaluated values of the kinetic parameters for the equation-(4) §4.4.3.

α	β	ω	k_{see}
+1,98	-0.0404	-2	3.22E-1597

4.4.4. Proposed Reaction Mechanisms for This Addition-Esterification Reaction Between Citric Acid (2 Moles) and a MSB (One Mole)

$$
\left.
\begin{aligned}
&1) \quad Ac + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \\
&2) \quad I_1 \underset{k_{-2}}{\overset{K_2}{\rightleftharpoons}} I_2 + H_2O \\
&3) \quad 2I_2 + SH + Ac \overset{k_3}{\rightarrow} AcSHX + H^+
\end{aligned}
\right\} \qquad (10)
$$

Applying quasi-steady-state theory to the reactive intermediates, and considering only the initial points for which the concentrations of I_2 intermediates and reaction products are assumed to be negligible on the mechanism (10), the following equation – (11) is deduced:

$$v = (k_1 \times [Ac]^2 \times [H^+]^2) - k_{-1} \times ([Ac]_0 - [Ac])^2 \qquad (11)$$

After linearization, the following equation-(12) is deduced;

$$\frac{v}{([Ac]_0 - [Ac])^2} = k_1 \times \frac{([Ac] \times [H^+])^2}{([Ac]_0 - [Ac])^2} - k_{-1} \qquad (12)$$

Based on the above experimental results, the following table 10 and figure 9 are drawn up.

Table 10. Values table of the equation-(12) deduced from experimental results Table 8.

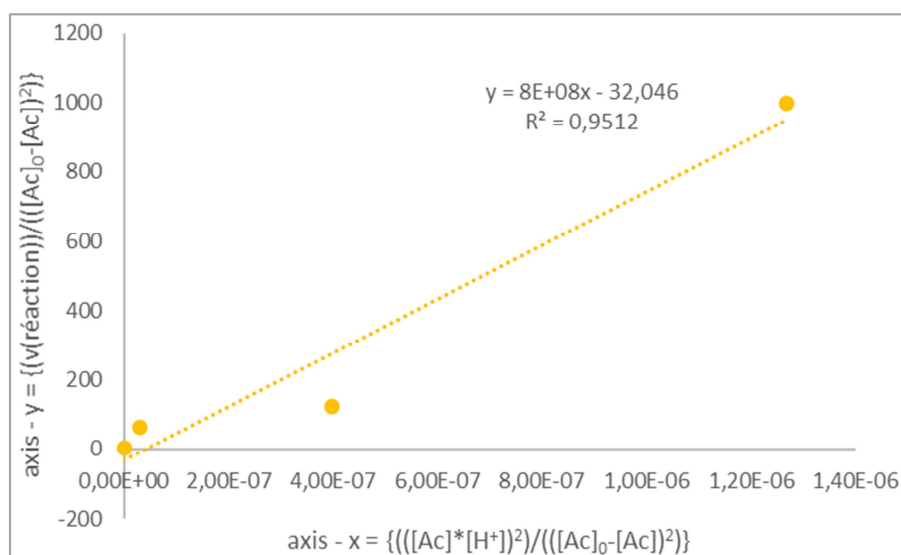| Axis - x $\{(([Ac]*[H^+])^2)/(([Ac]_0-[Ac])^2)\}$	1.26902E-06	3.97633E-07	3.0303E-08	5.3605E-12
Axis - y $\{(v(réaction))/(([Ac]_0-[Ac])^2)\}$	998.003992	121.8787158	62.5451741	4.44346896
k_1	8E+8			
k_{-1}	32.046			

Figure 9. *Curve corresponding to the values on table 10.*

4.4.5. Evaluation of Overall Kinetic Parameters for a Model Reaction Between Eleven Moles of Citric Acid and One MSB Mole

In this case, for the evaluation of the rate constants it was assumed that eleven citric acid molecules are attached to the sulfur of the MSB molecule, to get the complete model involving the formation of the stable configuration of the noble gas krypton from eleven citric acid molecules. Thus, the overall reaction can be written as follows in the equation (13).

$$11\,citric\ acid + 1MSB \rightarrow 1product \qquad (13)$$
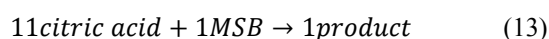
From this reaction, it could be deduced the Table 10 showing the MSB molecule advancement and the corresponding reaction speeds for this overall reaction above.

Table 11. *Reaction advancement and speed evolution for this model reaction Equation-(13).*

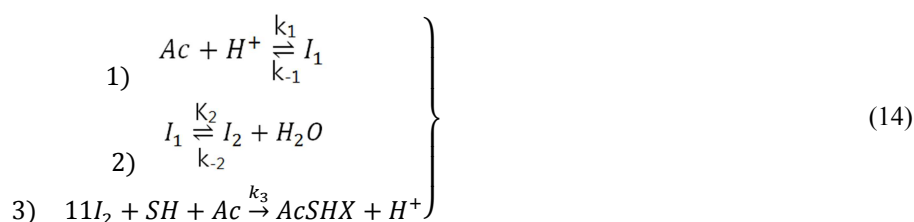| reaction time [mn]	1	3	5	10	15	30	60
n MSB(moles)	4.09E-04	4.09E-04	4.12E-04	4.37E-04	4.43E-04	4.44E-04	4.46E-04
[MSB] (mol/l)	2.48E-03	2.48E-03	2.50E-03	2.65E-03	2.69E-03	2.69E-03	2.70E-03
[H+] (mol/l)	2.15E-05	2.12E-05	1.97E-05	6.06E-06	3.03E-06	3.03E-06	1.52E-06
[citric acid]	2.65E-03	2.61E-03	2.43E-03	7.46E-04	3.73E-04	3.20E-04	1.87E-04
Reaction speed	4.65E-07	1.71E-07	8.57E-07	3.08E-06	6.85E-07	3.24E-08	4.09E-08

Application of the neperian logarithm function over the equation-(4) and considering the values of the entities' concentrations over the first four instants in Table 11, an equation system with four unknowns is established. Solving this equation system yielded results from which the values of the four kinetic parameters α, β, ω and k_{see} are deduced and evaluated with proportionality. These values are presented in the following table 12.

Table 12. *Evaluated values of the kinetic parameters for the equation 4 §4.4.5.*

α	β	ω	k_{see}
+2,38	-0,125	-2,4	1.84E-1872

4.4.6. Proposed Reaction Mechanisms for This Addition-Esterification Reaction Between Citric Acid (11 Moles) and a MSB Molecule

$$
\left.
\begin{aligned}
&1)\quad Ac + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \\[1em]
&2)\quad I_1 \underset{k_{-2}}{\overset{K_2}{\rightleftharpoons}} I_2 + H_2O \\[1em]
&3)\quad 11I_2 + SH + Ac \overset{k_3}{\rightarrow} AcSHX + H^+
\end{aligned}
\right\} \qquad (14)
$$

Applying quasi-steady-state theory to the reactive intermediates, and considering only the initial points for which the

concentrations of I2 intermediates and reaction products are assumed to be negligible on the mechanism (14), the following equation – (15) is deduced:

$$v = (k_1 \times [Ac]^{11} \times [H^+]^2) - k_{-1} \times ([Ac]_0 - [Ac])^{11} \tag{15}$$

Based on the above experimental results, the following table 13 and figure 10 are drawn up.

Table 13. *Values table of the equation-(15) deduced from experimental results Table 11.*

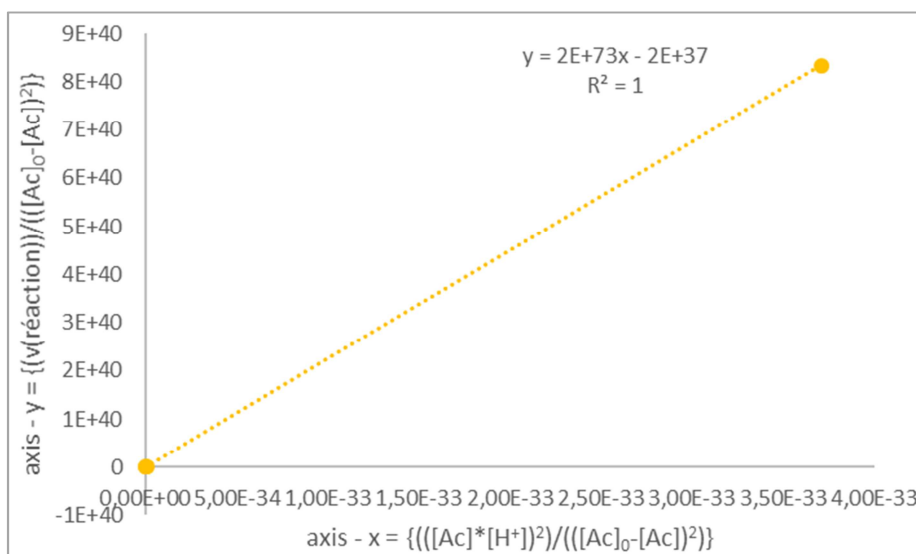| Axis - x $\{(([Ac]*[H^+])^{11})/(([Ac]_0-[Ac])^{11})\}$	3.71E-33		6.27E-36	4.45E-42	1.02E-62
Axis - y $\{(v(réaction))/(([Ac]_0-[Ac])^{11})\}$	8.34E+40		7.09E+37	1.29E+33	1.95E+24
k_1		2E+73			
k_{-1}		2E+37			

Figure 10. *Curve corresponding to the values on table 13.*

5. Synthesis of the Catalysts-Litter pn-Pozzolana-Citric Acid (PPCA)

The aim of this paragraph is to synthesize catalysts-litter pn-pozzolana-citric (PPCA) from the pn-pozzolana, which was synthesized and characterized according to the procedure described by the bibliography [9]. Thus, this synthesis followed three steps: the first step was the synthesis of the citric acid black polymer (pn) [10-12], the second step was the pn-pozzolana synthesis [11], and the third step was to deposit the citric acid molecules on the pn-pozzolana among the active sites by using two solvent water and ethanol.

5.1. The Synthesis and the Characterization of the Pn-Pozzolana

The pn-pozzolana synthesis and characterizations was done according to the procedure described on the bibliography [9] and the results were shown in the following table 14.

Table 14. *pn-pozzolana synthesis steps and characteristics.*

TREATMENTS	RESULTS
weighing of raw materials used	
Pozzolana size [μm]	< 0.25 [μm]
Pn - weight [g]	7.7770
alkene-equivalent content of pn [moles/g]	5.0649E-4
Pozzolana - weight [g]	2.1675
Water volume [ml]	18
drying and removal of water molecules from pozzolana	
Oven temperature speed	15°C/mn from ambient to 250°C
Drying-removal temperature [°C]	250
Drying-removal time [mn]	120
solubilisation of pn in water	
Water bath temperature [°C]	45
duration [mn]	120
pn-pozzolana synthesis	

TREATMENTS	RESULTS
Water bath temperature [°C]	95
duration	Until paste-dry mixture
Drying of the pn-pozzolana	
Oven temperature speed	3°C/mn from ambient to 75°C
Drying temperature [°C]	75
Duration [mn]	More than 60
Synthesized pn-pozzolana characteristics	
Synthesized pn-pozzolana weight [g]	9,6728
More accessible pn-equivalent on surface [%]	7,84
Pn-equivalent in structure and porosity [%]	92,16
Alkene equivalente concentration of the pn-pozzolana [molesC$^=$/g]	3,0194E-4

During this first synthesis, the pozzolana used is pulverous with a size less than 0.25 [µm]. It had been noticed that after the pn-pozzolana synthesis-mixing, the black citric acid polymers agglomerate around the pozzolana creating well-ordered structures until porous grains.

5.2. Catalyst-Litter pn-Pozzolana-Citric-Acid PPCA Synthesis by Citric Acid Dispersion-Deposition on the pn-Pozzolana

The dispersion-deposition of the citric acid molecules on the pn-pozzolana was done under two methods which differs by the used solvent water or ethanol-90°. The citric acid quantities-moles used during the PPCA synthesis was determined in such a way the moles ratio between the ethanol and the citric acid during the citric acid and the MSB molecules esterification-addition was retained and equals to 1072.39. Thus, the moles ratio between the pn-equivalent of the pn-pozzolana and the citric acid was equal to 76.5995. For the water quantities determination, the moles-ration between the distilled water and pn-equivalent was equals to

200 [9]. When the citric acid, distilled water and ethanol quantities were determined, the first step was to dissolve the citric acid in the used solvent (distilled water or ethanol-90°) according to the method selected. Do a water bath using a beaker 400ml, an assembly like the pn-pozzolana synthesis [9] such as the temperature was stabilized in the vicinity of 45°C in order not only to dehydrate and to evaporate the used solvents distilled water or ethanol but also to limit the citric acid polymers transformations. But, at the end of this first step the water bath temperature could be increased at 95°C (for the distilled water solvent) and at 84°C (for the ethanol solvent) in order to eliminate as far as possible the solvent without catching fire. The second step consisted to dry the synthesized PPCA-catalyst-litter in an oven at 75°C during 1hour minimum. Once dried, recover and weight the synthesized PPCA and proceed on their characterizations by the Boëhm titration to determine their acid and basic sites as described on the bibliography [13]. The results of these PPCA synthesis were shown in the following table 15.

Table 15. Catalyst-litter pn-pozzolana-citric acid PPCA synthesis.

Catalyst-litter pn-pozzolana-citric acid PPCA synthesis procedure and characterizations		
	SOLVENT-DISTILLATED WATER	SOLVENT-ETHANOL-90°
pn-pozzolana weight [g]	4.8116	4.5505
pn-equivalent weight [g]	3.8590	3.6496
pn-equivalent [moles]	2.4572E-3	2.3239E-3
Citric acid weight [g]	0.0063	0.0058
Citric acid [moles]	3.2791E-5	3.0189E-5
Solvent volume [ml]	8.8	27.12
Solvent quantities [moles]	488.89E-3	278.676E-3
$\frac{n_{pn}}{n_{Acide\ citrique}}$	74.94	76.98
$\frac{n_{ethanol}}{n_{Acide\ citrique}}$	-	9231.0444
$\frac{n_{eau}}{n_{Acide\ citrique}}$	14909.2739	19963,1321
$\frac{n_{eau}}{n_{pn}}$	198.9622	259.3343
$\frac{n_{ethanol}}{n_{pn}}$	-	119.9174
Initial-first dehydration evaporation temperature [°C]	45	
Final-second drying temperature [°C]	95	84
Oven drying temperature [°C]	75	
Catalyst-litter pn-pozzolana-citric acid PPCA synthesized characteristics		
Acid sites concentrations [moles/g]	5.7397E-3	3.4286E-3
Basic sites concentrations [moles/g]	3.3186E-3	1.0449E-3
Total sites concentrations [moles/g]	9.0583E-3	4.4735E-3
Alkene-equivalent concentrations [molesC$^=$/g]	5.2403E-4 (3.3256E-4)*	6.0873E-4 (3.4048E-4)*

* Values determined at the start of the color turning point into yellow transparent during HF-0,0026N titration [14, 15]

Noticed that these values (*) were in the vicinity of the corresponding pn-equivalent contents of the pn-pozzolana on

the table 14. The differences noticed on the start of the color turning point into yellow transparent values (*) and the final color titration transparent yellow could be assigned to the formation of additional alkenes sites either from the pn-pozzolana either from the citric acid molecules [14, 15].

6. Conclusion

The MSB - 3-Methyl-3-Sulfanylbutan-1-Ol molecule could be extracted from the cat-litter by the solvent ethanol. It was established that without considering the duration of the extraction the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol molecules mass concentration per total extraction volume was more important with the only one-long time extraction procedure (2,2 [$\mu mol.g^{-1}.ml^{-1}$]) than the two-short extraction procedure (2,2 [$\mu mol.g^{-1}.ml^{-1}$]). But, with considering the total duration of the extraction-time it was without doubt that the two-short extraction test was very efficiency 9.2784E-2 [$\mu mol.g^{-1}.ml^{-1}.h^{-1}$] against 2.9730E-2 [$\mu mol.g^{-1}.ml^{-1}.h^{-1}$] for the other test. Then, the kinetic study of the esterification-addition between the citric acid molecules and the MSB - 3-Methyl-3-Sulfanylbutan-1-Ols molecules indicated that the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol sulfur atom vacancy cases play an important role during this reaction. It was noticed that the concentration of citric acid increased the speed reaction and allowed to the formation of a stable sulfur+citricacid product consequently the protonic acid H^+ became a poison leading to the formation of carboxylic acid citric acid instead of sulfur+citricacid product. Indeed, the partial order of the protonic acid H^+ was all the time negative and in all mechanism model their concentration evolve uniformly with their conversion on time reaction recorded during the experimentation esterification-addition. After, analyzing the partial orders and the initial kinetic constants (k_1 and k_{-1}), the more probable mechanism was the mechanism of the model reaction between three moles of citric acid and one mole of MSB - 3-Methyl-3-Sulfanylbutan-1-Ol followed by the proposed reaction mechanisms addition-esterification reaction between citric acid (2 moles) and the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol molecule (one mole) (stable Neon configuration). The third model reaction confirmed that the protonic acid H^+ could be a poison. These results allowed to the synthesis of the material based on black citric acid polymers (pn), pozzolana and citric acid named PPCA (pn-pozzolana-citric-acid) which characteristics basics and acids sites permitted to deduce its capacity as a cat-litter.

Acknowledgements

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