

Research Article

Kinetic Study of PET Recycling into PAT and Ethanediol by Hydrolysis Catalyzed by Protonic Acid H^+ and Iron-Fe Catalysts

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Abstract

PET - Polyethylene Terephthalate is the main raw material used to manufacture PET - PETE plastic bottles. Since 2015, over 6.9 billion tons of plastic waste have been produced and only round 9% was recycled, 12% was incinerated and 79% accumulated in landfills or in nature. The present study involves recycling PET-based plastic materials into ethanediol and terephthalic acid by hydrolysis using two types of acid catalyst: the protonic H^+ acid sites of citric acid molecules and the Lewis acid sites of Iron-Fe molecules. The set-up used is a reflux system consisting of a 250ml flask placed in the flask heater at a temperature of 144 °C, with a straight cooler above it. Monitoring the progress of the reaction consisted in titrating the quantities of recycled PAT-Pure Terephthalic Acid molecules formed and the unsaturation in solution with HF-0.0026N hydrofluoric acid, then deducing the quantities of ethanediol molecules formed. The results recorded with the first experiment using the protonic acid H^+ sites of citric acid molecules as catalyst were quite conclusive; 3.0762E-03 moles of PAT had been regenerated per gram of initial charge per moles of protonic H^+ sites per minute. An optimization test was carried out, enabling us to estimate the quantities of Iron-Fe used in the three other tests with the Lewis Iron-Fe site catalyst, with Iron-Fe weight percentages of 15wt%, 58.42wt% and 92.65wt% respectively. It had been recorded that PET conversion increases slowly but surely with reaction time and that the amount of recycled PAT increases very strongly with the amount of catalyst used. Thus, the molar quantity of PAT regenerated per gram of initial charge per mole of Iron-Fe and per minute for the three quantities of catalyst mentioned above are respectively 1.1580E-04 (15wt%), 1.7809E-04 (58.42wt%) and 9.0591E-03 (92.65wt%), i.e. an increase at both ends of 7.723.06% compared with the 15wt% value. Kinetic study had been carried out on the test with 58.42wt% Iron-Fe catalyst, enabling not only to the determination of various kinetic constants but also the validation of a proposed reaction mechanism.

Keywords

Polyethylene Terephthalate-PET, Recycling, PAT-Pure Terephthalic Acid, Ethanediol, Reaction Mechanism, Iron-Fe, Citric Acid

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1. Introduction

The first part of this manuscript presents the physico-chemical characteristics of the raw material to be recycled, Polyethylene Terephthalate - PET, and the molecules recycled after hydrolysis, acid PAT-Pure Terephthalic and ethanediol. Next, we describe the experimental conditions for this recycling process, for which two acid catalysts were used, one a protonic Brønsted H^+ acid catalyst from the carboxylic acid functions of citric acid molecules, the other a Lewis Iron-Fe acid catalyst whose weight percentage was varied between 15wt%, 58.42wt% and 92.65wt%. The 58.42wt% Iron-Fe weight content test was kinetically monitored by taking samples and measuring out their recycled PAT, measuring out their unsaturation contents with HF-0.0026N hydrofluoric acid at 1mn, 3mn, 5mn, 15mn, 43mn, 60mn and 90mn. The final section presents the results of the various experiments carried out, followed by the determination of the various kinetic constants and the validation of a proposed mechanism. The equipment used in this study is a reflux set-up consisting of a 250ml flask heated with a flask heater and topped with a straight refrigerant system, a bottle of Malagasy white water from the STAR company, a grinder for grinding PET plastic bottles into powders and grindings with diameters ranging from 1mm to 2.5mm maximum, 250ml beaker, graduated eprouvette, graduated pipette, magnetic stirrer, magnetic rod, PET bottle eau vive Malagasy plastic, citric acid, burette, hydrofluoric acid HF-0.0026N, bromophenol blue indicator, thermometer, pH meter, iron-Fe mesh filament, distilled water.

2. The Polyethylene Terephthalate - PET

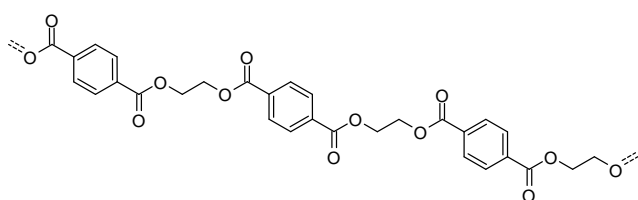


Figure 1. PET figure and its monomer composed of PAT and ethylene glycol combined by oxygen bridge.

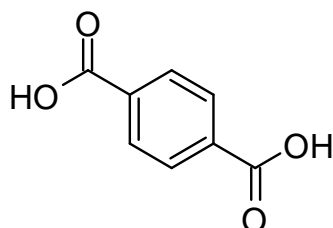


Figure 2. The molecule Pure Terephthalic Acid or benzene-1,4-dicarboxylic acid.

Polyethylene terephthalate, usually referred to PET (Figure 1), is a polymer whose monomer is composed of one mole of PAT, known as Pure Terephthalic Acid (Figure 2), and one mole of ethylene glycol (Figure 3), polymerized at both ends of the monomer's two acid functions.

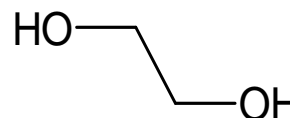


Figure 3. The ethylene glycol or ethane-1,2-diol molecule.

The specifications of the PET are given in the following Table 1:

Table 1. The physico-chemical specifications of the PET [1].

Specifications	Values
Glass-transition temperature	70 °C
Melting point	245 °C
Density	1.34 – 1.39 g/cm ³
Refractive index	1.57 – 1.58

3. The Pure Terephthalic Acid – PAT

3.1. The Specifications of the PAT

PAT is a diacid with a benzene ring, and is the monomer used in the manufacture of PET. It is practically insoluble in water, since it takes about 1 liter of water to dissolve just 17 mg of PAT. In other words, if the water solution is 3 mL, the amount of soluble PAT is 0.051 mg or 51 µg. On the other hand, PAT is soluble in polar solvents and basic solutions. The specifications of the PAT are given in the following table 2:

Table 2. The physico-chemical characteristics of Pure Terephthalic acid -PAT [1].

Specifications	Values
Shapes	White crystals and/or powder
Density	1.519
Specifications	Values
Solubility in water	0.065 [g/l] – 65 mg/l – 3.25

Specifications	Values
	mg/50 ml
pKa	3.54 – 4.34
Molar mass	166.132 g/mol
Melting point	402 °C
Auto-inflammation temperature	496 °C
Flash point	260 °C
Refractive index	1.51

3.2. The PAT Analysis Procedure

PAT molecules and ethane diol molecules must be titrated non-selectively with HF-0.0026N. The process for this determination of PAT and Et-2OH by HF-0.0026N is described and is presented thereafter with a ratio of 7.

Thus,

- (1) place titrant solution HF-0.0026N in the burette
- (2) take 0.1 ml to 0.2 ml of the solution from the reaction medium at the chosen instant V_{ech-t}
- (3) dilute the sample in the 250 ml beaker with 15 ml distilled water
- (4) add 3 to 4 drops of bromophenol blue and shake gently with a magnetic stirrer, solution turns purplish-blue
- (5) start titration with the burette's HF-0.0026N titrant solution
- (6) take the volume of titrant solution when the solution turns transparent-violet at time t note this value $V_{trans-t}$
- (7) continue dosing and take the volume of titrant solution from the burette when the solution turns yellow-yellow-green - note this value $V_{total-t}$ at time t
- (8) in the case that the reaction medium solution contains citric acid and $pH < 2$ under most experimental conditions, almost all three carboxylic acid functions are in the acid form during HF determination. Thus, m_{Ac} is the weight of citric acid used in the test

$$Ac_{moles\ total} = \frac{m_{Ac}}{192,12}$$

$$[Ac_{moles\ total}] = \frac{Ac_{moles\ total}}{V_{solution-t}} \quad (1)$$

This gives the quantity of citric acid in moles in the sample.

$$Ac_{moles\ ech} = [Ac_{moles\ total}] * V_{ech-t} \quad (2)$$

Thus, the quantity of HF reacting with these citric acid molecules in the sample at this $pH < 2$ ($pH = 1.52$) is given by the multiplicative factor evaluated at 0.03846 which corresponds to the acid functions of citric acid which are in non-dissociated basic dissociated acid forms, then

$$H^+_{moles\ Ac-non\ reacting\ ech} = 0.03846 \times Ac_{moles\ ech} \quad (3)$$

The number of moles of PAT in the sample at time t is equal to

$$PAT_{t-ech} - moles = \frac{(V_{total-t} - V_{trans-t}) \times 0,001 \times 0,0026}{7 \times H^+_{moles\ Ac-non\ reacting\ ech}} \quad (4)$$

$$PAT_{t-total} - moles = \frac{(PAT_{t-ech} \times V_{solution-t})}{V_{ech-t}} \quad (5)$$

$$Et_{2OH-total} - moles = PAT_{t-total} - moles \quad (6)$$

$$m_{PAT_{t-total}} = PAT_{t-total} - moles \times 166,132 - g \quad (7)$$

$$m_{Et_{2OH-total}} = Et_{2OH-total} - moles \times 62,07 - g \quad (8)$$

In fact, to fully assay one molecule of PAT and one molecule of Et-2OH, a total of seven-7 molecules of HF are required, so the number of moles of PAT = number of moles of Et-2OH = number of moles of HF divided by seven-7.

And the titration volume from purplish to transparent corresponds to the quantities of alkenes formed during the reaction.

$$C^- - moles\ ech = V_{trans-t} \times 0,001 \times 0,0026 \quad (9)$$

$$C^-_{total} - moles = \frac{(C^- - moles\ ech \times V_{solution-t})}{V_{ech-t}} \quad (10)$$

Taking into account that the molar mass of PAT is 166.132 and that the molar mass of Et-2OH is 62.07 g/mol (with a density of 1.11 g/ml).

Knowing that the total volume of the solution at time t is given by the determination procedure in paragraph §3.1. below and is equal to $V_{(solution-t)}$ then the concentration of PAT and Et-2OH at each time is equal to

$$[PAT_{t-total}] = \frac{PAT_{t-total} - moles}{V_{solution-t}} = [Et_{2OH-total}] \quad (11)$$

4. PET Recycling Process into PAT and Ethane Diol

The recycling procedure adopted in this study is the hydrolysis of PET at high temperature in a reflux assembly using acid catalysts. Two kinds of acid catalysts are used, firstly Brönsted protonic H^+ acid catalysts from the carboxylic acid functions of citric acid molecules, and secondly Lewis acid catalysts from the vacancies of iron-Fe molecules. In the first case, we're in a heterogeneous catalysis situation in which the Brönsted H^+ protonic acid catalysts are in a different liquid phase to the PET recycling reactant, which is in a solid phase. Whereas in the second case, we are in a situation of homogeneous catalysis during which the acid catalysts Lewis va-

cancies of the Iron-Fe molecules is in the same solid phase as the reagent to be recycled PET.

Various experimental conditions were tried out in an attempt to define this PET recycling method, which is based on cracking PET at the oxygen bridges of the PAT monomer by activating them with an acid site catalyst. Two types of catalyst were tested:

1. A H^+ proton source catalyst, in this case citric acid, used as a heterogeneous catalyst.
2. A homogeneous Lewis acid site catalyst, Iron-Fe, in the same solid phase as the PET to be recycled.

In all cases, distilled water was used as solvent.

4.1. Experimental Conditions and Results for the First Test with Protonic H^+ Catalysts of Citric Acid Molecules

Referring to the experimental conditions of the different esterification of plants with citric acid described in the bibliographies [2-9], a relationship had been noticed between the rate constant k and the ratio between the quantities of H^+ and

equivalent alkenes $[H^+/C^-]$.

Thus, the weight of the reactant charge, for which the alkene-equivalent concentration C^- is predetermined had been fixed. Consequently, the quantity of alkenes in the fixed charge was determined. Next, the $[H^+]/[C^-]$ ratio was set to give the optimum-maximum k value, from which the H^+ concentration was determined, the pH of which was evaluated by means of a curve. Then, the evaluation of the mass of citric acid to be used and the corresponding quantity of water to get the chosen pH is calculated using an Excel file. The quantity of H^+ is deduced from the H^+ concentration and the volume of solution to be used.

Take a 250 ml flask and add the distilled water from the experiment, then solubilize the quantity of citric acid in it and top it all off with the right condenser cooling system. Raise the temperature of the flask heater to the desired reaction temperature and then place the whole set-up in the flask heater. Then take the sample volume at each reaction time chosen to study the kinetics of the PET recycling reaction. The experimental conditions for the first test with citric acid H^+ protons are presented in the following Table 3:

Table 3. Experimental conditions for PET recycling with proton catalysts - H^+ from citric acid molecules.

Experimental conditions	Values
Reactor	Reflux assembly (250 ml flask - Flask heater - Straight condenser)
Temperature	144 °C
PET load weight	4.0608 g
Hydrolysis duration [mn]	60
$[C^-]$ – PET	0.019791 mol/g
Ratio $[H^+]/[C^-]$	0.29
Distillated water solvent volume [ml]	200
$[C^-]_{\text{solution}}$ [moles/L]	0.4018
$[H^+]$ [moles/L]	0.1177
pH	3.415
Citric acid weight	0.0261 g
M_{Ac}/M_{PET}	6.4273E-3

The experimental results from this initial experiment are presented in the following Table 4.

Table 4. Experimental results of the first experiment.

Titration HF-0.0026N	Flask reactor – Balloon 250 ml	Duration [mn]	Citric acid weight [g]
Test1 – Protonic acid H^+ - citric acid		60	0.0261
Initial load PET weight [g]	4.0608	Moles H^+ -total	moles Ac – citric acid

Titration HF-0.0026N	Flask reactor – Balloon 250 ml	Duration [mn]	Citric acid weight [g]
		4.08E-04	1.36E-04
Initial volume H ₂ O [ml]	200		moles Ac - Ech
Final volume H ₂ O [ml]	185.66	[H ⁺]	1.36E-06
Echantillon-Ech sample volume [ml]	2	2.04E-03	moles Ac-ech × 0.03846 = H ⁺ non titrated - pH=1.52
[HF] - mol/l ⁻¹	0,0026	colors solutions to be titrated	5.22E-08
color indicator	bromophenol blue	purplish blue	
	4	Transparent	alkenes in solution
Titration volume [ml]	13	yellow-green	C=O; benzene; C-OH/PAT
PAT-sample [moles]	3.29E-06		
PAT regenerated-total [moles]	3.05E-04		
Molar mass PAT [g/mol]	1.66E+02	PET Conversion%	
Total regenerated PAT weight [g]	5.07E-02	1.25%	
PAT regenerated per total load weight [moles/g]	7.52E-05		
PAT regenerated -totalcharges / [moles _{PAT} /g/ molesH ⁺]	1.85E+03		
PAT regenerated per minute -totalcharges / [moles _{PAT} /g/ molesH ⁺ /mn]	3.08E+01		
[Ac]	6.79E-04		
Masse finale-PET [g]	4.01E+00		
[PET] [g/L]	20.304		
[PET] _{final} [g/L]	20.05026065		

The regeneration yield is very low indeed, equal to 0.19 - 1.25% in sixty minutes, i.e. only 7.5223E-05 moles of PAT regenerated per initial total mass of feedstock. However, the turn-over is quite high, i.e. 1.8457E-01 moles of PAT regenerated per initial total mass of feedstock and per moles of H⁺ proton catalysts. These results, and the relationship between the rate constant *k* and the ratio between the quantities of H⁺ and equivalent alkenes [H⁺/C⁻] deduced from the various experiments on esterification with citric acid molecules [2-9] suggest to a further decrease in the [H⁺]/[C⁻] ratio (Table 3) in order to increase the rate constant, bearing in mind that in the previous experimental condition the quantity of protonic H⁺ catalytic acid is much greater than the possible optimization, which perhaps favors trans-esterification between citric acid and PET bridges as the cracking mode of PET. These conditions could favor trans-esterification reaction between citric acid and PET bridges as a means of PET cracking. Thus, an optimization of the experimental condition with

citric acid could take place and this led us to try using the Fe catalyst.

4.2. Experimental Conditions and Results of Tests with Lewis Acid Sites of Pure Iron-Fe Atoms

The experimental conditions and results of tests with Lewis acid sites of pure Iron-Fe molecules are presented in the following Table 5. It had been experimented and deduced that divided iron particles proved to be less efficient than irons organized in mesh form for PET recycling. In the following experiments, filamentary irons-Fe organized in mesh form are placed in the reflux reactor so as to overhang the PET to be recycled, thus promoting the collisions between the solid reactant-PET and the solid catalyst-Iron-Fe.

Table 5. The experimental conditions of the experiments carried out.

	Fe-15%	Fe – 58.42%	Fe – 92.65%
Initial weight of the PET load [g]	3.9403	3.68	0.0216
Catalyst weight Iron-Fe [g]	0.6956	5.17	0.2721
Iron-Fe Quantities [moles]	1.25E-2	9.26E-2	4.87E-3
% weight of iron	15	58.42	92.65
Initial volume of H ₂ O [ml]	200	200	25

Table 6. Experimental results of the various experiments undertaken.

	Fe-15wt%		Fe – 58.42wt%		Fe – 92.65wt%	
Conversions	60mn	1.44%	1mn	3.35%	120mn	87.99%
			3mn	3.69%		
			5mn	6.37%		
			15mn	7.38%		
			43mn	8.72%		
			60mn	16.40%		
			90mn	17.80%		
Regenerated PAT [moles _{PAT} /g _{PET}]	Fe-15wt%		Fe – 58.42wt%		Fe – 92.65wt%	
	8.6534E-5		60mn	9.8913E-4	5.2963E-3	
			90mn	1.0699E-3		
			60mn	1.0685E-02	1.0871E+00	
Total regenerated PAT [moles _{PAT} /g _{LOAD} /moles _{Fe}]	6.9479E-03		90mn	1.1558E-02		
			60mn	1.7809E-04	9.0591E-03	
Total regenerated PAT [moles _{PAT} /g _{LOAD} /moles _{Fe} /mn]	1.1580E-04		90mn	1.2842E-04		

An increase in the amount of iron correlates with an increase in conversion (Figure 4). Iron thus plays an important role in PET regeneration, as oxygen atoms enables the adsorption onto the Lewis acid sites of iron atoms to form a reaction intermediate which subsequently promotes the regeneration of PAT and ethane-diol molecules (Figure 1-Figure 3).

As a result, the molar amount of PAT regenerated per gram of load-PET per moles of Fe catalyst per minute increases with the catalytic iron-Fe content in the reaction medium. This shows and confirms that as the amount of catalytic iron-Fe increases, the probability of contact between PET and iron atoms increases, and PET regeneration over time increases (Figure 5).

First of all, an experiment was carried out solely to determine the nature of the Iron-Fe catalyst, including its mass, before and after the reaction, while air-drying the Iron-Fe

catalyst before weighing it. It was found that the weight of the catalyst increased by 0.66%. This increase is due to the existence and long-term materialization of existing bonds between the Fe-Fe catalyst and the PET reagent, thus forming the reaction intermediate presented in Mechanism 1. Indeed, several bibliographies and the very basis of heterogeneous and homogeneous catalysis assert the ability of intermediate metals including Iron-Fe to form reaction intermediates with their reactants by chemisorption before giving reaction products [10-14], an intermediate form whose enthalpy of formation is much lower than that of the reactant-complex activated without these metal catalysts and thus leading to the very significant increase in reaction rates with catalysts. Then, in addition to this, during the experiments carried out on this PET recycling using the Iron-Fe catalyst, the factors which positively and effectively influence the reaction rate had been optimized:

1. The contact surface between the Iron-Fe (in grid form) and the PET reactants to be recycled was increased by finely grinding the latter.

2. The Iron-Fe catalyst was placed in the reaction vessel so as to overhang and cover the PET reagents to be recycled.

3. The reaction temperature, which will have a direct influence on the endothermic reaction to form the reaction intermediates, was chosen at over 120 °C, thus creating sufficient agitation of the reaction medium.

4. Finally, as a direct consequence of these first three factors, the effective collision frequency (Collision Theory) [10] between the Iron-Fe catalyst and the PET reagent to be recycled increases as the Iron-Fe content rises, and explains the maximum conversion 87.99% recorded at an Iron-Fe weight content close to 92.65wt%.

Figure 6 is showing the evolution of conversion as a function of reaction time catalyzed by the Lewis acid sites of the Iron-Fe atoms at 58.42wt%, indicates that this evolution increases, but very slowly, with reaction time.

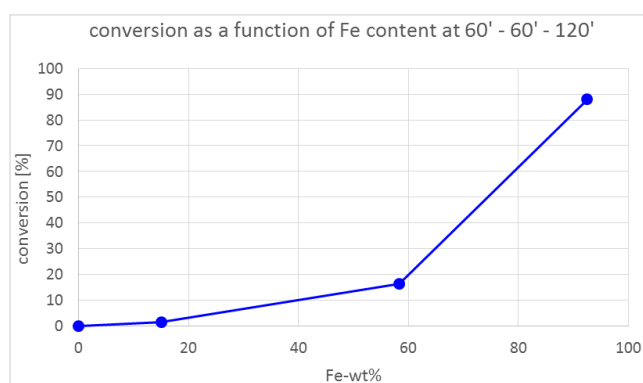


Figure 4. PET conversion as a function of Fe content.

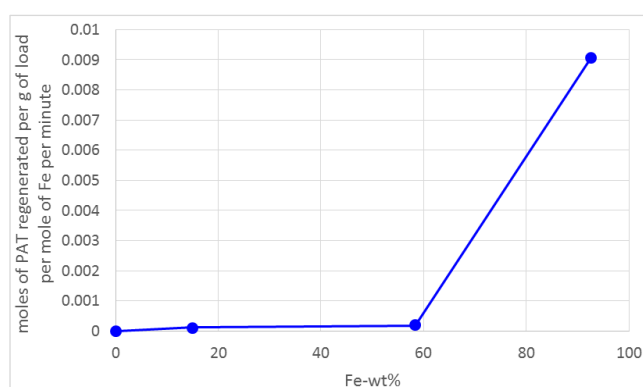


Figure 5. Molar quantity of PAT regenerated per gram of charge per mole of Fe per minute.

A time-dependent increase in PET conversion is observed (figure 6).

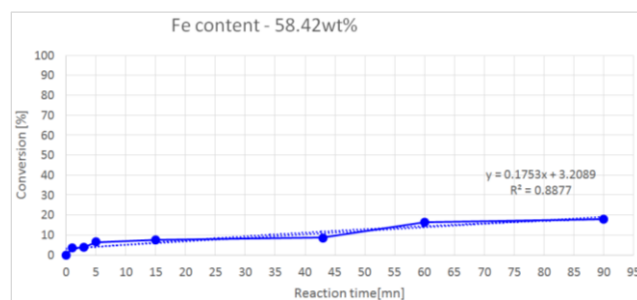


Figure 6. PET conversion as a function of reaction time for iron-Fe content-58.42%.

5. Kinetic Study of PET Recycling Using the Results of the Experiment with Iron-58.42wt%

5.1. Global Kinetic Study of the PET Recycling Without Taking Into Account the Iron-Fe Catalyst

The global PET regeneration reaction without taking into account the Iron-Fe catalysts is:



Thus, the global rate of this reaction as a function of the rate constant k is equal to

$$Vitesse = k \times [H_2O]^\alpha \times [PET]^\beta \quad (13)$$

Seeing that the amount of water used in the recycling reactions is in excess of the amount of PET, we can estimate and apply another rate constant k_{H_2O} such that

$$k_{H_2O} = k \times [[H_2O]^\alpha] \quad (14)$$

The rate expression became

$$Vitesse - Speed = k_{H_2O} \times [PET]^\beta = -\frac{d[PET]}{dt} \quad (15)$$

By solving this differential equation (15) with respect to PET concentration, it is possible to consider three cases:

- 1) If the global order with respect to PET is zero ($\beta = 0$), then it is necessary and sufficient that the variation of the initial PET concentration $[PET]_0$ minus $[PET]$ as a function of time is a straight line.
- 2) If the overall order with respect to PET is equal to one ($\beta = 1$), then it is necessary and sufficient that the variation of the initial PET concentration $PET \ln([PET]_0)$ minus $\ln([PET])$ as a function of time is a straight line.
- 3) If the global order with respect to PET is equal to two ($\beta = 2$), then it is necessary and sufficient that the variation

of PET concentration $\text{PET } 1/[\text{PET}]$ minus $1/[\text{PET}]_0$ as a function of time is a straight line.

The different values of these parameters are shown in the fol-

lowing table 7.

$$[\text{PET}]_0 = 18.4 \text{ [g/L]}$$

Table 7. Results of global PET regeneration kinetic studies Fe-58.42wt%.

Fe – 58.42%wt		[PET] [g/L]	Zero Order [PET] ₀ - [PET]	Order 1 LN [PET] ₀ - LN[PET]	Order 2 1/[PET] - 1/[PET] ₀
1mn	3.35%	1.7783E+01	6.1706E-01	3.4111E-02	1.8859E-03
3mn	3.69%	1.77E+01	6.7877E-01	3.7587E-02	2.0817E-03
5mn	6.37%	1.72E+01	1.1724E+00	6.5839E-02	3.6986E-03
15mn	7.38%	1.70E+01	1.3575E+00	7.6643E-02	4.3291E-03
43mn	8.72%	1.68E+01	1.6044E+00	9.1231E-02	5.1914E-03
60mn	16.40%	1.54E+01	3.0236E+00	1.7952E-01	1.0687E-02
90mn	17.80%	1.51E+01	3.2704E+00	1.9570E-01	1.1748E-02

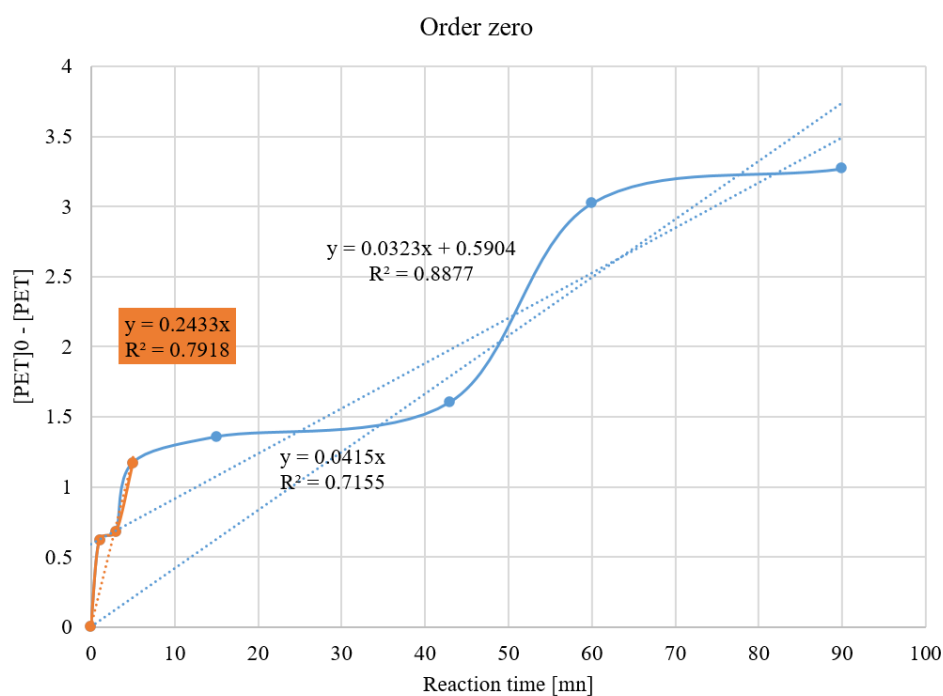


Figure 7. Evolution of the curve case global order with respect to PET is zero.

Comparing the R^2 values for the different orders, it is clear that this reaction is a complex reaction of global order 2 with respect to PET, considering that the water molecules are in excess with respect to PET.

Thus, initially the observed constant $k_{H_2O} = 8 \times 10^{-4} [l \times g^{-1} \times mn^{-1}]$.

The volume of water used is 200 ml so; $n_{moles H_2O} = \frac{200}{18.015} = 11.1019 \text{ moles}$.

As the reactor is a 250 ml capacity flask with a reflux sys-

tem, the estimated concentration of water during the reaction at 141 °C is equal to

$$[H_2O] = \frac{11.1019}{(250 \times 0,001)} = 44.4074 \text{ mol/l}$$

From equation 14, assuming $\alpha=1$, we have the approximate value of k such that

$$k = \frac{k_{H_2O}}{[H_2O]} = \frac{8 \times 10^{-4}}{44,4074} = 1.8015 \times 10^{-5} [l^2 \times g^{-2} \times mn^{-1}] \quad (16)$$

By decreasing the concentration of water, i.e. the number of moles of water, the rate constant must increase.

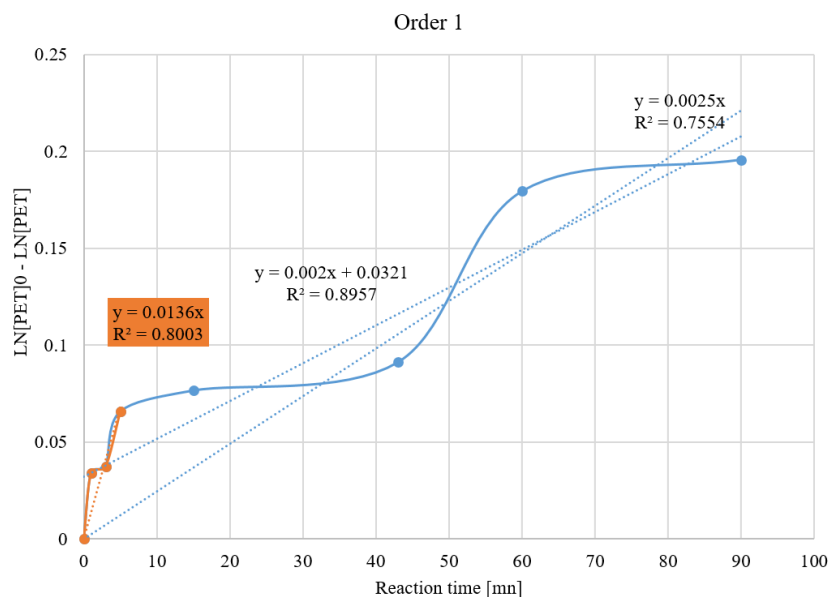


Figure 8. Evolution of the curve case global order with respect to PET is equal to one.

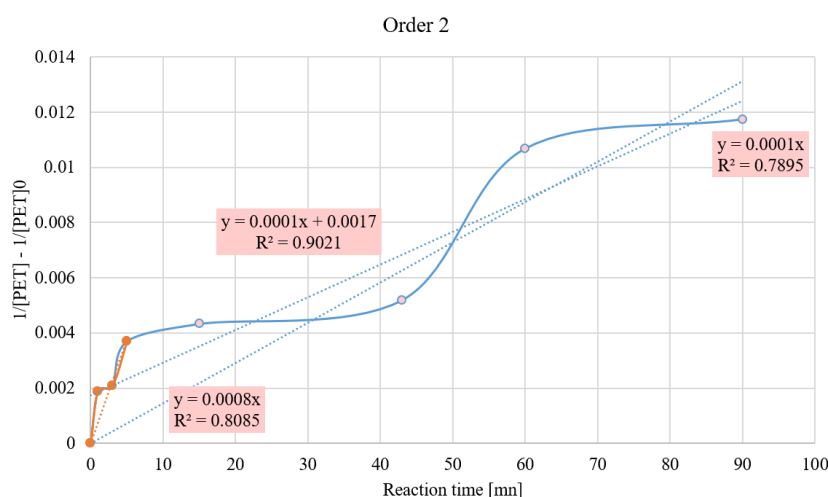


Figure 9. Evolution of the curve case global order with respect to PET is equal to two.

5.2. Global Kinetic Study of the PET Recycling Reaction Taking into Account the Iron-Fe Catalyst and Water

Taking into account the quantities of Iron-Fe catalyst and the quantities of water involved in this regeneration reaction, equation 12 becomes



Knowing that Iron is the catalyst of the reaction, it regenerates itself by participating in this reaction, the global speed

taking into account water and iron-Fe catalysts of this reaction is

$$Vitesse - Speed = -\frac{d[PET]}{dt} = k \times [H_2O]^\alpha \times [PET]^\beta \times [Fe]^\gamma \quad (18)$$

By applying the logarithm function to equation 18, it becomes

$$\ln(Vitesse - Speed) = \ln\left(\frac{d[PAT]}{dt}\right) = \ln k + \alpha \ln[H_2O] + \beta \ln[PET] + \gamma \ln[Fe] \quad (19)$$

By applying and using equation 18 to the experimental results (Table 8), there will be the following four-equation

linear equation system to solve and determine the values of the kinetic constants k , α , β and γ .

Table 8. The experimental results.

Time reaction interval	V_{PAT}	$[H_2O]$	$[PET]$	$[Fe]$
[0-1]	3.7143E-03	0.0074	8.0832E-04	0.4628
[1-3]	1.8571E-04	0.0082	8.0551E-04	0.4627
[3-5]	1.4857E-03	0.0141	7.8307E-04	0.4626
[5-15]	1.1143E-04	0.0163	7.7466E-04	0.4625
[15-43]	5.3061E-05	0.0193	7.6344E-04	0.4624
[43-60]	5.0252E-04	0.0364	6.9893E-04	0.4623
[60-90]	4.9524E-05	0.0394	6.8771E-04	0.4622

$$\begin{cases} 1x_1 - 4,9024x_2 - 7,1206x_3 - 0,7704x_4 = -5,5956 \\ 1x_1 - 4,8071x_2 - 7,1240x_3 - 0,7707x_4 = -8,5913 \\ 1x_1 - 4,2606x_2 - 7,1523x_3 - 0,7709x_4 = -6,5119 \\ 1x_1 - 4,1140x_2 - 7,1631x_3 - 0,7711x_4 = -9,1021 \end{cases}$$

Solving this system of equations using the free Matrix calculator application on the net gives the following results:

$$x_1 = \ln k = 1,36E4 \rightarrow k = e^{1,36E4} \quad (20)$$

$$x_2 = \alpha = 25,6 \quad (21)$$

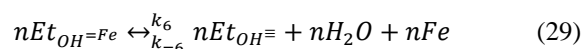
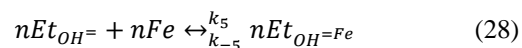
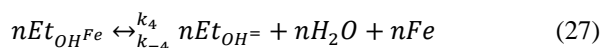
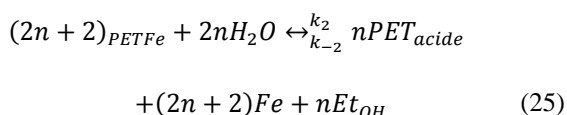
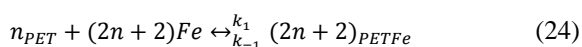
$$x_3 = \beta = 319 \quad (22)$$

$$x_4 = \gamma = 1,45E4 \quad (23)$$

6. Validation of the Proposed Reaction Mechanism for the Regeneration of PET to PAT

The following mechanism (mechanism 1) is proposed to study this PET regeneration using Iron with SA acid sites as catalyst. Determining the rate expression from this mechanism and comparing this rate expression with experimental results would validate the mechanism.

Mechanism 1 - Proposed reaction mechanism for the regeneration of PET to PAT and ethanediol



n_{PET} : PET composed of n PAT monomers

$PETFe$: complex between iron-Fe and PET

Et_{OH} : Ethane diol

PET_{acide} it's recycled PAT-pure terephthalic acid

$Et_{OH=Fe}$ complex formed between iron-Fe and ethanediol

$Et_{OH=}$: The first product of the 1st dehydration of the ethanediol

$Et_{OH=Fe}$: complex formed between Iron-Fe and $Et_{OH=}$

$nEt_{OH\equiv}$: The second product by dehydration of $Et_{OH=}$

The expressions for the speeds of the various steps in the above reaction mechanism are:

$$v_1 = k_1[PET][Fe]^{2n+2} - k_{-1}[PETFe]^{2n+2} \quad (30)$$

$$\begin{aligned} v_2 = & k_2[PETFe]^{2n+2}[H_2O]^{2n} - \\ & k_{-2}[PET_{acide}]^n [Fe]^{2n+2} [EtOH]^n \end{aligned} \quad (31)$$

$$v_3 = k_3[EtOH]^n [Fe]^n - k_{-3}[EtOHFe]^n \quad (32)$$

$$v_4 = k_4[EtOHFe]^n - k_{-4}[EtOH=]^n [Fe]^n [H_2O]^n \quad (33)$$

$$v_5 = k_5[EtOH=]^n [Fe]^n - k_{-5}[EtOH=Fe]^n \quad (34)$$

$$v_6 = k_6[EtOH=Fe]^n - k_{-6}[EtOH\equiv]^n [Fe]^n [H_2O]^n \quad (35)$$

The kinetically limiting step is the surface reaction step 3, so the velocity of this step is the slowest and the other steps are virtually at equilibrium and their velocities are equal to zero.

Thus, from equation (30) we deduce:

$$\begin{aligned} v_1 &= k_1[PET][Fe]^{2n+2} - k_{-1}[PETFe]^{2n+2} = 0 \Leftrightarrow \\ k_1[PET][Fe]^{2n+2} &= k_{-1}[PETFe]^{2n+2} \\ \rightarrow [PETFe] &= \left(\frac{k_1}{k_{-1}}\right)^{\frac{1}{2n+2}} [PET]^{\frac{1}{2n+2}} [Fe] = \\ K_1^{\frac{1}{2n+2}} [PET]^{\frac{1}{2n+2}} [Fe] \end{aligned} \quad (36)$$

such as K_1 is the adsorption equilibrium constant of the step 1

From the equation 31 it is deduced:

$$\begin{aligned} v_2 &= \\ k_2[PETFe]^{2n+2} [H_2O]^{2n} - \\ k_{-2}[PETacide]^n [Fe]^{2n+2} [EtOH]^n &= 0 \\ \Leftrightarrow k_2[PETFe]^{2n+2} [H_2O]^{2n} &= \\ k_{-2}[PETacide]^n [Fe]^{2n+2} [EtOH]^n \\ [PETFe] &= \left(\frac{k_2}{k_{-2}}\right)^{\frac{1}{2n+2}} \frac{[PETacide]^{\frac{n}{2n+2}} [Fe]^{\frac{n}{2n+2}} [EtOH]^{\frac{n}{2n+2}}}{[H_2O]^{2n}} \\ \Leftrightarrow [PETFe] &= K_2^{\frac{1}{2n+2}} \times \frac{[PETacide]^{\frac{n}{2n+2}} [Fe]^{\frac{n}{2n+2}} [EtOH]^{\frac{n}{2n+2}}}{[H_2O]^{2n}} \end{aligned} \quad (37)$$

avec K_2 is the adsorption equilibrium constant of the step 2

From the equation (33) it is deduced:

$$v_4 = k_4[EtOHFe]^n - k_{-4}[EtOH=]^n [Fe]^n [H_2O]^n = 0$$

$$\Leftrightarrow k_4[EtOHFe]^n = k_{-4}[EtOH=]^n [Fe]^n [H_2O]^n$$

$$\Leftrightarrow [EtOHFe] = \left(\frac{k_{-4}}{k_4}\right)^{\frac{1}{n}} [EtOH=] [H_2O] [Fe]$$

$$\Leftrightarrow [EtOHFe] = (K_4)^{\frac{1}{n}} [EtOH=] [H_2O] [Fe] \quad (38)$$

tel que K_4 is the adsorption equilibrium constant of the step 4

From the equation 23 it is deduced:

$$v_5 = k_5[EtOH=]^n [Fe]^n - k_{-5}[EtOH=Fe]^n = 0$$

$$\Leftrightarrow k_5[EtOH=]^n [Fe]^n = k_{-5}[EtOH=Fe]^n$$

$$\Leftrightarrow [EtOH=Fe] = \left(\frac{k_5}{k_{-5}}\right)^{\frac{1}{n}} [EtOH=] [Fe]$$

$$\Leftrightarrow [EtOH=Fe] = (K_5)^{\frac{1}{n}} [EtOH=] [Fe] \quad (39)$$

Such as K_5 is the adsorption equilibrium constant of the step 4

From the equation 35 it is deduced:

$$v_6 = k_6[EtOH=Fe]^n - k_{-6}[EtOH\equiv]^n [Fe]^n [H_2O]^n = 0$$

$$\Leftrightarrow k_6[EtOH=Fe]^n = k_{-6}[EtOH\equiv]^n [Fe]^n [H_2O]^n$$

$$\Leftrightarrow [EtOH=Fe] = \left(\frac{k_{-6}}{k_6}\right)^{\frac{1}{n}} [EtOH\equiv] [Fe] [H_2O]$$

$$\Leftrightarrow [EtOH=Fe] = (K_6)^{\frac{1}{n}} [EtOH\equiv] [Fe] [H_2O] \quad (40)$$

The law of conservation in Iron-Fe allows us to write the following equation (41):

$$[Fe]_{initial} = [Fe]_{vacant} + [PETFe] + [EtOHFe] + [EtOH=Fe] \quad (41)$$

$$\Leftrightarrow [Fe]_{initial} = [Fe] + K_2^{\frac{1}{2n+2}} \times \frac{[PETacide]^{\frac{n}{2n+2}} [Fe]^{\frac{n}{2n+2}} [EtOH]^{\frac{n}{2n+2}}}{[H_2O]^{2n}} + (K_4)^{\frac{1}{n}} [EtOH=] [H_2O] [Fe] + (K_5)^{\frac{1}{n}} [EtOH=] [Fe]$$

$$\Leftrightarrow [Fe] = \frac{[Fe]_{initial-i/interval}}{(1+K_2^{\frac{1}{2n+2}} \times \frac{[PETacide]^{\frac{n}{2n+2}} [Fe]^{\frac{n}{2n+2}} [EtOH]^{\frac{n}{2n+2}}}{[H_2O]^{2n}} + (K_4)^{\frac{1}{n}} [EtOH=] [H_2O] + (K_5)^{\frac{1}{n}} [EtOH=])} \quad (42)$$

This means,

$$v_{3-\frac{i}{interval}} = k_3[EtOH]^n [Fe]^n - k_{-3}[EtOHFe]^n$$

$$\Leftrightarrow v_{3-\frac{i}{interval}} =$$

$$\frac{k_3[EtOH]^n [Fe]^n_{initial-\frac{i}{interval}}}{(1+K_2^{\frac{1}{2n+2}} \times \frac{[PETacide]^{\frac{n}{2n+2}} [Fe]^{\frac{n}{2n+2}} [EtOH]^{\frac{n}{2n+2}}}{[H_2O]^{2n}} + (K_4)^{\frac{1}{n}} [EtOH=] [H_2O] + (K_5)^{\frac{1}{n}} [EtOH=])} - \frac{k_{-3}K_4^n [EtOH=]^n [H_2O]^n [Fe]^n_{initial-\frac{i}{interval}}}{(1+K_2^{\frac{1}{2n+2}} \times \frac{[PETacide]^{\frac{n}{2n+2}} [Fe]^{\frac{n}{2n+2}} [EtOH]^{\frac{n}{2n+2}}}{[H_2O]^{2n}} + (K_4)^{\frac{1}{n}} [EtOH=] [H_2O] + (K_5)^{\frac{1}{n}} [EtOH=])} \quad (43)$$

when $n \rightarrow +\infty$ in the vicinity of + 30 thus the equation 43 could be

$$v_{3-\frac{i}{interval}} = \frac{k_3[EtOH]^n[Fe]_{initial-\frac{i}{interval}}^n}{(1+\frac{[PETacide]^{\frac{1}{2}}[EtOH]^{\frac{1}{2}}}{[H_2O]^{2n}}+[EtOH=][H_2O]+[EtOH=])} - \frac{k_{-3}K_4^n[EtOH=]^n[H_2O]^n[Fe]_{initial-\frac{i}{interval}}^n}{(1+\frac{[PETacide]^{\frac{1}{2}}[EtOH]^{\frac{1}{2}}}{[H_2O]^{2n}}+[EtOH=][H_2O]+[EtOH=])} \quad (44)$$

$$\text{Such as } X_1 = \frac{[EtOH]^n[Fe]_{initial-\frac{i}{interval}}^n}{(1+\frac{[PETacide]^{\frac{1}{2}}[EtOH]^{\frac{1}{2}}}{[H_2O]^{2n}}+[EtOH=][H_2O]+[EtOH=])} \quad (45)$$

$$\text{To validate this proposed mechanism, we can plot the curve } v_{3-\frac{i}{interval}} = f(X_1) \quad (46)$$

But, after rearrangement, we can also write,

$$\left(\frac{v_{3-\frac{i}{interval}} \times (1+\frac{[PETacide]^{\frac{1}{2}}[EtOH]^{\frac{1}{2}}}{[H_2O]^{2n}}+[EtOH=][H_2O]+[EtOH=])}{[Fe]_{initial-\frac{i}{interval}}^n} \right) = k_3[EtOH]^n - k_{-3}K_4^n[EtOH=]^n[H_2O]^n$$

To validate this proposed mechanism, it is also possible to plot the curve

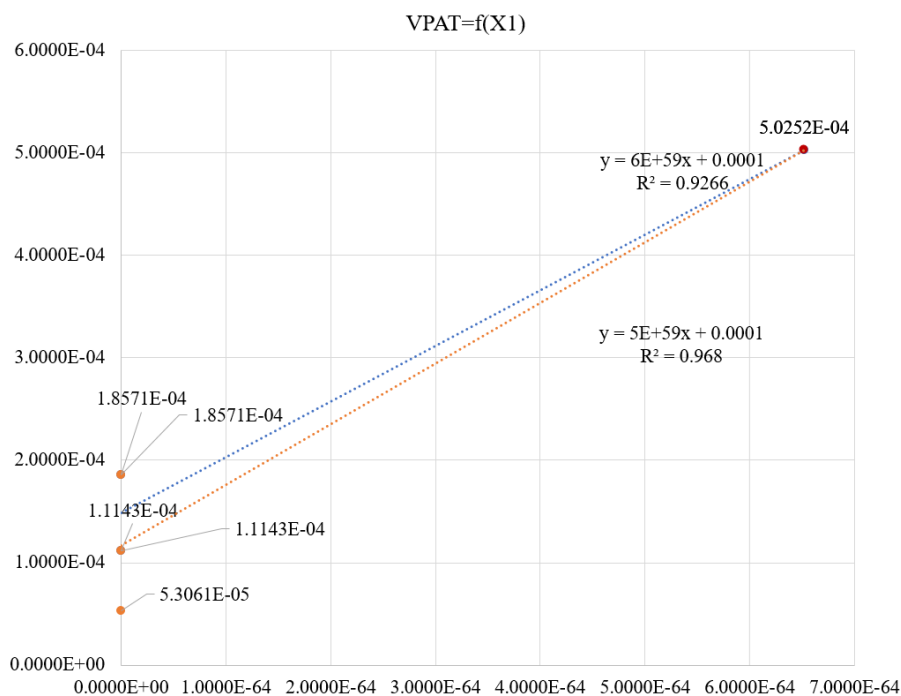
$$X3 = \left(\frac{v_{3-\frac{i}{interval}} \times (1+\frac{[PETacide]^{\frac{1}{2}}[EtOH]^{\frac{1}{2}}}{[H_2O]^{2n}}+[EtOH=][H_2O]+[EtOH=])}{[Fe]_{initial-\frac{i}{interval}}^n} \right) = f([EtOH]^n) \quad (47)$$

Referring to the experimental results in the following Table 9 and assuming that the number of maximum limiting monomers making up PET is equal to $n=30$ or trenta-mere.

Table 9. Experimental results of PET recycling kinetics using Iron-Fe catalyst in water.

Time reaction Interval - mn	V _{PAT}	[H ₂ O]	[PET]	PAT	EtOH	X1	[Fe]	X2	X3	EtOH - n
[0-1]	3.7143E-03	0.0074	8.0832E-04	3.7143E-03	3.7143E-03	5.6230E-105	1.0074E+01	1.5584E-43	8.2445E+28	1.24813E-73
[1-3]	1.8571E-04	0.0082	8.0551E-04	4.0857E-03	4.0857E-03	1.5443E-102	1.0082E+01	2.7802E-42	2.6192E+26	2.17791E-72
[3-5]	1.4857E-03	0.0141	7.8307E-04	7.0571E-03	7.0571E-03	1.8521E-88	1.0141E+01	4.3800E-35	2.3074E+20	2.87652E-65
[5-15]	1.1143E-04	0.0163	7.7466E-04	8.1714E-03	8.1714E-03	1.1206E-84	1.0163E+01	3.8032E-33	2.3254E+17	2.33851E-63
[15-43]	5.3061E-05	0.0193	7.6344E-04	9.6571E-03	9.6571E-03	2.3128E-80	1.0193E+01	6.2331E-31	8.0557E+14	3.51123E-61
[43-60]	5.0252E-04	0.0363	6.9893E-04	1.8200E-02	1.8200E-02	6.5212E-64	1.0364E+01	1.8534E-22	4.8862E+07	6.34076E-53
[60-90]	4.9524E-05	0.0393	6.8771E-04	1.9686E-02	1.9686E-02	7.1418E-62	1.0394E+01	2.1265E-21	4.6296E+05	6.67629E-52

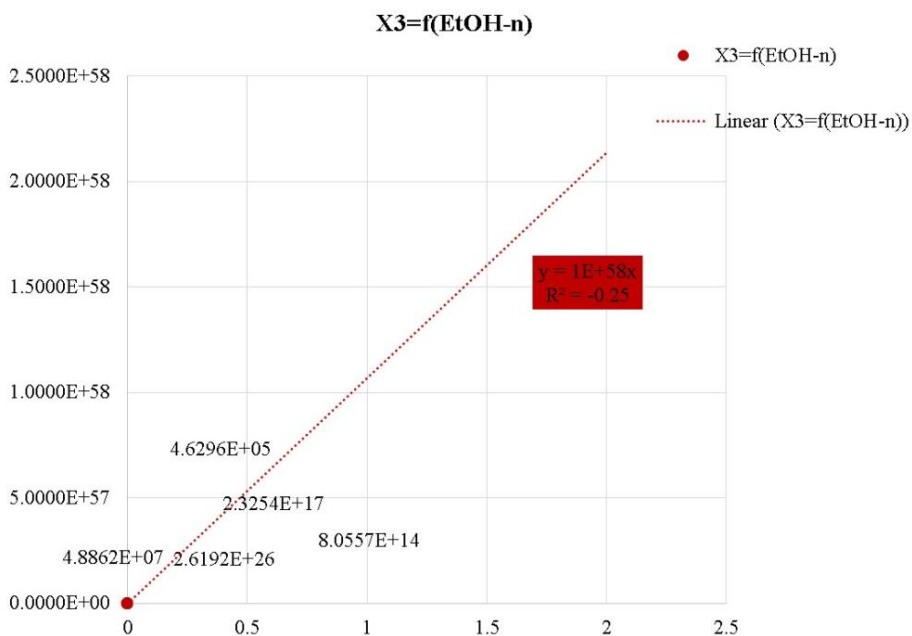
By plotting the curve given by equation (46), an increasing straight line [Figure 10] validates the proposed six-step mechanism for the regeneration of PET to PAT and Ethane diol following mechanism 1.



In consequence, the speed constant k_3 is equal to $6E+59 [l^{59} \times mol^{-59} \times mn^{-1}]$ for $n=30$ or trenta-mere PET.

Figure 10. First method to determine the speed constant k_3 by straight line to valid the mechanism 1.

Subsequently, by plotting the curve given by equation (47), a straight line whose trend line passes through the origin [Figure 11] also validates the proposed six-steps mechanism for the regeneration of PET to PAT and Ethane diol according to mechanism 1.



In consequence, the speed constant k_3 is equal to $1E+58 [l^{59} \times mol^{-59} \times mn^{-1}]$ for $n=30$ or trenta-mere PET.

Figure 11. Second method to determine the speed constant k_3 by straight line to valid the mechanism 1.

7. Conclusion

The results recorded and presented in this manuscript demonstrated the considerable capacity of the protonic Brönsted H⁺ acid sites of citric acid molecules and the Lewis acid sites of Iron-Fe to catalyze the reaction to recycle PET into PAT and ethanediol by hydrolysis. Kinetic monitoring on the 58.42wt% Iron-Fe catalyst showed that the amount of PAT recycled increased slowly but surely with time, reaching a PET conversion of only 17.80% at 90 min. This conversion also increased with the amount of catalyst used, and while it was 1.44% at 60 min for an Iron-Fe mass percentage of 15%, it rose to 87.99% at 120 min for an Iron-Fe mass percentage of 92.65%. During testing, it was found that the initial particle size of PET influences the speed and efficiency of conversion. Finally, the deduced kinetic constants presented in this manuscript and the reaction mechanism proposed in this manuscript were validated by the experimental results and would enable optimization of the parameters, reagents and catalysts involved in recycling PET to PAT and ethanediol under similar experimental conditions.

Abbreviations

PET	Polyethylene Terephthalate
PAT	Pure Terephthalic Acid
Fe	Iron Atom
Et-2OH = Et _{OH}	Ethanediol = Ethylene Glycol
Trans-	Transparent
ech (echantillon)	Sample
ln	Neperian Logarithm

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Author Contributions

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Raherimandimby Joachim: Formal Analysis, Methodology, Resources, Validation, Visualization

Raobijaona Baholy: Supervision, Validation, Visualization

Ratsimba Marie Hanitriniaina: Project administration, Supervision, Validation, Visualization

Conflicts of Interest

The authors declare no conflicts of interest.

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