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PHOTOCATALYTIC REDUCTION OF CO₂
BACHELOR / Thesis

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Summary

The concentration of CO₂ in the atmosphere is nowadays a worldwide problem, because is one of the gases contributing to global warming. It is a fact that CO₂ is increasing every time more and more in the atmosphere due to several industrial activities and the own carbon cycle. From this point of view, it is wanted to suggest the photoreduction of CO₂ in water with natural zeolites (in this case clinoptilolite) as a possible solution.

In this research two different types zeolites were tested, the difference was the particle size, and also two different modifications of them. In order to catch as much CO₂ as possible it was experimented with the solubility of CO₂ in water and to convert as much as CO₂ into organic compounds several photoreduction were developed.

The results show that it is possible to convert CO₂ into organic matter performing a photoreduction with clinoptilolite. It was found out that the best conditions for a more efficient photoreduction are with 0,1 g of zeolites as catalyst, although there is not a big difference between the particle size of zeolites, the better working photocatalyst was the zeolites with particle size less than 0,25 mm. About the temperature of the photoreduction can be achieved same results with cold and warm water, but depends on the speed wanted for the reaction, cold reaction are slower than warm reactions.

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1. List of abbreviation and symbols

Ag₂SO₄: Silver sulphate

CaCO₃: Calcium carbonate

CAS: Chemical Abstract Service

CaO: Calcium oxide (quicklime)

Ca(OH)₂: Calcium hydroxide

CCS: Carbon Capture and Storage

CdS: Cadmium sulphide

CdSe: Cadmium selenide

CeO₂: Cerium dioxide

CFC: Chlorofluorocarbon

CH₄: Methane

CHCl₃: Chloroform

CO₂: Carbon dioxide

COD: Chemical Oxygen Demand

Cu₂O: Copper oxide

DAC: Direct Air Capture

E_a: Activation energy

EPA: Environmental Protection Agency (USA)

ESRL: Earth System Research Laboratory

FeCl₃: Iron chloride

Fig. : Figure

GCMS: Gas Chromatography with Mass Spectrophotometer

GHG: Greenhouse Gases

H₂CO₃: Carbonic acid

HFC: Chlorofluorocarbon

Hg: Mercury

HgSO₄: Mercury sulphate

H₂SO₄: Sulphuric acid

IGCC: Integrated Gasification Combined Cycle

IUPAC: International Union of Pure and Applied Chemistry

k: Kinetic constant

K₂Cr₂O₇: Potassium dichromate

Mo: Molybdenum

Na: Sodium

Na₂CO₃: Sodium carbonate

NaOH: Sodium hydroxide

NIOSH: National Institute for Occupational Safety and Health

N₂O: Nitrogen oxide

PbS: Lead (II) sulphide or also known as galena

PFC: Prefluorinated compounds

ppm: Parts per million

ppmv: Parts per million per volume

PT: Polythiophene

Os: Osmium

OSHA: Occupational Health and Safety Administration

Re: Rhenium

Rh: Rhodium

Ru: Ruthenium

SF₆: Sulphur hexafluoride

SiO₂: Silicon dioxide

TiO₂: Titanium dioxide

TOC: Total organic carbon

TWA: Permissible exposure limit for an employee to a chemical substance or physical agent

UNFCCC: United Nation Framework Convention on Climate Change

UV: Ultraviolet

V: Vanadium

ZnO: Zinc oxide

ZrO₂: Zinc dioxide

ZnS: Zinc sulphide

2. Glossary

Adsorption: adhesion of atoms, ions or molecules from gas, liquid or dissolved solid to a surface. It is a surface-based process, where it is created a film of the adsorbate on the surface of the adsorbent.

Absorption: separation process in which gaseous component is separated from a gas stream by the use of a liquid. The gaseous component comes into contact with the liquid and is absorbed from the gas phase into the liquid phase.

Absorbent or solvent: liquid used for absorption.

Activated carbon: material which is characterized for having a large number of microporous.

Anatase: one of the three minerals formed of titanium dioxide, it crystallizes in tetragonal system.

Calcination: heating to high temperatures in air or oxygen. (IUPAC)

Catalysis: a modification and especially increase in the rate of a chemical reaction induced by material unchanged chemically at the end of the reaction.

Catalyst: substance that accelerates a chemical reaction without being consumed as a reactant.

Causticization: process used for converting a solution of soda (sodium carbonate) with lime (calcium hydroxide) into sodium hydroxide and calcium.

Chalcogenide: chemical compound consisting of at least one chalcogen anion and at least one more electropositive element, group 16 of the periodic table.

Chlorophyll: term used for several closely related green pigments found in cyanobacteria and the chloroplasts of algae and plants.

COD: commonly used to indirectly measure the amount of organic compounds in water. The bases of COD is that nearly every organic compound.

Conduction band: quantifies the range of energy required to free an electron from its bond to an atom.

Conjugated polymers: organic macromolecules which consist at least of one backbone chain of alternating double- and single-bonds.

Crystal system: minerals crystallize according to one of seven motifs, known as crystal systems.

Desorption: the opposite of sorption, is a phenomenon whereby a substance is released from or through a surface.

Erythrosine: organic compound, specifically a derivative of fluorine. It is cherry-pink synthetic, primarily used for food colouring.

Exothermic reaction: Reaction which one emerges heat while is occurring.

Greenhouse gas: gas which absorbs and emits radiation within the thermal infrared range and contributes to climate change. These gases are water vapour, methane, carbon dioxide, nitrous oxide, ozone and CFC.

Ion exchange capacity: measure of the ability of an insoluble material to undergo displacement of ions previously attached and loosely incorporated into its structure by oppositely charged ions present in the surrounding solution.

Photosynthesis: process used by plants and other organisms to convert light energy, normally from the Sun, into chemical energy that can be later released to fuel the organisms' activities.

Photon: elementary particle, the quantum of light and all other forms of electromagnetic radiation.

Porosity: fraction of volume of holes over the total volume of the material.

Redox: chemical reaction which one or more electrons are transferred between the reagents, inducing a change in the oxidation states.

Rose bengal: organic compound. Its sodium salt is commonly used in eye drops and and thereby identify damage to the eye.

Rutile: mineral composed primarily of titanium dioxide, the most common natural form of TiO₂.

Slaker: process which lime reacts with water or moist air producing CaOH.

Specific gravity: ratio of the density of a substance to the density (mass of the same unit volume) of a reference substance. The usual standard of comparison for solids and liquids is water at 4° C which has a density of 1000 kg/l.

Surfactant: compound that lower the surface tension.

Syngas: gaseous fuel obtained from substances rich in carbon subjected to a chemical process at high temperature. Contains varying amounts of CO and H₂.

Stripping column: physical separation process where a liquid stream is removed by a vapour stream. The liquid and the vapour stream can have concurrent or countercurrent flows.

Thionin: family of small proteins found solely in plants.

3. Objectives

The main objective of this research is to know if it is possible to develop a photoreduction with natural zeolites, more specifically with Clinoptilolite, in order to reduce the CO₂ concentration in air and convert it into organic compounds such as methane, methanol, ethane, etc.

Secondary objectives are:

- Figure out the best conditions to dissolve CO₂ in water, temperature, pH and bubbling time.
- Find the best conditions to perform photoreduction and to know the parameters which affects photoreduction with Clinoptilolite.
- Study the kinetics of the photoreduction with different types of zeolites, order and rate of the reaction.
- Find the activation energy of the photoreduction performed with different types of zeolites.

4. Background

As it is known nowadays we are living in a world which one depends on fossil fuels, not only for energy also for all the plastic industry, coatings, paintings, cosmetics and many other sectors. Since the industrial revolution we are consuming these fuels in such frantic pace that we are extinguishing these sources. Human influences are expected to continue changing the atmospheric composition through the 21st century. Greenhouses gases such as CO₂, CH₄, N₂O, SF₆... are the main cause of global warming. The GH gas representing the largest contribution of human activities is CO₂, emissions from fossil fuel combustions, inducing the increase of CO₂ in the atmosphere concentration.

The assessment of total CO₂ emissions is approximately 23Gt per year worldwide [1]. Emissions from transport are increasing the last few years, more than emissions from industry or other sectors; actually transport sector is the second larger sector which emits more CO₂. Transport emissions are mainly generated by a multiplicity of small and distributed sources, which implies the possibility of capture and storage of carbon dioxide easily.

But the main consequence is the CO₂ that we are releasing into the atmosphere due to the burning of fuel. This CO₂ is causing to the earth serious problems such as the global warming, hereby researchers are trying to find the way to mitigate this problem and to decrease the concentrations of CO₂ in the atmosphere.

So back to nature, it can be observed that plants are able to do the process what we are seeking, convert the CO₂ in organic matter, with solar light. So based on plants, researchers are trying to perform a process similar to photosynthesis, instead of chlorophyll with different catalyst and also with solar light.

In this research it is wanted to promote a little more in this field and contribute to the development of a more sustainable world.

5. Introduction

5.1. Carbon dioxide

Carbon dioxide is a chemical compound formed by two atoms of oxygen attached symmetrically to an atom of carbon by two double bonds (O=C=O). Carbon dioxide is the main gas which contributes to the atmosphere pollution, greenhouse gas, as it is the result of several processes of fermentation (wine, beer...) and the main component in the combustion gases.

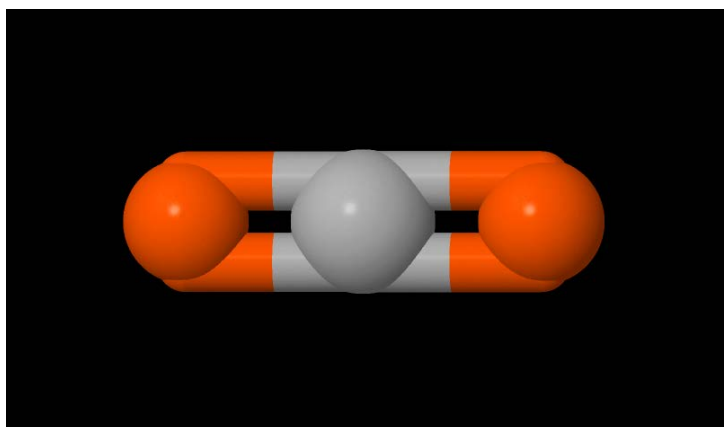


Fig. 5.1: Molecule of CO₂ (black atom is the C and red ones are O) [2]

5.1.1. Properties

Table 5.1: Properties of CO₂ [3]

CAS No.	124-38-9
Formula	CO ₂
Appearance	Colourless, odourless gas.
Stability	Stable. Incompatible with chemically active metals, such as alkali metals.
Exposure levels	NIOSH REL: TWA 5000 ppm (9000 mg/m ³) ST 30,000 ppm (54,000 mg/m ³) OSHA PEL: TWA 5000 ppm (9000 mg/m ³)

Physical properties

Table 5.2: Physical properties of CO₂ [3]

Molecular weight	44,01 g/mol
Experimental melting point	-56.5 °C
Experimental boiling point	-78 °C (Sublimes)
Experimental vapour pressure	56.5 atm (42940 mmHg)
Solubility in water (ml/100 ml at 20°C)	88

5.1.1.1. Solubility in water

The solubility of CO₂ in water is one of the most studied phenomena in all the physical chemistry. The system carbon dioxide-water is complex and very important for the biological life in earth.

First the CO₂ dissolves into water according the reaction (Eq. I)



Once the CO₂ is dissolved in water, begins the equilibrium between the carbonic acid and the carbon dioxide dissolved.



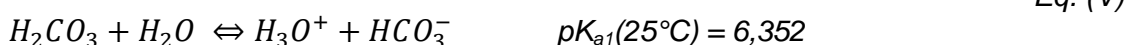
This reaction is kinetically slow, actually almost all the CO₂ remains as solvated molecular CO₂ only a small fraction of CO₂ is converted to H₂CO₃.

$$K = \frac{[H_2CO_3]}{[CO_2]} \cong 1,7 \cdot 10^{-3} s^{-1} \quad \text{Eq. (III)}$$

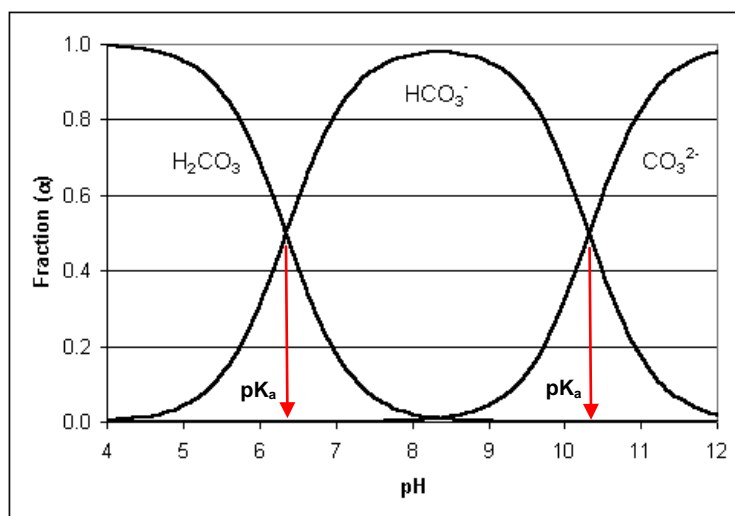
The equilibrium condition is quantified by the molar solubility K₀ (Henry's law), where the partial pressure of CO₂ has to be in atm, K₀ is the solubility in mol·l⁻¹·atm⁻¹ and [H₂CO₃] is the concentration of CO₂ dissolved in mol/kg of water. [4]

$$K_0 = \frac{[H_2CO_3]}{p_{CO_2}} \quad \text{Eq. (IV)}$$

The dissociation of carbonic acid runs in two steps due to the fact that it is a weak acid:



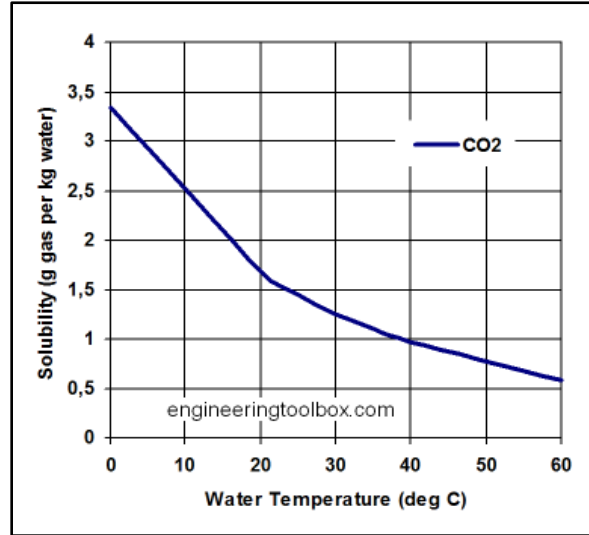
Where the $pK_{ax} = -\log K_{ax}$. In the graph 5.1 it can be seen how the fraction (α) of each compound change in relation of the pH.



Graph 5.1: Equilibrium diagram of carbonic acid [5]

These carbonate anions can easily form precipitates reacting with anions such as Ca²⁺ or Mg²⁺ which can pull the equilibrium more to the right resulting in the acidification of the water. [6, 7, 8]

The solubility of CO₂ depends also on the pressure and temperature, about pressure it is not going to be detailed because it is not interesting in this research; it is going to be working always with atmospheric pressure so it is going to give all the graphs and data for 1atm of pressure. About temperature, it can be said that at high temperatures the solubility decreases because of the movement of the atoms and at low temperatures the molecules are quite and it is easier to dissolve other molecules.



Graph 5.2: Evolution of solubility of CO₂ in water in relation to water temperature (°C) [9]

In table 5.3 it can be seen how the solubility of CO₂ changes in relation of the pH and the temperature. It can be seen that the best conditions for dissolving CO₂ in water are neutral pH and cold water.

Table 5.3: Relation between pH, temperature and solubility of CO₂ [10]

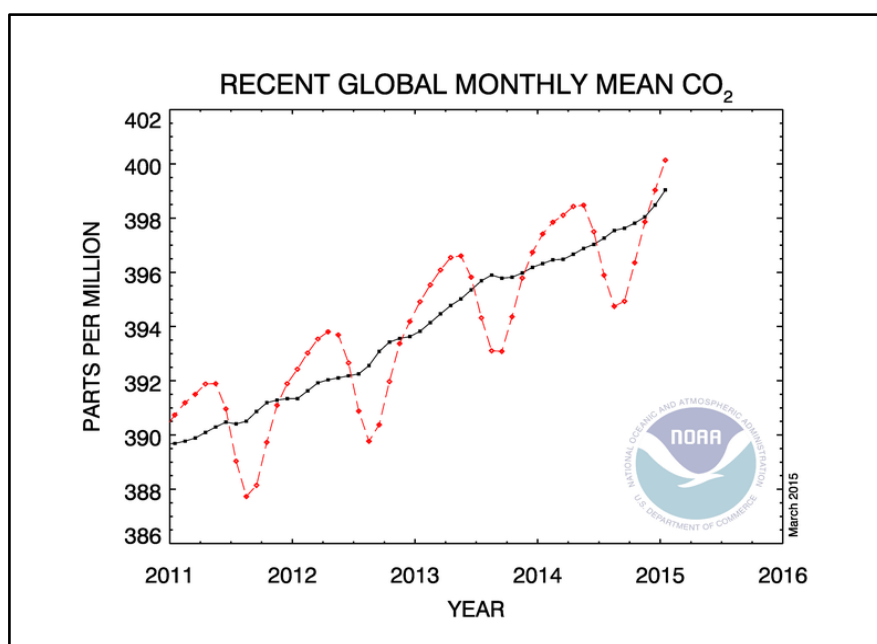
pH	Temperatures (°C)						
	5	10	15	20	25	30	35
6.0	2.915	2.539	2.315	2,112	1.970	1.882	1.839
6.2	1.839	1.602	1.460	1.333	1.244	1.187	1.160
6.4	1.160	1.010	0.921	0.841	0.784	0.749	0.732
6.6	0.732	0.637	0.582	0.531	0.495	0.473	0.462
6.8	0.462	0.402	0.367	0.335	0.313	0.298	0.291
7.0	0.291	0.254	0.232	0.211	0.197	0.188	0.184
7.2	0.184	0.160	0.146	0.133	0.124	0.119	0.116
7.4	0.116	0.101	0.092	0.084	0.078	0.075	0.073
7.6	0.073	0.064	0.058	0.053	0.050	0.047	0.046
7.8	0.046	0.040	0.037	0.034	0.031	0.030	0.030
8.0	0.029	0.025	0.023	0.021	0.020	0.019	0.018
8.2	0.018	0.016	0.015	0.013	0.012	0.012	0.011
8.4	0.012	0.010	0.009	0.008	0.008	0.008	0.007

Tucker (1984).
 *Factors should be multiplied by total alkalinity (mg/L) to get carbon dioxide (mg/L).
 For practical purposes, CO₂ concentrations are negligible above pH = 8.4.

5.1.2. CO₂ in the atmosphere

Carbon dioxide is naturally part of the atmosphere but human activities are altering the carbon cycle by adding more CO₂, both by adding CO₂ to the atmosphere and by the ability of natural sinks, like forest, to remove CO₂ from the atmosphere.

The concentration of CO₂ in the atmosphere has been measured continuously since 1958, it has been discovered that follows an oscillating line known as the "Keeling Curve" due to Dr. Charles David Keeling, professor at Scripps Institution of Oceanography. Keeling was the first who measure carbon dioxide and he figured out that atmospheric CO₂ concentrations were increasing. Before industrial era (1800s) atmospheric CO₂ concentration was between 275 and 280 ppm, in 1958 Dr. Keeling measured 315 ppm and nowadays it was registered 400,14 ppm in January 2015 as ESRL reported.



Graph 5.3: Evolution of the atmospheric concentration (ppm) of CO₂ in the last years [11]

5.1.3. The greenhouse effect

The greenhouse effect is a natural process that consists in the absorption and re-radiated of some part of sun's energy by greenhouse gases leaving the radiation stucked which induces an increase of temperature of the earth's surface. Although a finite amount of CO₂ is stored in the sea, fossil fuels, living matter and atmosphere the poles are melting and the global temperature is still increasing more and more every year.

The greenhouse effect consists in 6 basic steps, as it can be seen in fig 5.4 the problem we are facing nowadays is that human activities are increasing the concentration of greenhouses gases.

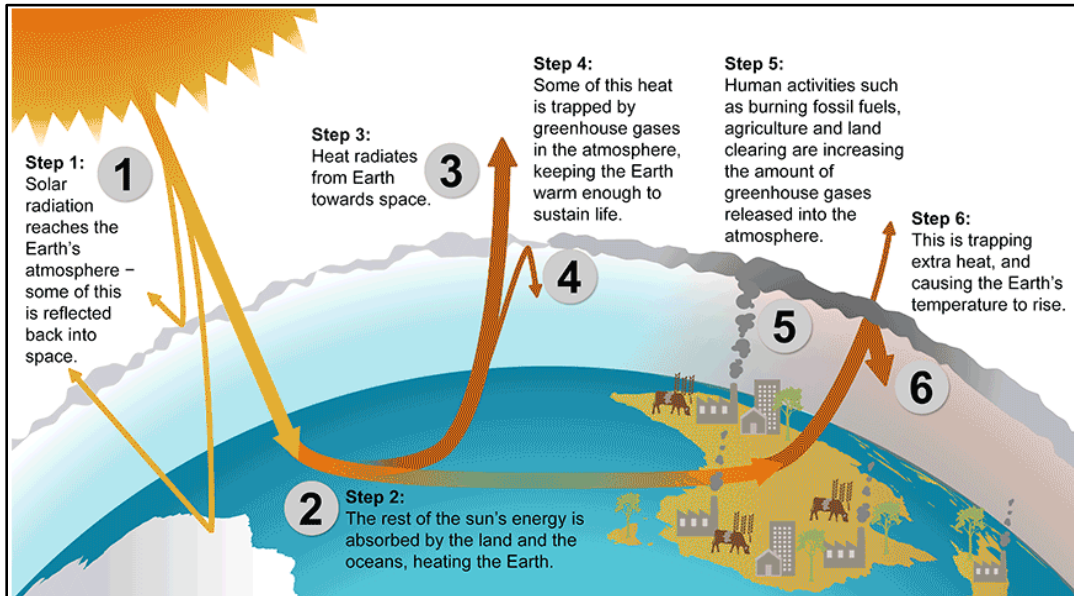


Fig. 5.2: Scheme of greenhouse effect [12]

5.1.3.1. KYOTO Protocol

The Kyoto protocol about the climate change is a protocol and an international agreement which aims the reduction of the emission of the six main greenhouse gases: CO₂, CH₄ and N₂O and industrial fluorinated gases HFC, PFC and SF₆.

On 11th of December of 1997, industrial countries pledged to reduce the greenhouses emissions. Governments agreed reducing 5% of the global emissions between 2008 and 2012, taken by reference the data in 1990. It does not mean that every country which take part of the Kyoto protocol have de reduce its emission one 5%, each country has its own percentage, but the global emission has to be 5% reduced. Recognizing that developed countries are the most responsible of the emissions of GHG in the atmosphere because of the 150 years of industrial activity, the Protocol burden them more under the principle of "common but differentiated responsibilities".[13]

If it is taken the example of Slovakia and Spain it can be seen in table 5.3 the data of the emission of both countries of CO₂, and the protocol target, seen that Spain doesn't pledge with the Kyoto Protocol and Slovak Republic does.

Table 5.4 Different year data of the emission of CO₂ in Slovakia and Spain [14]

	1990 (Mt of CO ₂)	2010 (Mt of CO ₂)	% changed	Kyoto Protocol target (%)
Slovak Republic	56,7	31,9	-43,8	-8
Spain	205,2	266,6	29,9	-15

5.1.4. Carbon dioxide capture

Since every time it is taking more awareness about climate change, researchers are doing high progresses in carbon dioxide capture field. Nowadays exist different technologies for this purpose in two directions, depending on where CO₂ comes from the two approaches are capture of atmospheric CO₂ and capture of CO₂ from fossil fuel power plants.

5.1.4.1. Carbon dioxide capture from fossil fuel power plants

Roughly 40% of all CO₂ emissions come from fossil fuel burning power plants, these plants are an easy target for CO₂ capture. But this sort of capture presents several disadvantages such as how to handle impurities in the flue gas stream or how to handle large quantities of CO₂ formed in the fuel combustion. [15][16]

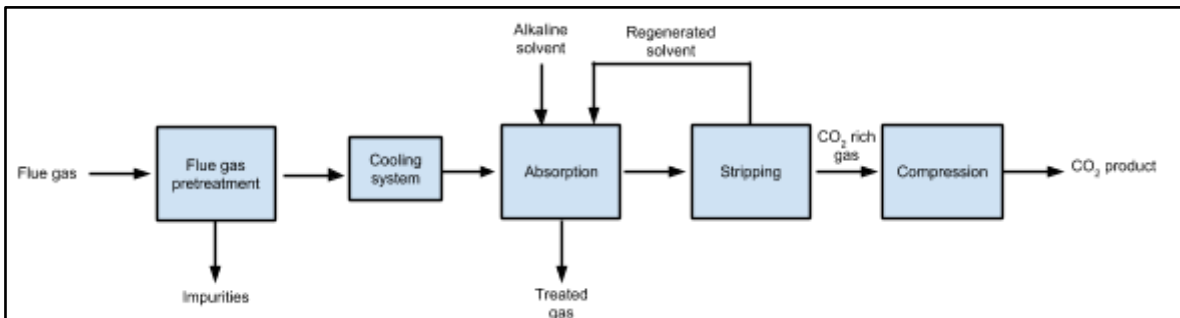
Carbon capture and storage (CCS) systems are generally a three step process:

1. Capture and compression from combustion exhaust (This step is the one that could account for 70-90% of the totalling operating costs of a CCS system)
2. Transportation (usually via pipeline)
3. Utilization

The most common approaches for capture of CO₂ are explained below:

1. Post-combustion: capture of CO₂ from flue gases created during fuel combustion with air. Can be treated with:
 - a. *Chemical absorption*: is the preferred method to capture CO₂ from post combustion CO₂ flue gas streams. It is need at the beginning a

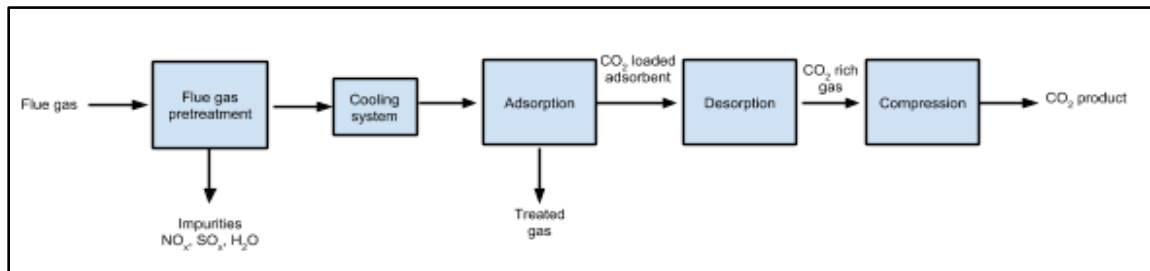
pretreatment step in order to remove as much impurities as possible, after this step the gas is cooled and sent it to the absorption column employing alkaline solvents to neutralized the absorbed CO₂. After that, the CO₂ goes to a stripping column where it is heated to break down the intermediate compounds. [15]



Graph 5.4: Scheme of chemical absorption

- b. *Adsorption*: it is particularly important to dry the flue gas before adsorption, thus first step is pretreatment where the impurities has to be removed, after pretreatment, the gas should be cooled to around room temperature. The gas is sent to an adsorption column and after that to a desorption step.

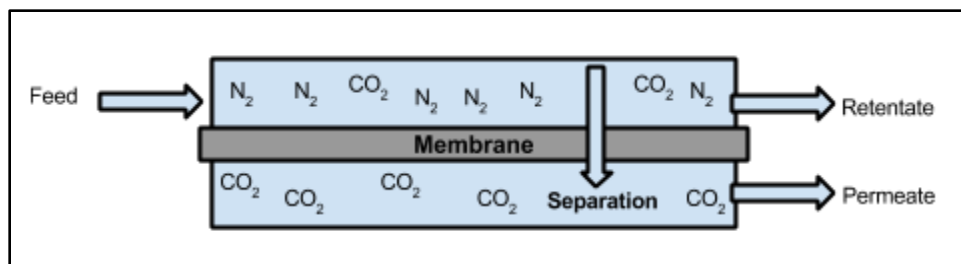
Adsorbents approaches are (1) zeolites, (2) activated carbon, (3) amine functionalized adsorbents and (4) metal organic frameworks (MOFs). [15]



Graph 5.5: Scheme of adsorption

- c. *Membrane separation*: this process is currently available; the stream is at atmospheric pressure which is the main difference between the other processes. The membrane acts like a filter to remove one or more gas components because of the different pressure between the feed side and

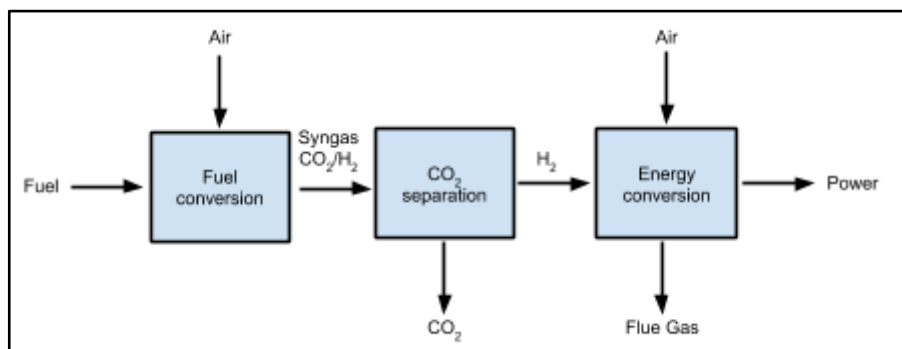
the permeable side. This method needs also a step of pretreatment to remove impurities.



Graph 5.6: Scheme of a membrane separation process

The two approaches of this process are the organic membranes, the inorganic and the mixed ones. Permeability and selectivity are the properties who rule this separation process.

- d. *Cryogenic distillation*: this technology has been used for years to separate the compounds of the air, but it's relatively new the idea for post combustion capture of CO₂.
2. Pre-combustion: capture of CO₂ from a synthesis gas (syngas) before fuel combustion. It applies to integrated gasification combined cycle (IGCC) power plants. The primary fuel is first 'gasified' in order to produce syngas, then the syngas is converted to CO₂ and H₂ from which CO₂ is separated.

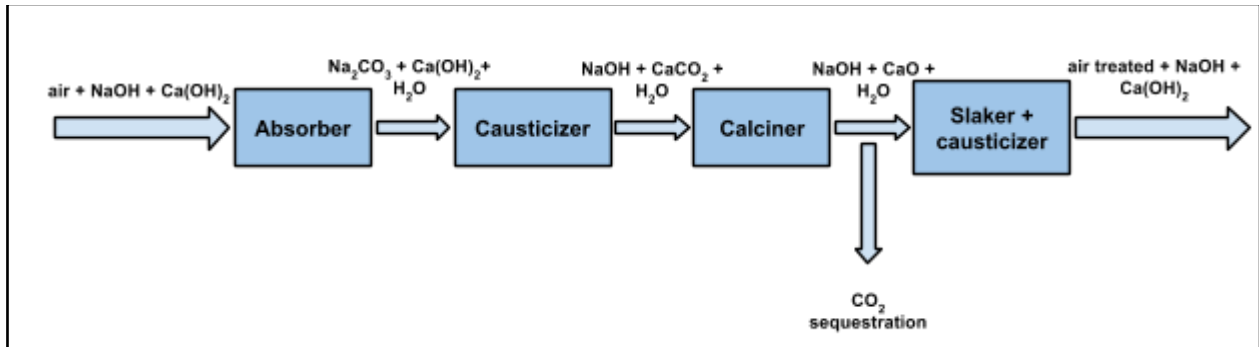


Graph 5.7: Scheme of pre-combustion carbon dioxide capture

5.1.4.2. Atmospheric carbon dioxide capture

On the other hand, there is also the approach to capture atmospheric CO₂, the difference between this air and the latter one rely on the concentration of CO₂, atmospheric air has less concentration of CO₂ than the ones which provides a fuel power plant.

Atmospheric CO₂ can be captured via different methods one of them, the most popular nowadays is the capture using sodium hydroxide spray. The CO₂ and the NaOH reacts and it is converted to Na₂CO₃, after 4 steps (1) absorption, (2) causticization, (3) calcination and (4) a mixed step with a slaker and a causticizer. In the third step, CaCO₃ is converted in CaO and CO₂ through a calcination process, making possible that CO₂ released at a pressure close enough to atmospheric pressure and allowing the sequestration of it. [17]



Graph 5.8: Scheme of atmospheric CO₂ capture using NaOH

5.2. Photocatalytic reduction

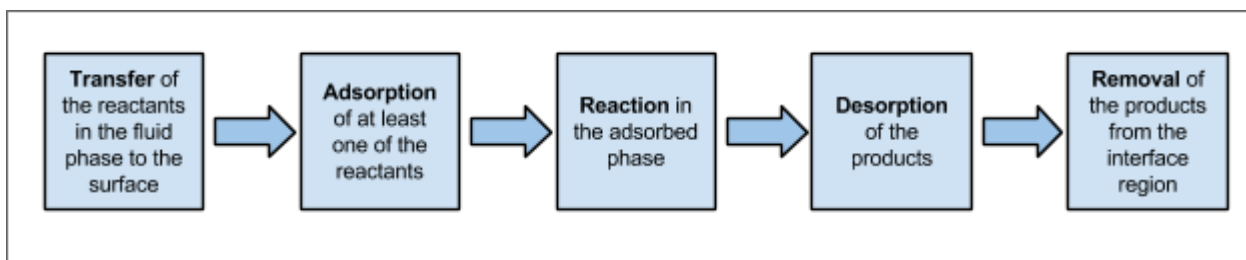
Photocatalytic reduction is an innovative technology which is based on the double aptitude of the catalysts to adsorb both reactants and efficient protons. The difference between photocatalytic reduction and classic catalysis lies in the activation mode, while classic catalysis has a thermal activation, photocatalytic reduction is activated by photons.

There are two types of: heterogeneous and homogeneous. The first one has the catalyst and the reactants in a different phase form, whereas the second one has the reactants and the photocatalysts exist in the same phase.

5.2.1. Principles of heterogeneous photocatalytic reduction

Heterogeneous photocatalytic reduction can be carried out in various media: gas, pure organic phase or aqueous phase.

The overall process can be decomposed into five different steps:



Graph 5.9: Scheme of Photocatalytic reduction process

There is also a step of activation, which is not considered in the previous scheme but now is going to be detailed. The photocatalytic activity is initiated by the absorption of light energy equal or higher than the band gap energy by semiconductors catalysts of the chalcogenide type (oxides, for instance TiO₂, ZnO, ZrO₂, CeO₂...or sulphides like CdS or ZnS for example). Unlike metals which have continuum electronic states, semiconductors have a gap of energy where there are no energy levels available to promote recombination of an electron and hole produced by photoactivation in the solid. The void, which extends from the top of the filled valence band to the bottom of the vacant conduction band, is called band gap. When excitation occurs across the band gap, there is a sufficient lifetime in the nanosecond scale, for the created electron-hole undergo charge transfer to adsorbed species on the semiconductor surface from solution or gas phase contact. If the semiconductor remains intact and the charge transfer to the adsorbed species is continuous and exothermic the process is called heterogeneous.[18]

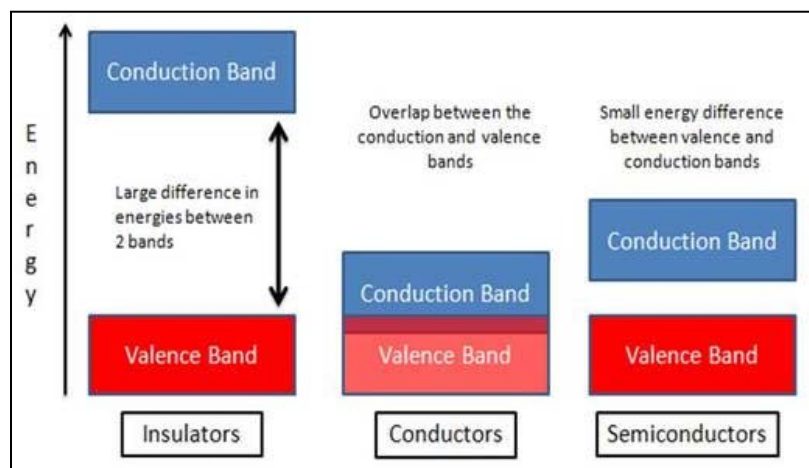
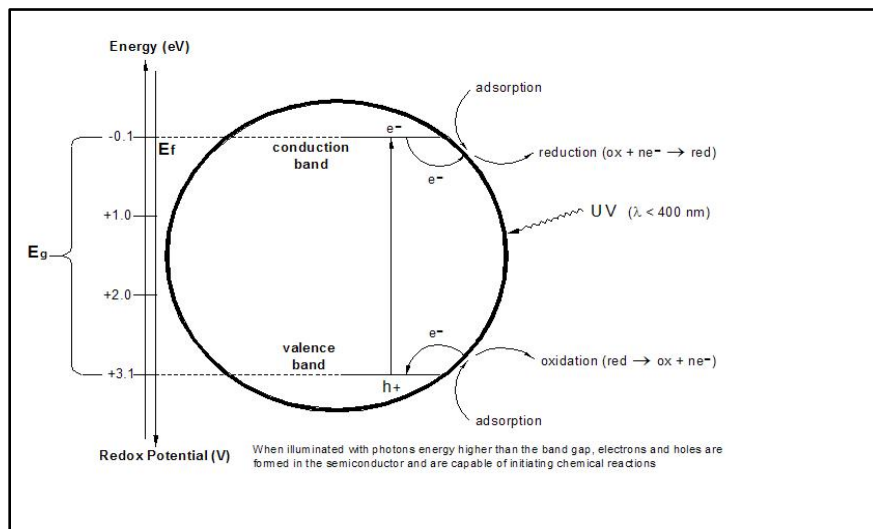


Fig 5.3: Scheme of conduction and valence band in different sort of materials [19]

At the same time occurs a spontaneous adsorption, according to the redox potential of each adsorbate, in the fluid phase. A electronic transfer proceeds towards acceptor molecules and photoholes are transferred to donor molecules. [20]



Graph 5.10: Scheme of photocatalytic reduction process in a molecular level [20]

In fig. 5.4 it is the reactions of the photocatalytic reduction and the respective reduction potentials:

reaction	$E^{0'}$ (V) vs SCE ^a
$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCO}_2\text{H}$	-0.85
$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.77
$\text{CO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{C} + 2\text{H}_2\text{O}$	-0.44
$\text{CO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.72
$\text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.62
$\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.48

^a $E^{0'}$ potentials are reported at pH 7.

Fig. 5.4: Reaction of CO₂ in photocatalytic reduction and the respective reduction potentials [21]

Photocatalytic reduction has several applications, including sterilization of surfaces, photocatalytic reduction with TiO₂ can kill bacteria and other pathogens, cancer treatment,

is one of the most important topics that is associated with photoreduction, cleaning odours, cleaning atmosphere are the main applications. [22]

5.2.2. Photoreduction of CO₂ with TiO₂

Titania has been used as a photocatalyst because of its many advantages including low price, high photostability, no toxicity and superior redox ability.[23] The earliest work that it has been found it was reported by Renz, at University of Lugano (Switzerland), who reported in 1921 that titania is partially reduced during illumination with sunlight in the presence of an organic compound such as glycerol. The proposed reaction was: [24]



Titania is still the preferred because of several advantages such as its low toxicity, ability to resist photo-corrosion, versatility in terms of applications and especially for the abundant availability and quantum yield. Several investigations are making great discoveries about the modification or sensitize TiO₂ in order to operate under irradiation of much larger visible light regions under sunlight. [25, 26]

5.2.2.1. The need for modifications

Unlike natural photosynthesis, photoreduction of CO₂ with TiO₂ use only 3-4% of the solar light that reaches earth, necessitating the use of a UV light source. For this reason, significantly investigations are underway to modify or sensitize TiO₂ to operate under irradiation of much larger visible light regions of sunlight. [25]

Apart of the needed of other regions of the spectrum, the life of the electron-holes pares is very short and the efficiency of the reaction decrease. Nobel metals have been reported to be very effective for enhancement of TiO₂ photoreduction, greatly reducing the possibility of electron-hole recombination, resulting in efficient separation and stronger photocatalytic reaction. [27]

Table 5.5: Characteristics of different modifications in titania [28]

Modifications	Characteristics	Examples
Doping of metals/ metal ions	<ul style="list-style-type: none"> • Increase the photocatalytic activity for both oxidation and reduction reactions • Acts as electron traps and facilitates carrier separation, photoreactivity increases • Introduces impurity states and induce visible light absorption 	Fe ³⁺ , Mo ⁵⁺ , Ru ³⁺ , Os ³⁺ , Re ⁵⁺ , V ⁴⁺ and Rh ³⁺
Doping of anions	<ul style="list-style-type: none"> • Narrowing of a band gap due to mixing of <i>p</i> states of dopants (N, S) with O 2<i>p</i> states in the valance band of TiO₂ • Introduces impurity states above the valance band of titania • Induces visible light absorption 	N, S ^{30,31} , C ^{32,23} , F ^{34,35} and B ^{36,37}
Coupling with semi-conductors	<ul style="list-style-type: none"> • A narrow band gap semiconductor, with appropriate energy levels, absorbs visible light and transfers excited electrons into the conduction band of titania • UV light source not needed 	Cu ₂ O, PbS, CdS and CdSe
Sensitization with light harvesting compounds/ dyes	<ul style="list-style-type: none"> • Certain organic dyes can absorb visible light and inject photo-excited electrons into the conduction band of titania • Besides visible light activity, effective separation of charge carriers is achieved 	Chlorophyll, erythrosine B, thionin or rose bengal

5.2.2.2. Materials and Methods

Due to the big amount of different types of TiO₂ is going to be detailed the method to prepare RM-TiO₂ as a representative example.

Preparation of catalysts:

RM-TiO₂ was prepared by sol-gel method, by slow drop wise addition of titanium isopropoxide into the hydrolysis medium consisting of cyclohexene, anionic surfactant (Triton-X-114) and distilled water. Molar ratio of cyclohexene: Triton:water:titanium isopropoxide was 11:1:1:1. The solution was stabilized for 15 minutes and then allowed to gel at ambient temperature for 24 hours, followed by calcination in air at 400°C for 4 hours to obtain RM-TiO₂.

Photocatalytic reaction:

The photocatalytic reactor (Fig. 5.1) was used to follow the reduction of CO₂ under radiation in UV-visible range 300-700 nm from a Hg lamp.

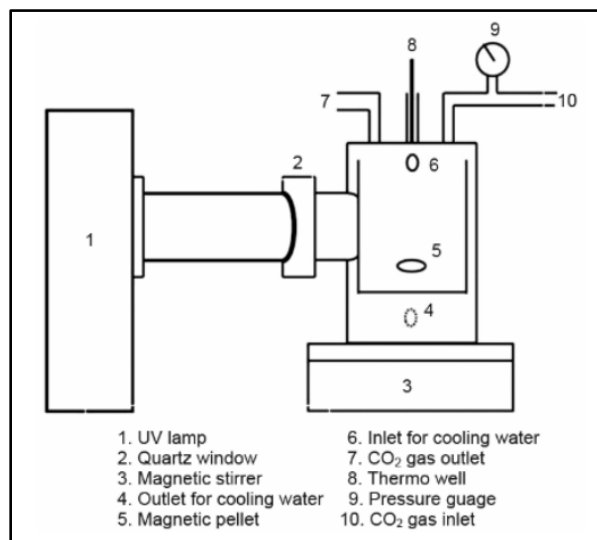


Fig. 5.5: Scheme of the photoreduction process made by Jeyalakshmi, V. Mahalakshmy, R. Krishnamurthy, K.R. Viswanathan, B published in Indian Journal of Chemistry[28]

Aqueous alkaline solution (at pH-13.0) was then saturated with pure CO₂ by continuous bubbling for 30 minutes after which the pH turned 8.0. After every two hours, gas samples were taken out and analysed by gas chromatography. Blank experiments were also done in order to ensure that the product formed was due to the photoreduction of CO₂. [28]

5.2.2.3. Experimental results with TiO₂

As there is a lot of modified TiO₂ is going to be shown some representative results of TiO₂ based photocatalysts.

K. Rajalakshmi, V. Jeyalakshmi, K.R. Krishnamurthy and B. Viswanathan published on 13th of January of 2012 in the Indian Journal the article '*Photocatalytic reduction of carbon dioxide by water on titania: Role of photophysical and structural properties*'. In table 5.1 is shown the physico-chemical characteristics of the catalysts and in table 5.2 is shown the results achieved. Their research was about photoreduction with three materials as photocatalysts, P-25, hydrophilic fumed titanium dioxide [29], Hombikat which is a nanocrystalline anatase titanium dioxide developed for photocatalytic applications [30] and RM-TiO₂ which is based on coarse rutile titanium dioxide powder [31].

Table 5.6: Results published in 2012 by K. Rajalakshmi and co, physic chemical characteristics [32]

Sample	Phase comp. (%)	Surface area (m ² /g)	Crystal size (nm)	Band gap (eV)
P-25	Anatase (85) Rutile (15)	50	22	3.02
Hombikat UV-100	Anatase	311	9	3.04
RM-TiO ₂	Anatase	48	12	3.06

Table 5.7: Results published in 2012 by K. Rajalakshmi and co. [32]

Catalyst	Yield ^a (μmol/g)			Total CO ₂ consumed
	CH ₄	CH ₃ OH	C ₂ H ₅ OH	
P25	0.7	914	0	915
Hombikat UV-100	0.3	118	53	216
RM TiO ₂	0.6	130	59	249

^aYields after 6 h of irradiation.

As it can be seen in table 5.7, methane and methanol is the major product formed for the three photocatalysts. The most effective catalyst is P25 which has the bigger crystal size and the smallest band gap among the three photocatalysts.

The same authors of the last article wrote '*Titania based catalysts for photoreduction of carbon dioxide: Role of modifiers*' on 12 June 2012. They publish the results of some photoreduction of CO₂ by water on metal doped semiconductor oxides (table 5.7).

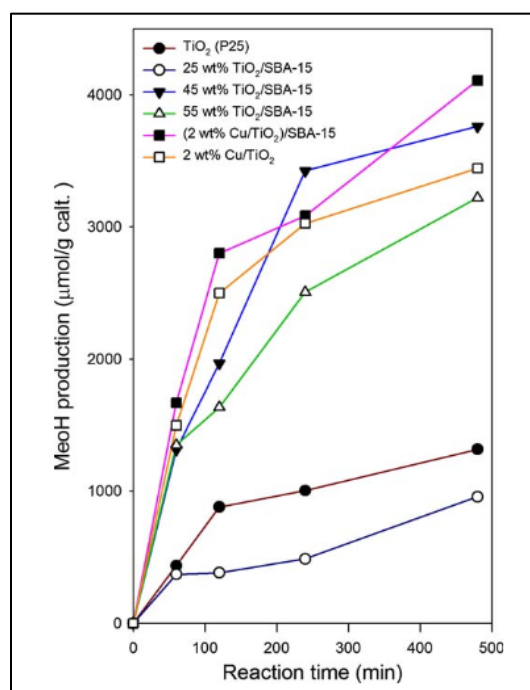
Table 5.8: Results published on 2012 by K. Rajalakshmi and co. [28]

Catalyst	Ratio of initial rates of product formation CH ₄ :H ₂ :CO
Pt/TiO ₂	1.2 : 8.0 : 0.0
Pt/SrTiO ₃	1.0 : 1.0 : 0.0
Rh/SrTiO ₃	1.0 : 250.0 : 0.0
Ag/SrTiO ₃	1.0 : 7.0 : 15.0
Pt-Ru/SrTiO ₃	1.0 : 6.0 : 1.2

It can be seen that the most effective catalyst is Pt/TiO₂, because what is wanted the major amount of methane or hydrocarbons possible, the H₂ formation is not due to the CO₂ photoreduction is because of water hydrolysis and CO is not the most valuable product it can be obtained.

Regarding reaction time, in 1999 Yang, H.-C.; Lin, H.-Y.; Chien, Y.-S.; Wu, J.C.-S.; Wu, H.-H. published their investigation about photoreduction of CO₂. They publish some results with different catalysts and different times of irradiation.

They experiment with different doped titanium dioxide and they performed the photoreduction with a peak light intensity at 365 nm mounted on an inner irradiation quartz cell. The photoreduction of CO₂ with water was performed in 550 ml aqueous 0.1 N NaOH solution containing about 0.05 g catalyst at 42°C. The initial pH value of 0.1 N NaOH solution was approximately pH 13. Then, CO₂ was bubbled through the reactor for at least 30 min to purge air and to saturate the solution. The pH value of the CO₂-saturated NaOH solution was nearly pH 7. To maintain CO₂ saturation during the reaction, CO₂ gas was bubbled into the reactor continuously, and the pH value of the solution was kept near pH 7 during the reaction. [33]



Graph 5.11: Relation between the methanol production and the reaction time [33]

It can be seen in the graph 5.11 the clear relation of the time, at more time higher production of CO₂ with all the catalysts.

About kinetics, various photocatalytic processes have been described by different kinetic models such as pseudo zero order, pseudo first order and second order models. The reason of pseudo relays in the kinetics constant, as it is needed a lot of simplifications, the k is called apparent kinetic constant.

The commonest decay models that are observed in photoreduction studies are the zero and the first order rate laws. Normally, the zero order is observed at surface saturation. Basically, the rate of a zero order reaction does not vary with concentration. Consistence of photocatalytic degradation reactions with second order model is not expected but this unusual case was reported in the photocatalytic degradation of Auramine O aqueous solutions over ZnO catalyst owing to constraints in fitting the kinetic data to other than the second order kinetics. [34]

About the activation energy is 0 or almost zero, about a few kilojoules. It depends on the range of temperatures, about -44 to 0°C the activity is decreasing and the E_a becomes positive, for temperatures between 20 and 80°C the E_a is very small (few KJ) and for high temperatures E_a becomes negative, the exothermic adsorption of the reactive becomes favoured and it is limiting the reaction. [35]

5.3. Zeolites

Zeolites are crystalline solid structures composed of pores and corner-sharing aluminosilicate (AlO₄ and SiO₄) tetrahedrons. The pores structure is characterized by cages approximately 12 Å in diameter, which are interlinked through channels about 8 Å. This structure give special properties to zeolites, adsorption, ionic-exchange, molecular sieve and catalytic properties, which make them ideal for the development of task such as filtering, odour removal, water softener or gas absorption. [36]

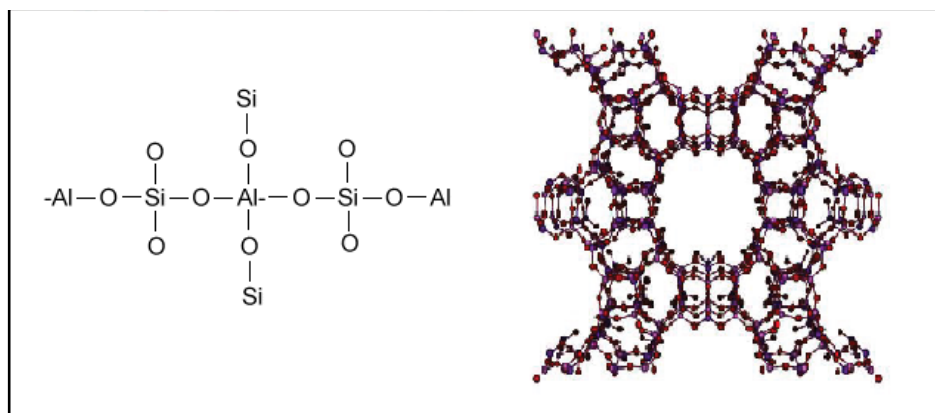


Fig. 5.6: Basic structure of zeolites [37]

Zeolites are able to absorb large amount of CO₂ due to the presence of alumina in the silica structure which induces a negative framework charge which is compensated for with exchangeable cations in the pore space. These alkali cations enable zeolites to absorb acid gases such as CO₂.

To date more than 150 zeolites have been synthesized (some of the most common artificial are zeolites A, X, Y and ZMS-5) and more than 40 types of natural zeolites have been reported (some of the most common clinoptilolite eronit, chabazite, mordenite and philipsite). [36]

5.3.1. History

In 1756, Fredrich Cronstet discovered the zeolites. He called the material 'Zeolites' from the Greek ζέω (*zéo*) and λίθος (*lithos*), meaning boiling stone, because he observed that after heating the material about 200°C it produced steam of water that have been absorbed before by the zeolite. From 1770s to 1800s several authors worked describing the properties of zeolites, in 1840 Damour observed that zeolites could be reversibly dehydrated without an apparent change in their transparency or morphology and in 1862 St. Claire Devill reported the first hydrothermal synthesis of levynite zeolite.

Friedel in 1896 observed that liquids like alcohol, benzene and chloroform were occluded by dehydrated zeolites thus he developed the idea that the structure of dehydrated zeolites consists of open spongy frameworks.

Weigel and Steinhoff in 1925 reported the first molecular sieve effect and in 1960s was when the commercial production began. [34, 36]

5.3.2. Natural zeolites

During the development of the earth layers of volcanic ash were exposed to high temperatures and pressure which provided the perfect conditions to create diverse groups of zeolites. The advantage of these groups of zeolites rely on its origin as it is a natural mineral it has a low toxicity, minimum biological risk and high stability. Because of its properties it can be used for agriculture and human and animal health, for instance several products has been developed using Clinoptilolite for a people who have diabetes and vascular diseases. [39]

Cuba, USA, Russia, Japan, Italy, South Africa, Hungary and Bulgaria have important resources of these minerals.

5.3.3. Artificial zeolites

Zeolites were first synthesized in the 1930s, but it was not until the 1960s when synthetic zeolite market materialized, when their large-scale began use for catalytic cracking in the petroleum refining.

Zeolites can be manufactured from kaolinitic clays thermally converted and suspended with sodium hydroxide and adding SiO₂. The main advantage of the synthetic zeolites is that controlling the process optimizes the zeolites for different applications. Higher SiO₂ generally gives greater hydrothermal stability, stronger-acid catalytic activity and greater hydrophobicity as adsorbents whereas lower SiO₂ gives greater cation exchange capacity and higher absorbance for polar molecules.


Artificial zeolites also have the advantage of the purity, impurities are costly to remove and natural zeolites have variable phase of purity and also chemical impurities which can make synthetic zeolites more attractive for specific applications.[38]

5.3.4. Clinoptilolite

In this research it has been working with the zeolite Clinoptilolite, it is a natural zeolite that belongs to a group called heulandite. Due to the high amount of pore spaces, high resistance to extreme temperatures and chemically neutral basic structure is suitable for several applications such as chemical sieve, feed and food additive and gas odour absorber.

It is a white, green, orange to red or colourless mineral, but the colour can change as function of the composition (see table 5.4). It is a serie of three minerals with the same name: clinoptilolite-Ca, Clinoptilolite-K and clinoptilolite-Na the mix of these three minerals form the actual clinoptilolite, however the composition of Na, Ca and K can vary depending on the place and on the age of the rock.

Table 5.9: Pictures of clinoptilolites from different places [37]

		
<p>Clinoptilolite-K Richardson's Ranch north of Madras, Jefferson County, Oregon, USA. Width of view 5 mm.</p>	<p>Clinoptilolite-Ca Cape Lookout, Tillamook Co., Oregon, USA</p>	<p>Clinoptilolite-Na Rodalquilar, Nijar, Almería, Andalucía, Spain</p>

5.3.4.1. Properties

Clinoptilolite has properties such as ion exchange capacity, high absorption level, dehydration activity and easily shapeable features which make it very important in plant production. The chemical composition and some properties of Clinoptilolite are detailed below in table 5.5.

Table 5.10: Properties of clinoptilolite and location in central Europe [37]

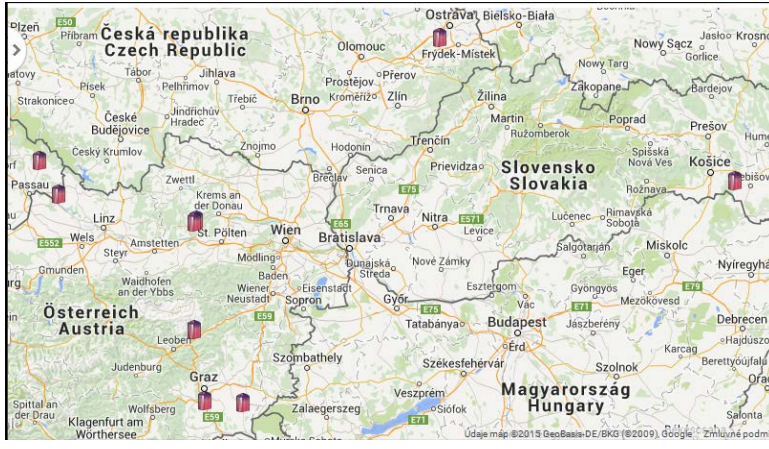
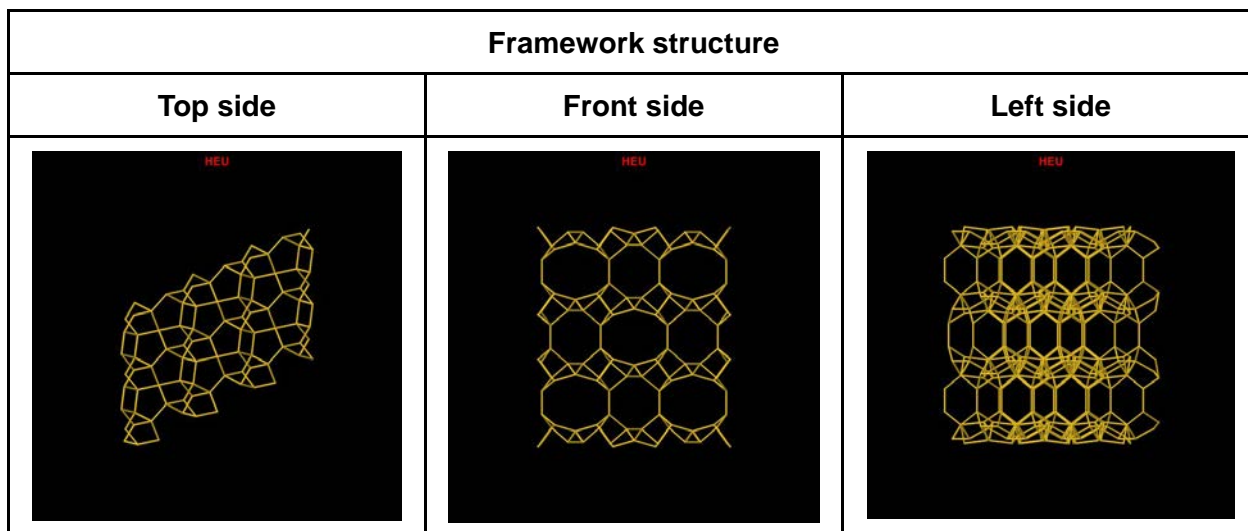
Chemical formula	(Ca,Na,K) ₂₋₃ Al ₃ (Al,Si) ₂ Si ₁₃ O ₃₆ •12(H ₂ O)
Empirical formula	Ca _{1.9} Na _{1.76} K _{1.05} Mg _{0.17} Al _{6.72} Si _{29.2} O ₇₂ •23.7(H ₂ O)
Composition	Potassium: 1,50% Sodium: 1,48% Calcium: 2,78% Magnesium: 0,15% Aluminium: 6,61% Silicon: 29,91% Hydrogen: 1,74% Oxygen: 55,84%
Crystal system	Monoclinic-prismatic C2/m
Porosity	34%
Specific gravity	2,15-2,25 g/cm ³
Bulk density	1,15 g/cm ³
Ion exchange capacity	2,16 meq/g
Location in central Europe [40]	

Table 5.11: Structure of clinoptilolite from different sides [37]



5.3.4.2. Applications

As it has been said before, clinoptilolite has several applications; one of the most important is in the field of agriculture. Clinoptilolite improves the efficiency of used fertilizers, promotes better plant growth and enhances the yield, helps to retain nutrients and improves the long term soil quality.

This zeolite also has properties of gas absorber thus can be used as control odours or collecting them. For instance clinoptilolite is used in intensive animal husbandry sheds in order to reduce the content of ammonia and sulphuric acid. It can be used in filtration systems or simply over the water surface being that is totally harmless to water life.

Water absorption is also one of the important properties of clinoptilolite. Zeolites can hold water up to 60% of their weight due to his high porosity of the crystalline structure. Water molecules in the pores could easily evaporate without damage to such structures. This property makes also clinoptilolite the best candidate for carry agricultural pesticides. [36]

Clinoptilolite absorb toxins which can be dangerous to animals, it is demonstrated that the use of this zeolite as animal feed additive improves the weight gain and increases feed conversion ratios. Clinoptilolite application is not restricted to animals but an anti-diarrheic drug (ENTEREX) has also been developed for humans. [41]

6. Experimental part

6.1. Materials, reagents and equipments

6.1.1. Thiophene and polythiophene

One of the materials used for doping the clinoptilolite is thiophene, it is a cyclic compound which its molecular formula is C₄H₄S and its molecular weight 84,14g/mol. [42] It is one of the simplest aromatic compounds and it shares some chemical properties with benzene. At room temperature it is colourless, liquid and with an odour reminiscent of benzene. [43]

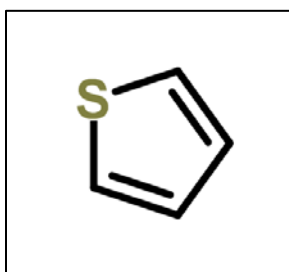


Fig. 6.1: Molecule of thiophene [44]

The boiling point of thiophene is 84°C (Oxford University Chemical Safety Data), the melting point is -38°C (Oxford University Chemical Safety Data) its density is 1,065g/l at 20°C and it is miscible in ethanol, ether, benzene and acetone [44]. Thiophene is a chemically stable compound it does not undergo the oxidation of typical a sulphides, but it undergoes electrophilic substitution: nitration, halogenation and sulfonation. [43]

If thiophene is polymerized, polythiophene (PT), it can act like an organic semiconductor material, PT is an environmentally stable conjugated polymer which gives rise to cation radicals through photoactivation when rapid subsequent reactions are stimulated by a released electron. [45]

There are three approaches for polymerization of thiophene: (1) electropolymerization, (2) metal-catalyzed coupling reactions and (3) chemical oxidative polymerization. [46] In this research it is going to be used the third approach, because it is wanted to polymerize the thiophene in the cavities of the zeolites in the laboratory, hereby chemical oxidation is the fastest and easiest way to do it. Chemical oxidative polymerization consists in adding a salt of a transition metal with the same oxidative potential of the monomer in a solution of

chloroform or pyrrole with the monomer, in this research it is going to be used Fe³⁺ as the transition metal and chloroform.

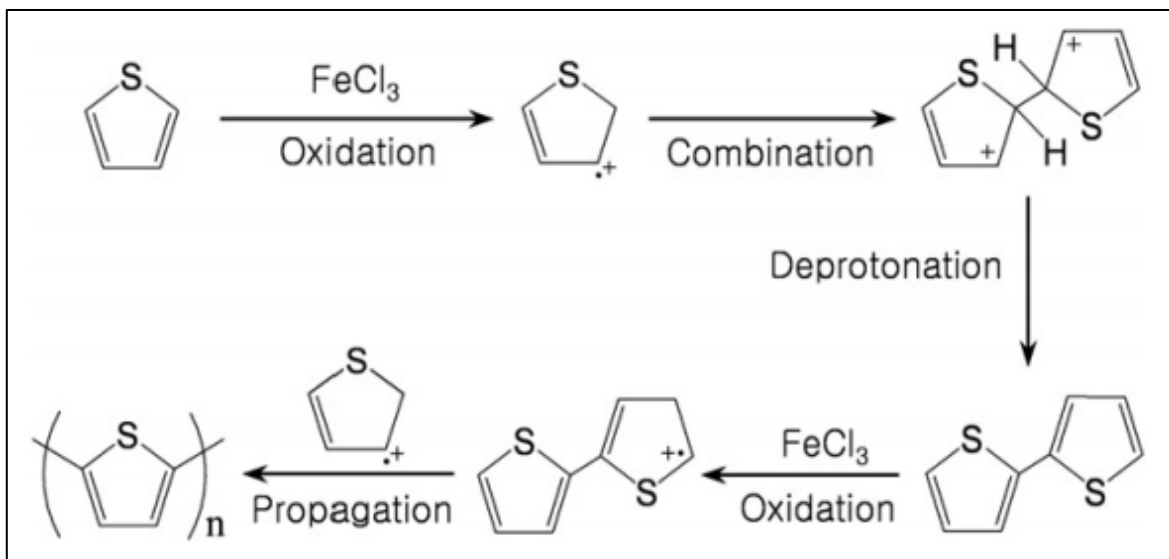


Fig. 6.2: Reaction of polymerization of thiophene [47]

It can be seen in fig. 6.2 the reaction of polymerization of PT, which is a three step chain reaction. First stage consists of an oxidation breaking a double bond and adding a charge in one carbon, the second step consist of a combination where couple of molecules are joined, then a third step is running by forming again the double bond before broke it by deprotonation. The process is repeated until one of the reagents is wasted.

In this research the important characteristic of PT is the absorption spectrum because on this will depend the lamp, and if it is running or not with only solar light

.In fig. 6.3 it can be seen also the relation between the temperature and PT absorption parameter. It can be seen that if the temperature increases the wavelength rises and the absorption decreases.

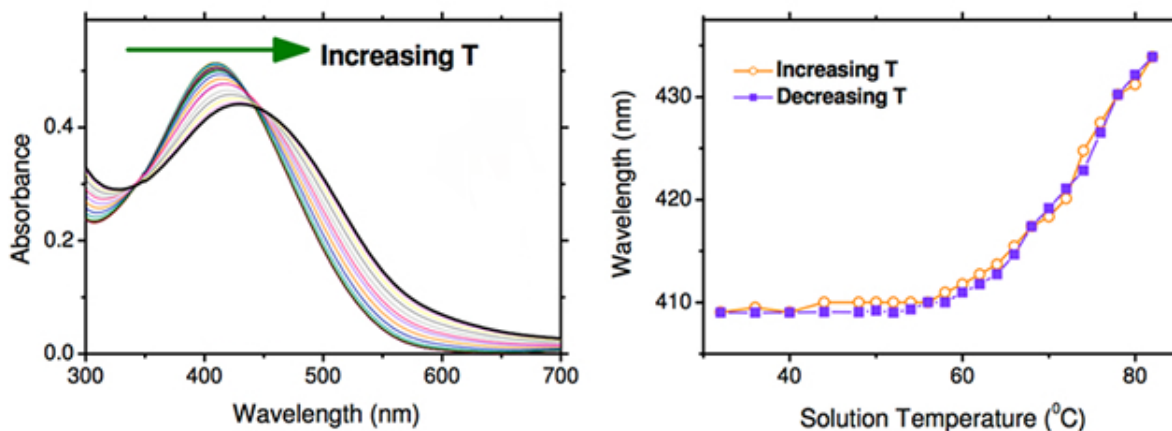


Fig. 6.3: Absorption spectrum of polythiophene and dependence on temperature

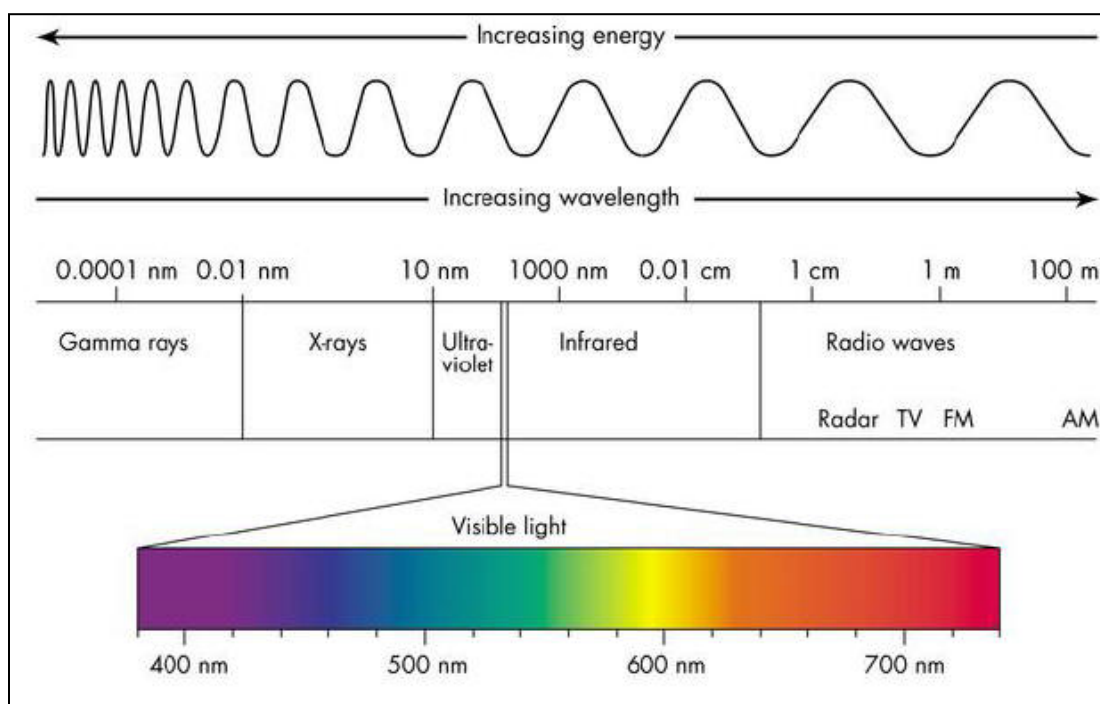


Fig. 6.4: Light spectrum [48]

It can be seen in fig. 6.3 that PT absorbs light from a little less than 400nm to 500nm approximately, corresponding to UV and visible light as it can be seen in fig. 6.4. The spectrum of solar light is from 300 nm up to 2000 nm with the biggest energetic part between 300 nm and 1000 nm [49], so it means that PT is a optimal polymer for photoreduction because its absorption spectra is within the border which sun emits.

6.1.2. Iron chloride

Iron chloride or ferric chloride (FeCl₃) is an inorganic compound formed by three atoms of chlorine attached into one atom of iron. Its molecular weight is 162,204 g/mol, it is dark brown [50]. The melting point of the FeCl₃ is 37°C [51] that is the reason this compound should be saved in the fridge.

Iron chloride is used in order to induce the redox reaction and to help the polymerization of tiophene by oxidation. Polymerization with FeCl₃ is more suitable in this research because it is not essentially to have the pure monomer of tiophene, it is better for large scale and gives high weight monomers. [52]

6.1.3. Chloroform

Chloroform CHCl₃ is a chemical reagent which molecular weight is 119.37764 g/mol it is liquid at room temperature colourless and it has a characteristic smell. [53]

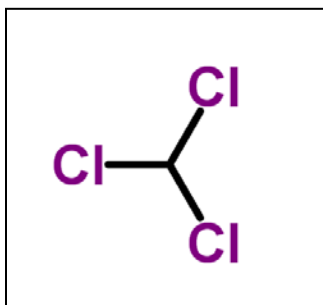


Fig. 6.5: Molecule of chloroform

It is used chloroform in this research because tiophene is soluble in that.

6.1.4. Reagents

- NaOH solution 0,1M: Solution made from solid NaOH pellets, it was weighted 1 g of NaOH and it was placed into a volumetric flask and filled with distilled water until the meniscus line (100 ml).
- HCl solution 0,1M: Solution made from a concentrated solution of HCl (36%). It was placed with a pipette 2,15 ml of the previous solution into a volumetric flask and filled with distilled water until the meniscus line (100 ml).

6.1.5. Equipment

- General volumetric material of laboratory such as funnel, spatula, Erlenmeyer flasks, beakers, etc.
- Precision balance METTLER
- Magnetic stirrer
- Ultrasonic mixer SILVERCREST
- Lamp which the following spectrum

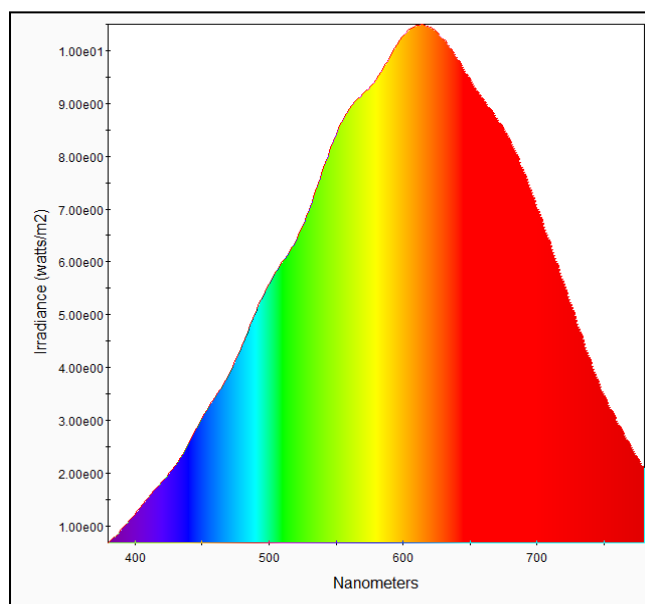


Fig. 6.6: Lamp spectrum

- Thermometer
- Spectrophotometer for COD

6.2. Methods

6.2.1. Measurement of the CO₂ and HCO₃⁻ dissolved in water

In order to know the conditions for dissolving the maximum amount of CO₂ in water, it has been made several experiences changing the conditions. The methodology was almost the same, only some parameters detailed below were changed.

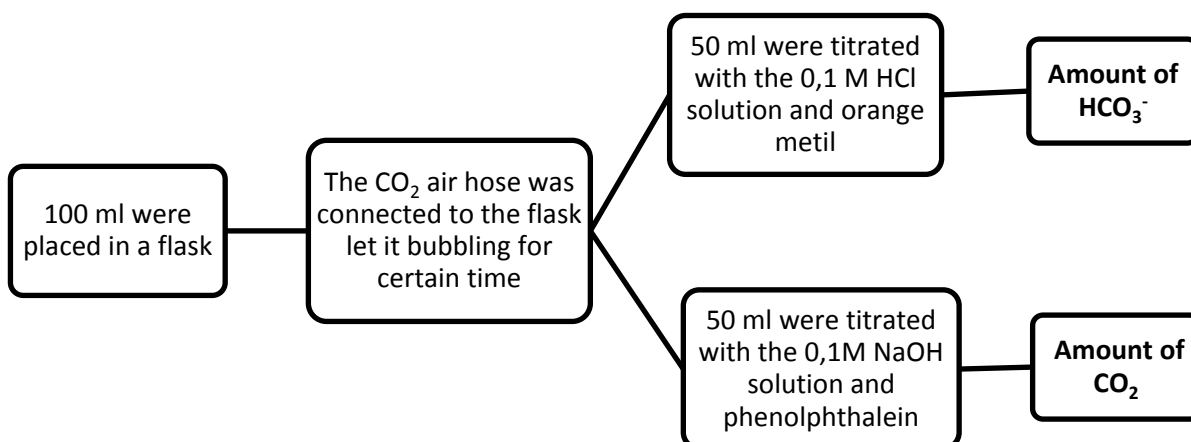
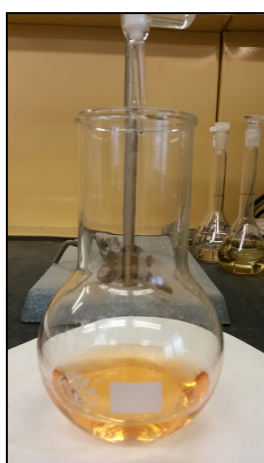


Fig 6.7: Process scheme of the titrations

Bubbling CO₂

After titration with orange metil



After titration with phenolphthalein

Fig. 6.8: Pictures of the different steps of the process

6.2.2. Modification of the zeolites

Clinoptilolite was modified polymerizing tiophene with FeCl₃ at room conditions. First 5 g of zeolites were weighted with the precision balance and placed into a flask, in the next step 50 ml of chloroform were added too and a magnetic bar in order to mix it with the ultrasonic mixer and afterwards with a magnetic mixer (except the first zeolites, which didn't remain on the magnetic mixer). The solution was mixed 30 min and 1 g of FeCl₂ was added. After 1 hour mixing the tiophene was added, passed 1 hour and 30 minutes after adding the first millilitre of tiophene if the solution is not dark enough another millilitre it is

added. The mixture was left 4 hours in the ultrasonic mixer and then it was placed in the magnetic stirrer and was mixed all the night and part of the morning, 10 hours in total.

Next step was filtration of the mixture with distilled water, a funnel and filtration paper, until the water of the filtration was totally transparent. Then the zeolites were putted in the oven at 100°C and let it dry for 1h. When the zeolites were totally dry they were placed into a jar.

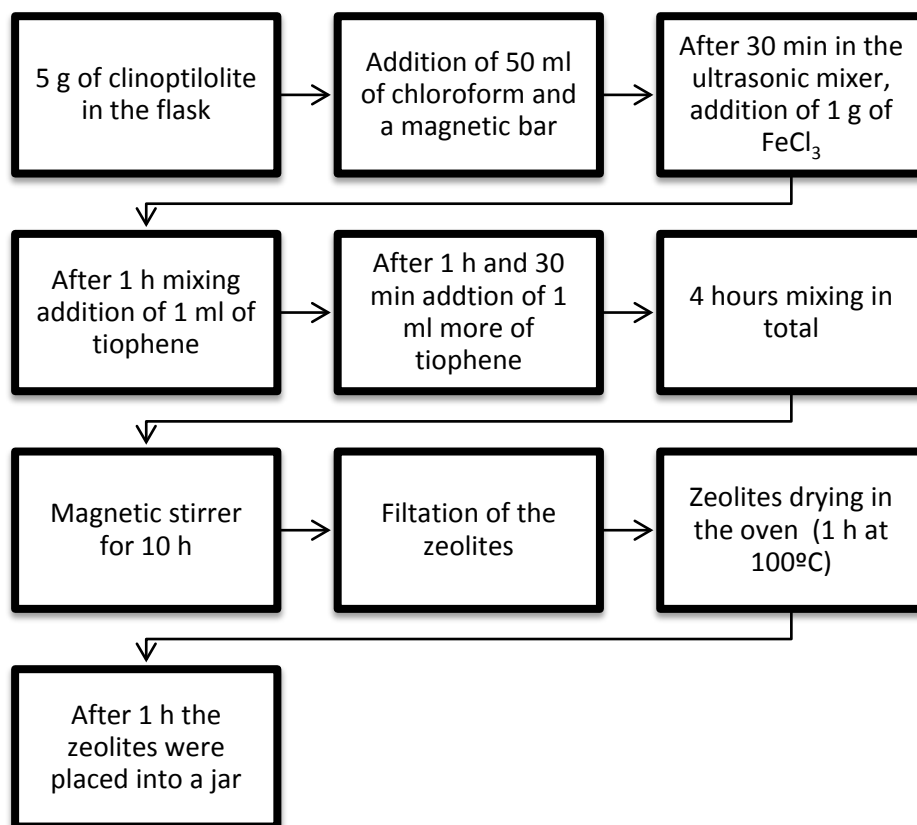


Fig. 6.9: Process scheme for doping the zeolites

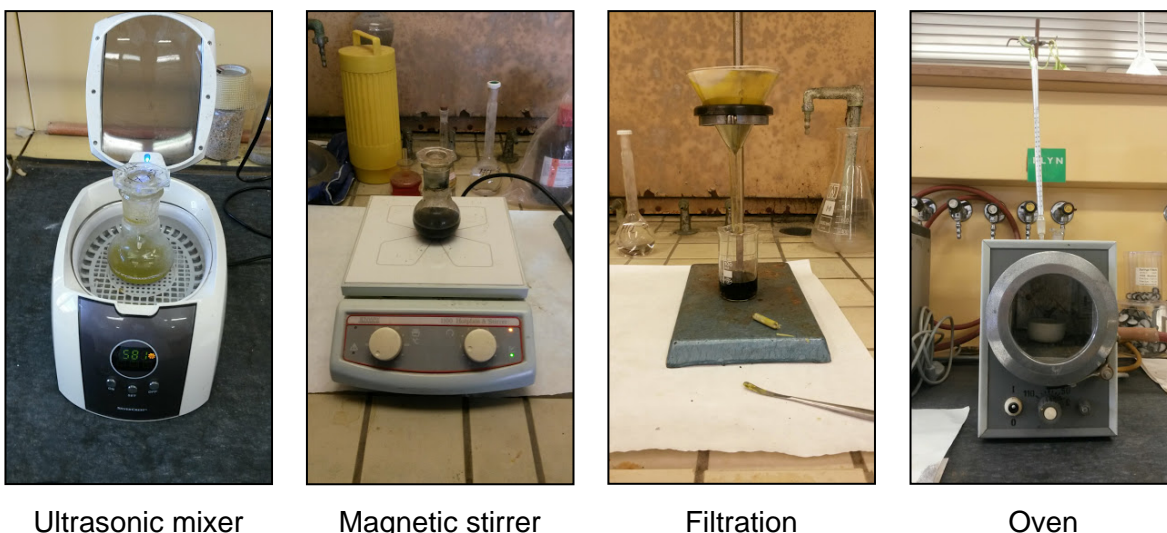


Fig. 6.10: Pictures of the different steps of doping the zeolites

6.2.2.1. Types of zeolites

In this research it has been working with two types of zeolites, the first one is a kind of zeolite which one has smaller particles and other ones that has bigger size of particles. Among the first group it is also a difference between the doping of the zeolites, below it is shown the characteristics of each one.

Table 6.1: Characteristics of the different types of zeolites

1st zeolites	Particles size:	<0,25 mm
	Type of modifying:	As it is explained in 6.2.2 but without the step of magnetic mixer for 10 h.
2nd zeolites	Particles size:	<0,25 mm
	Type of modifying:	Standard procedure (6.2.2)
3rd zeolites	Particles size:	0,3 - 1 mm
	Type of modifying:	Standard procedure (6.2.2)



Fig. 6.11: Picture of the different zeolites, from first zeolites to third zeolites starting from left

6.2.3. Evaluation of the relation between the pH and CO₂ dissolved in water

For the study of the relation of pH in the solubility of CO₂ it was done a series of experiments like the one explained in the part 6.2.1, but only measuring the CO₂ and changing the pH of the water adding NaOH for basic water and HCl for acid water.

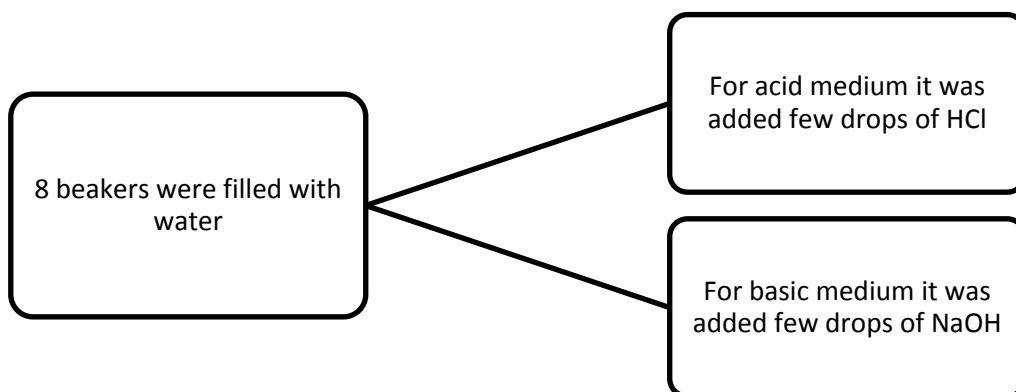


Fig. 6.12: Scheme of the process for changing the pH

After having the desired pHs CO₂ was bubbled for 20min and following the method explained in part 6.2.1 it was determined the amount of CO₂ dissolved.

6.2.4. Evaluation of the relation between the temperature and the CO₂ dissolved in water

In this case the experiment explained in the 6.2.1 part was repeated again only measuring the CO₂. It was also performed by a series of beakers with distilled water at different temperatures and it was bubbled CO₂ and then titrated.

6.2.5. Photocatalytic reduction of CO₂

The photoreduction was performed as the scheme 6.7 represents, first certain amount of the modified zeolites were weighted and placed into a flask filled with 100 ml of distilled water. The water with the zeolites was bubbled with CO₂ for 20 min, and after that the lamp was switched on and the really photoreduction started. From time to time the samples were taken. The total duration of the experiment was 4 hours.

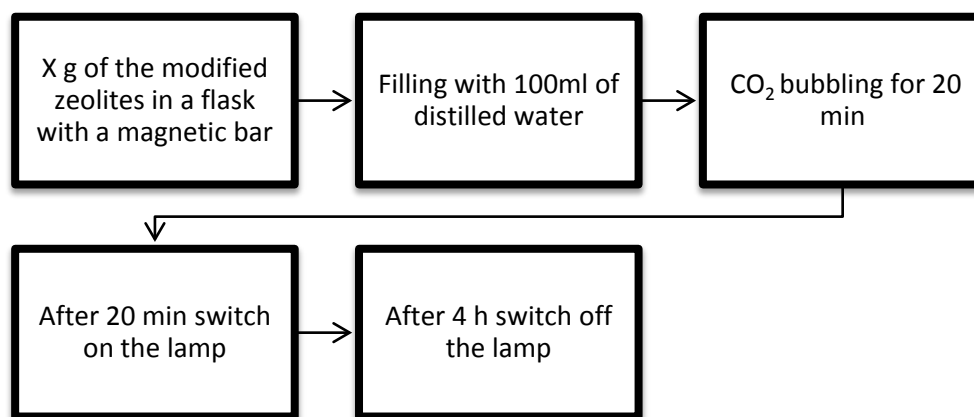
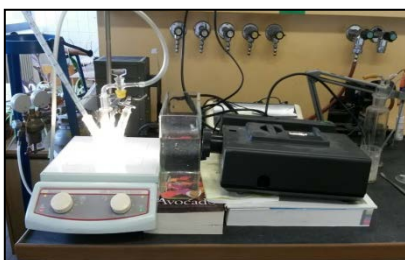


Fig. 6.13: Photoreduction scheme



Photoreduction



Photoreduction flask



Samples

Fig. 6.14: Photoreduction pictures

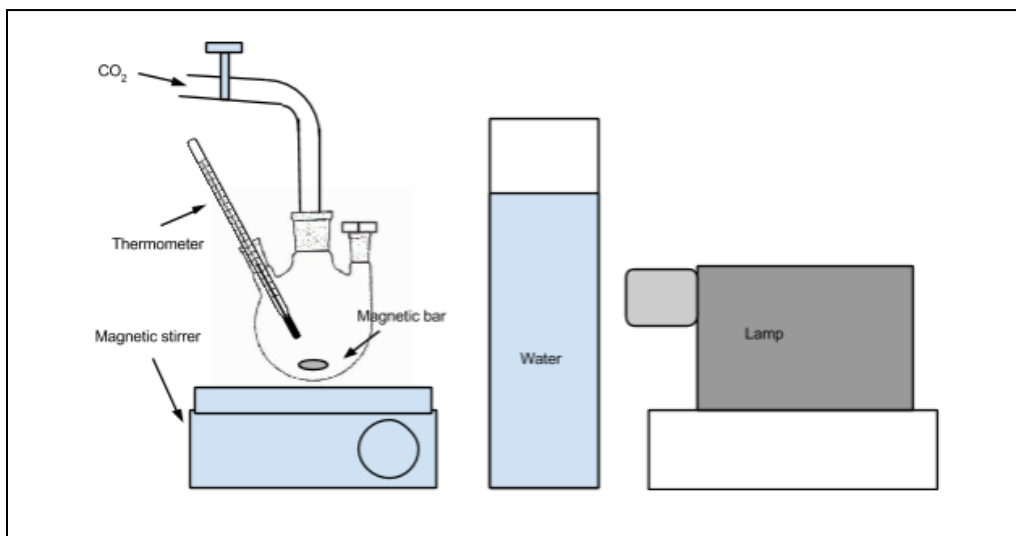


Fig. 6.15: Scheme of the experiment

6.2.5.1. Photocatalytic reduction with cold water

In order to perform the experiment with cold water, the photoreduction flask was placed into a cooling bath. A bigger flask was filled with cold water and ice and the flask with the zeolites and the water was settled inside.

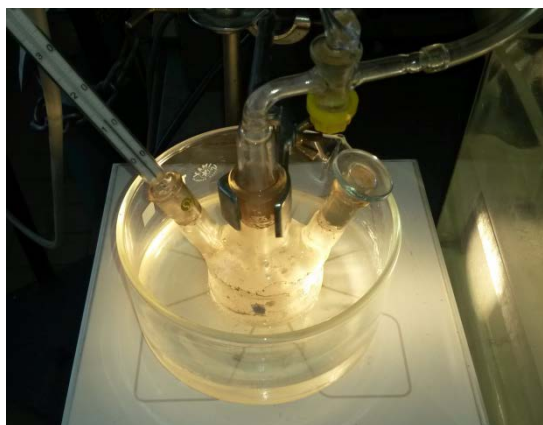


Fig. 6.16: Picture of the equipment for cold photoreduction

6.2.6. Measurement and calculation of the COD

For the determination of COD it was used the dichromate method. In order to proceed it is needed an oxidant solution, in this case it was prepared following the next steps:

1. It was added 10,2148 g of dry K₂Cr₂O₇, 167 ml of H₂SO₄ concentrated and 33 g of HgSO₄, into a beaker with 500 ml of distilled water.

2. The mixture was cooled down carefully and placed into a 1000 ml volumetric flask and filled it up with distilled water.
3. 10 g of Ag₂SO₄ were added into 1000 ml of concentrated H₂SO₄. The mixture was agitated couple of times and it was let dissolved slowly for approx. 24 hours.

Once the oxidant solution is ready, 2 ml of the sample which is wanted to analyse is placed onto this solution, it is mix it carefully, because is an exothermic reaction and the tub becomes very hot. The test tubes are placed in an over and they are heated at 148°C for 2 hours. When the test tubes are ready the absorbance can be measured with the spectrophotometer at a wave length of 600 nm.

Once the absorbance value is known, the COD value has to be calculated with the calibration curve of the machine which is:

$$E = ac + b$$

Eq. (VII)

Where E is the absorbance measured minus the absorbance of the blank, a and b are constants 0,0004 and 0,0069 respectively and c is the COD expressed in mg/l or ppm.

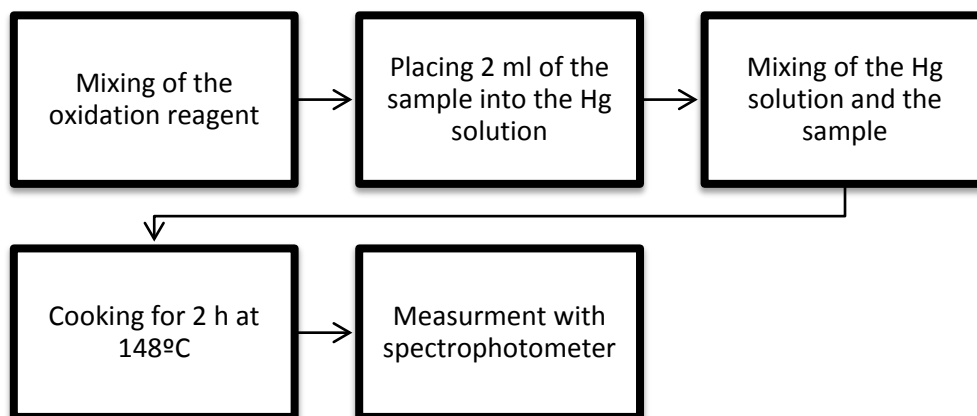
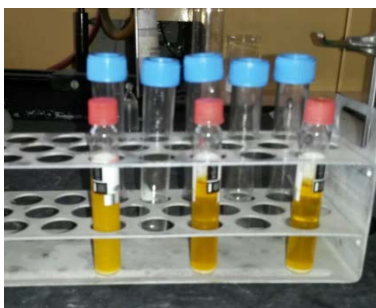


Fig. 6.17: Scheme of the measurement of COD



Oxidant reagent



Baker



Spectrophotometer

Fig. 6.18: Pictures of the different steps for the COD procedure

6.2.7. Kinetics

To determine the speed of the reaction (k) and the order of that, it was used the procedure explained in part 6.2.5. Samples were taken from time to time and titrated with the solution of NaOH and phenolphthalein, to know the amount of CO₂ reacted.

As there are a lot of reactions occurring at the same time in photoreduction it was decided to simplify the reaction as much as possible (Eq. VI). It was determined the disappearance of CO₂, counting all the organic compounds as one because the stoichiometry of every reaction is one (see fig. 5.4) and calculating all the constants of every reaction will be hard work, and it is only pretended to know the trend of the reaction in general [54]. It was also assumed that it is a one step reaction and that it is occurring on a uniform surface area.



6.2.7.1. Order and rate of the reaction

The order of the reaction helps to know the dependence on the reactants in the speed of the reaction. The rate of the reaction links the concentration or the pressure (if the reactant/s is/are gasses) with the kinetic constant.

The typical rate equation is:

$$r = k[A]^x[B]^y \dots \quad \text{Eq. (IX)}$$

Where r is the rate of the reaction ($\text{dm}^3 \cdot \text{s}^{-1}$), k is the kinetic constant (units for the kinetics constant: order 0 $\text{mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$, order 1: s^{-1} and order 2 $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$), $[A]$, $[B]$... are the concentration of the reagents and x , y are the stoichiometric coefficients of the reaction. If a mass balance it is applied in the case of photoreduction being N the reagents:

$$r_i = \frac{d[N_i]}{dt} \quad \text{Eq. (X)}$$

Other parameter that is interesting is the half time reaction ($t_{1/2}$); it measures the time it takes for the concentration of the substance to fall to half of its initial value.

There are several methods to calculate these parameters, in this research is going to be used the integrated form for the calculation of the kinetic constant and the differential form to calculate the rate of the reaction.

Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k [A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \rightarrow P$	second	$\frac{1}{2} \frac{d[A]}{dt} = -k [A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
$A + B \rightarrow P$	second	$\frac{d[A]}{dt} = -k [A][B]$	$kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$

Fig. 6.19: Equations to calculate the order of the reaction [55]

Zeroth order reaction	$t_{1/2} = \frac{[A]_0}{2k}$
First order reaction	$t_{1/2} = \frac{\ln 2}{k}$
Second order reaction	$t_{1/2} = \frac{1}{k[A]_0}$

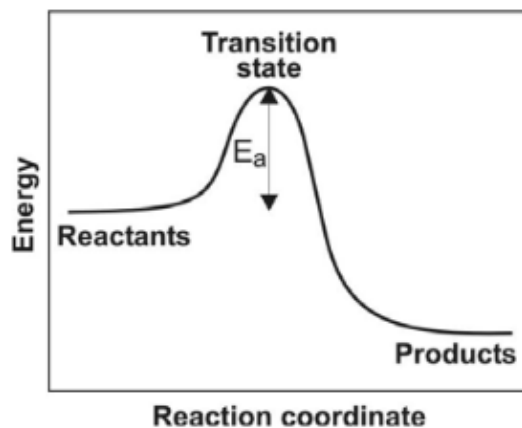
Fig. 6.20: Equations to calculate the half time [55]

In this research to know the order of the reaction was plotted the concentration of CO₂ against the reaction time, $\ln[\text{CO}_2]/[\text{CO}_{20}]$ against the time and $1/[\text{CO}_2]$ against time too. After having the curves it was checked the parameter R^2 and determining the order according to the curve which was better adjusted.

As it is said before, when we are talking about kinetics of photoreduction with that amount of simplifications what is calculated is the apparent k .

6.2.7.2. Measurement and calculation of the activation energy

The activation energy is the difference between the reactant and the transition states and describes the temperature dependence of the overall reaction rate. The higher activation energy means the higher dependence on the temperature and if the reaction has zero activation energy it means that has no relation between the temperature and the rate.



Graph 6.1: Activation energy

It was followed the same procedure of 6.2.7.1 with different temperatures. Once the kinetic constants were calculated it was applied the Arrhenius equation:

$$k = A \exp\left(-\frac{Ea}{RT}\right) \quad \text{or equivalently} \quad \ln k = \ln A - \frac{Ea}{RT} \quad \text{Eq. (XI)}$$

Where Ea is the activation energy, A is the Arrhenius constant and R is the constant of the gasses which is 8,3144 J/(mol·K). It was plotted the lnk against 1/T, the intercept is lnA and the slope is Ea/R.

If there is a limited amount of data, the case of this research, the equation can be simplified:

$$\ln \frac{k_1}{k_2} = \frac{Ea}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Eq. (XII)}$$

In this case the reaction is photoreduction so it can be expected that the rate of the reaction will be high and the energy reaction low due to the job of a catalyst is reducing the activation energy.

6.3. Results and discussions

6.3.1. Solubility of CO₂ in water

Several experiments were performed in order to figure out the relation between the temperature and the pH, and find the optimal conditions for dissolved the maximum amount of CO₂ in water to get the best possible yield.

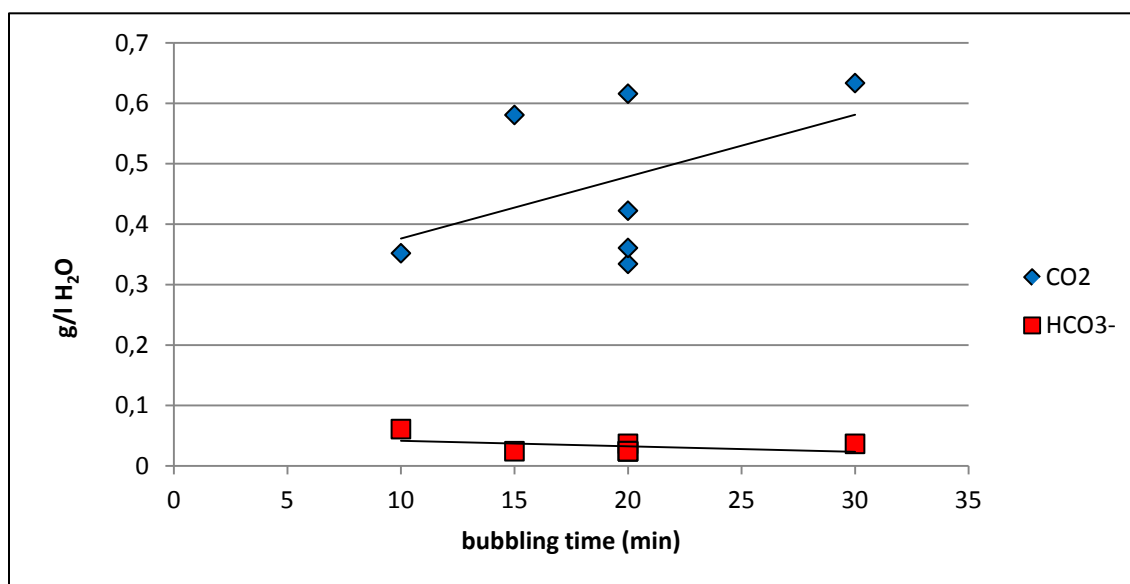
6.3.1.1. Temperature and bubbling time dependence

It was followed the procedure explained in 6.4.1, first the experiment was performed without any zeolite inside the flask and after zeolites were placed inside and the experiment was repeated to compare solubility.

The first parameter that was changed was the bubbling time; it was wanted to know the relation between the solubility of CO₂ and HCO₃⁻ and this variable.

Table 6.2: Results of the first experiment changing the bubbling time and without zeolites

bubbling time (min)	V _{NaOH} (ml)	V _{HCl} (ml)	g CO ₂ /l	g HCO ₃ ⁻ /l
10	4	0,5	0,352	0,061
20	7	0,3	0,616	0,0366
20	3,8	0,2	0,3344	0,0244
20	4,1	0,2	0,3608	0,0244
20	4,8	0,2	0,4224	0,0244
30	7,2	0,3	0,6336	0,0366
15	6,6	0,2	0,5808	0,0244

Graph 6.2: Relation between the bubbling time and the solubility of CO₂ and HCO₃⁻ without zeolites

It can be seen a slight trend for both compounds, but the opposite relation. For CO₂, it can be seen that as longer bubbling time more CO₂ dissolved. For HCO₃⁻ is the opposite, the longer bubbled less solubility of this compound.

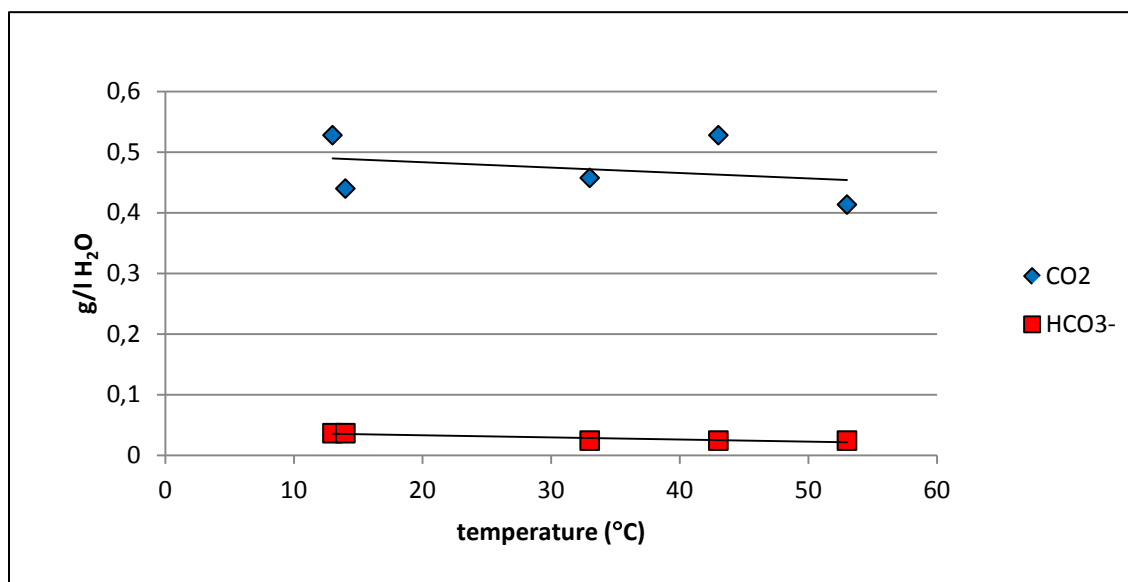
This decreasing relation of the solubility of HCO₃⁻ can be due to pH, as graph 5.1 shows the equilibrium of HCO₃⁻ changes with the pH, it can happen that as long as CO₂ is bubbled other compounds are forming and they change a bit the pH moving the equilibrium.

One drawback of this experiment is the volatility of CO₂, it can happen that part of the CO₂ dissolved in water is again converted into gas before titration not being able to measure all the amount of CO₂ dissolved.

The second parameter to change was the temperature, as it is shown in graph 5.2 it was wanted to know if in this case was also the same the higher temperature the less solubility and for lower temperatures the opposite.

Table 6.3: Solubility for different temperatures

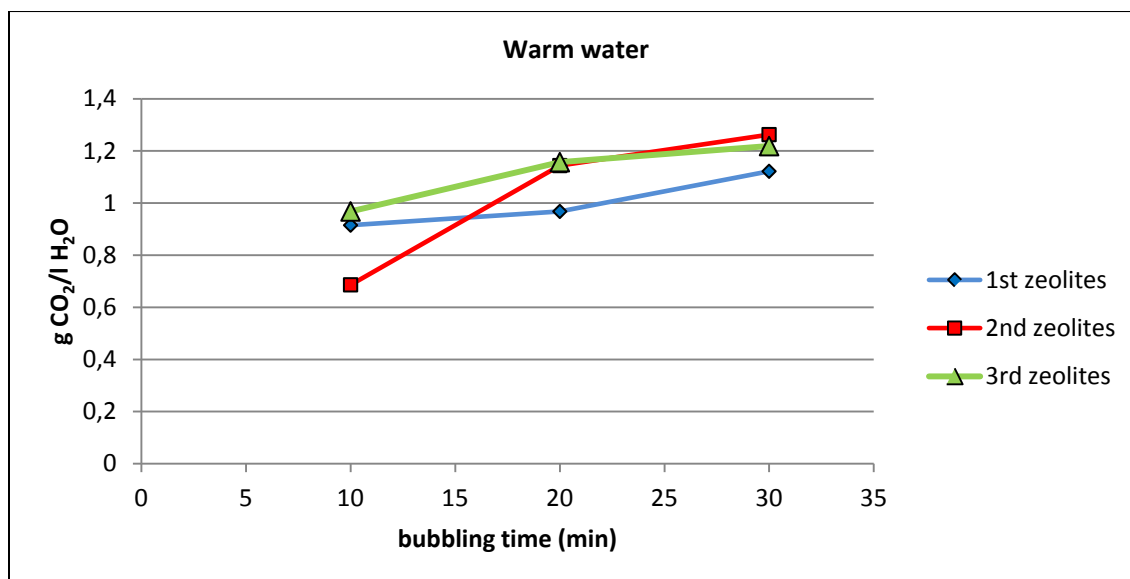
T (°C)	V _{HCl} (ml)	V _{NaOH} (ml)	g HCO ₃ ⁻ /l	gCO ₂ /l
13	0,3	6	0,0366	0,528
14	0,3	5	0,0366	0,44
33	0,2	5,2	0,0244	0,4576
43	0,2	6	0,0244	0,528
53	0,2	4,7	0,0244	0,4136



Graph 6.3: Relation between the bubbling time and the solubility of CO₂ and HCO₃⁻ without zeolites

Data reveal that there is not outstanding relationship between the temperature and the solubility, at least in these experiments. It can be seen in both compounds a low trend for decreasing the solubility at high temperatures but it cannot be said something clear. Perhaps it is needed more range of temperature to verify this relation or a constant temperature in all the experiments, in this case the temperature suffered small fluctuations.

After these experiments, all the zeolites were tested with the same procedure explained before. The experiments were performed with 0,15 g of zeolites, with different temperatures, warm water, which means from 20 to 23°C and cold water, which means from 13 to 16,5°C and changing the bubbling time.



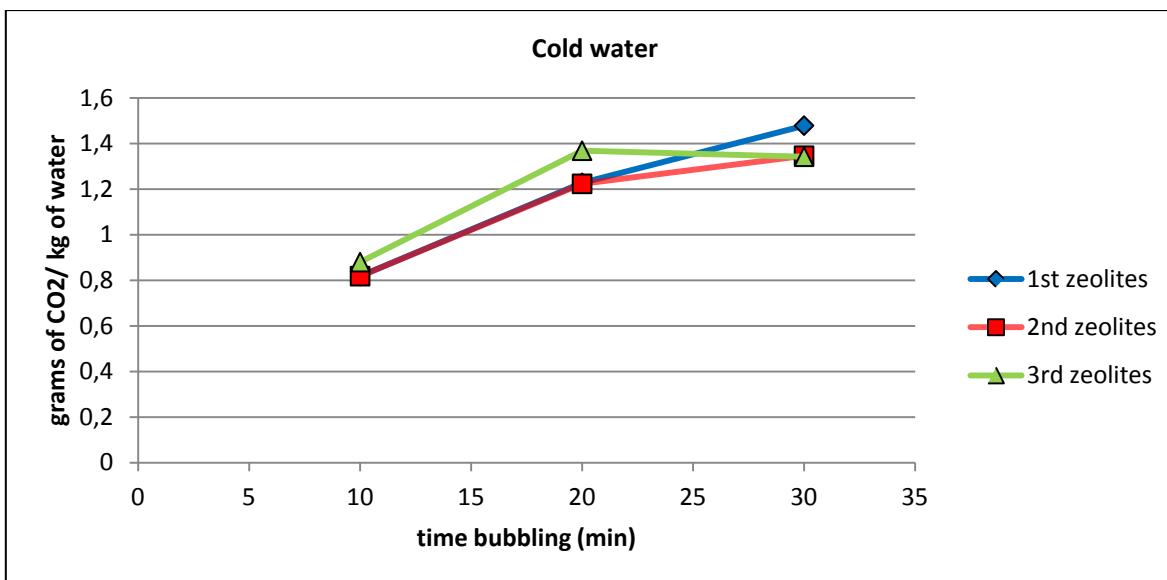
Graph 6.4: Plots of the amount of CO₂ dissolved with different zeolites, bubbling times and warm water

Table 6.4: Results for the CO₂ dissolved in warm water with different zeolites

Warm water			
	1 st zeolites	2 nd zeolites	3 rd zeolites
time bubbling (min)	g of CO ₂ /l water	g of CO ₂ /l water	g of CO ₂ /l water
10	0,9152	0,6864	0,968
20	0,968	1,144	1,1572
30	1,122	1,2628	1,2188

It can be seen in graph 6.4 the different between the zeolites with warm water. For 10 min bubbling the zeolites which dissolves more CO₂ are the third ones very close to the first ones and the worst for that time are the second one. But for 20 min it changes, now the zeolites which absorb less amount of CO₂ are the first ones and the third and the seconds are able to dissolve equal amount of CO₂. Last but not least, for the longest time bubbling, 30 min, the zeolites which absorb more amount of CO₂ are the second ones, followed by the third one and the worst ones are the first ones.

The second zeolites are the ones which have more slope on the first part of the calibration curve, it means that they can absorb CO₂ quicker the first 20 min, and the first and the third ones absorb the CO₂ more slowly. Although the last 10 min almost all the slope are the same, so the speed of dissolving CO₂ is approximately the same.



Graph 6.5: Plots of the amount of CO₂ dissolved with different zeolites, bubbling times and cold water

Table 6.5: Results for the CO₂ dissolved in cold water with different zeolites

Cold water			
	1 st zeolites	2 nd zeolites	3 rd zeolites
time bubbling (min)	g of CO ₂ /l water	g of CO ₂ /l water	g of CO ₂ /l water
10	0,8184	0,8184	0,88
20	1,2276	1,2232	1,3684
30	1,4784	1,3464	1,342

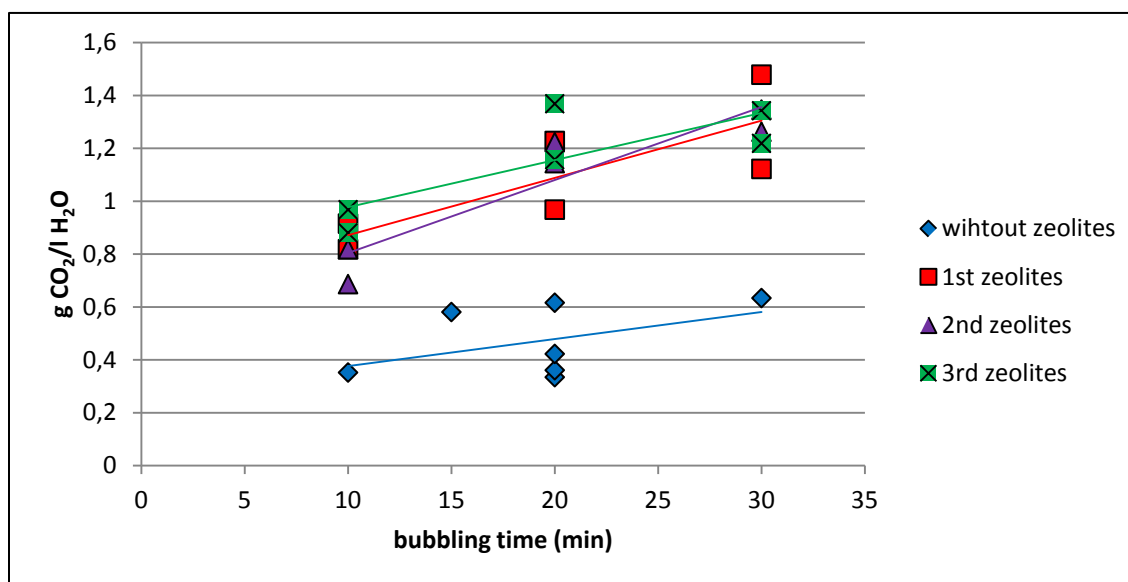
With cold water it can be seen that the trend is the same as warm water, but in this case the amount of CO₂ dissolved is bigger. For 10 min bubbling, the zeolites which can dissolve more amount of CO₂ are the third one, and the first ones and the second ones can dissolve exactly the same grams of CO₂ per litre of water. For 20 min bubbling the best zeolites are the third ones, and for 30 min the first ones.

Within the first 20 min, the slopes of the three zeolites are the same; it means that the zeolites with cold water absorb the same amount of CO₂ per minute. The last part the first zeolites are the ones who can absorb the CO₂ quicker, and the third ones and the second ones are decreasing the speed.

The solubility of CO₂ was compared also with and without zeolites. It can be seen in graph 6.9 that the solubility with the zeolites inside the flask are better than without zeolites.

Table 6.6: Data of the solubility of CO₂ with the different zeolites and without them

Time (min)	Solubility g CO ₂ /l of water			
	Without zeolites	1st zeolites	2nd zeolites	3rd zeolites
10	0,352	0,9152	0,6864	0,968
10		0,8184	0,8184	0,88
15	0,5808			
20	0,3344	0,968	1,144	1,1572
20	0,3608	0,1227	1,2232	1,3684
20	0,4224			
20	0,616			
30	0,6336	0,1122	1,2628	1,2188
30		0,1478	1,3464	1,642

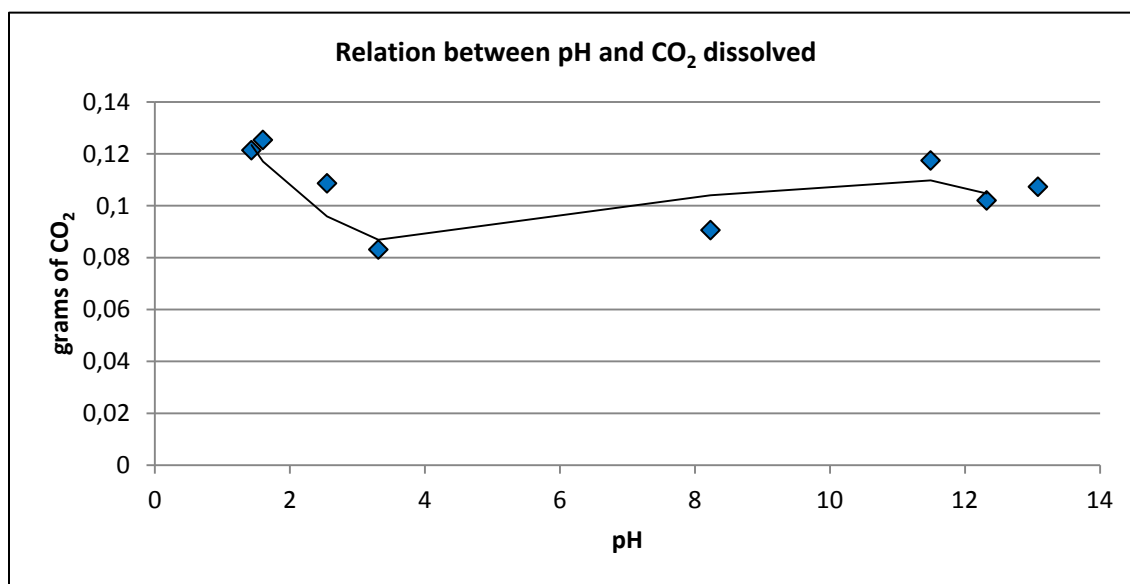
**Graph 6.6: Comparison of the solubility with different types of zeolites and without zeolites**

There are different values for the different zeolites and also for different bubbling times. For a bubbling time of 10 min, the zeolites which absorb more amount of CO₂ are the third ones and the same with 20min bubbling. However for 30 min bubbling the zeolites which absorb more amount are the first ones.

The amount of CO₂ dissolved in water without zeolites is always the lower value, it can happen that due to the cavities of the zeolites they are able to capture more amount of CO₂ and only with water it becomes into gas again very fast.

6.3.1.2. pH dependence

Regarding pH, it cannot be concluded anything as it can be seen in graph 6.6. It can be seen that for acid pH there is one maximum at pH 1,6 and then the solubility of CO₂ starts to decrease as the pH starts to neutralize. About basic pH the maximum is at pH 11,49 but it cannot be seen any relation between the whole scale of pH (from 0 to 14) and the grams of CO₂ absorbed.



Graph 6.7: Relation between the pH and the CO₂ dissolved in water

Table 6.7: Results of the grams of CO₂ absorbed with different pH

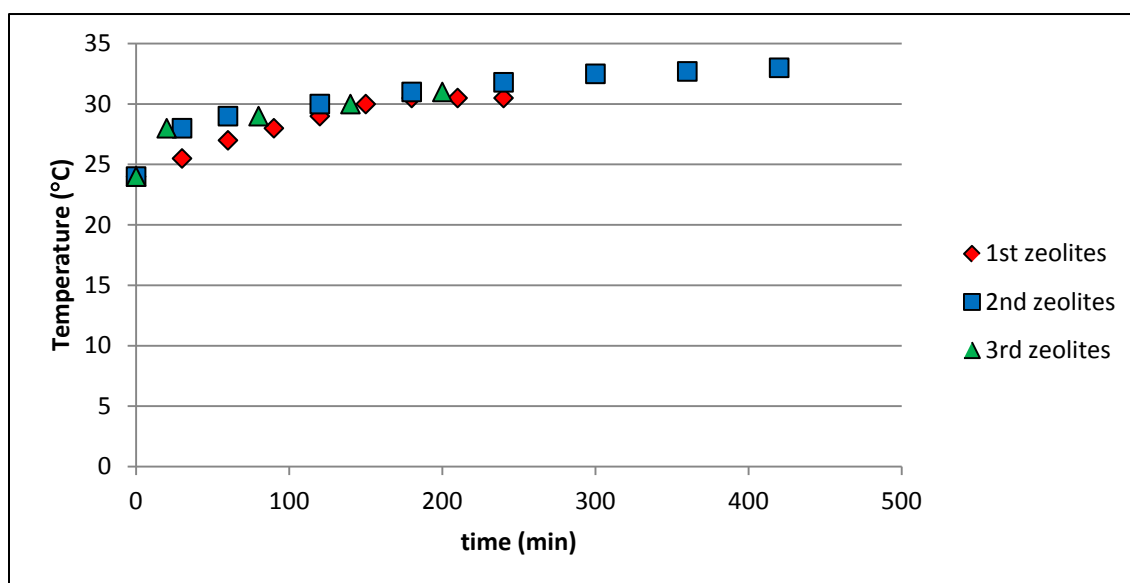
T(°C)	pH	V _{NaOH} (ml)	g CO ₂
23	13,08	24,4	0,10736
22	12,32	23,2	0,10208
22	11,49	26,7	0,11748
22	8,23	20,6	0,09064
21,5	3,31	18,9	0,08316
22	2,55	24,7	0,10868
22	1,6	28,5	0,1254
22	1,43	27,6	0,12144

6.3.2. Photoreduction

6.3.2.1. Temperature dependence

It can be seen in graph 6.8 the evolution of the temperature while photoreduction is occurring, the temperature increases with the time, so probably it is an exothermic reaction. It can be seen also that with all the zeolites the temperature follows the same trend, and with the second zeolites is when the photoreduction achieve more temperature.

In these experiments the water was bubbled 30 min, and it was done with the three different zeolites, the amount of zeolites was 0,15 g.



Graph 6.8: Evolution of the temperature while photoreduction is occurring

Table 6.8: Results of the experiments for the evaluation of the temperature

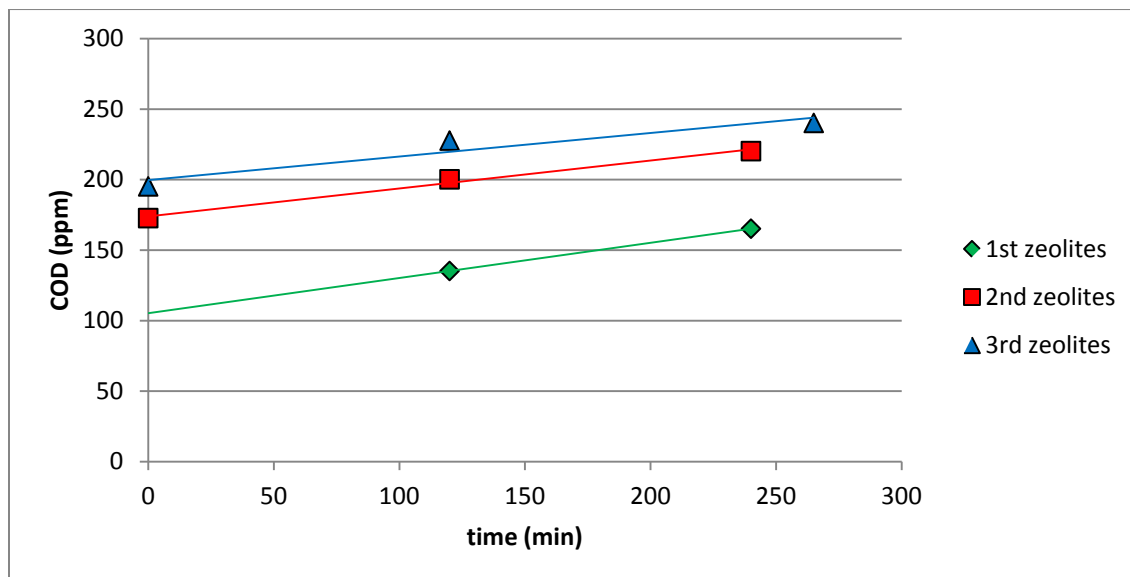
Time (min)	Temperature (°C)		
	1 st zeolites	2 nd zeolites	3 rd zeolites
0 ¹	24	24	24
30	25,5	28	28
60	27	29	-
90	28	-	29
120	29	30	140
150	30	-	31
180	30,5	31	
210	30,5	-	
240	30,5	31,8	
300		32,5	
360		32,7	
420		33	

6.3.2.2. COD

The COD was calculated as it is explained in 6.2.6 part, several experiments were performed to know how parameters like temperature, amount of zeolites or time affects to the conversion of CO₂ into organic matter.

Three experiments were made for the three zeolites with the same amount of zeolites, 0,15 g and 20 min bubbling CO₂ and taking samples every two hours and at the beginning, after bubbling, to know the evolution of the COD. It can be seen in graph 6.14 that the zeolites which had better value for the COD were the 2nd ones and the 3rd ones, while the 1st ones, had low COD value. It can mean that the most efficient zeolites for photoreduction are the 2nd and the 3rd ones.

¹ Time 0 means the point which it is started to bubble the CO₂ into the water.



Graph 6.9: Relation between the COD, the photoreduction time and the sort of zeolite

Table 6.9: Results of the experiments for the COD relation between the different zeolites

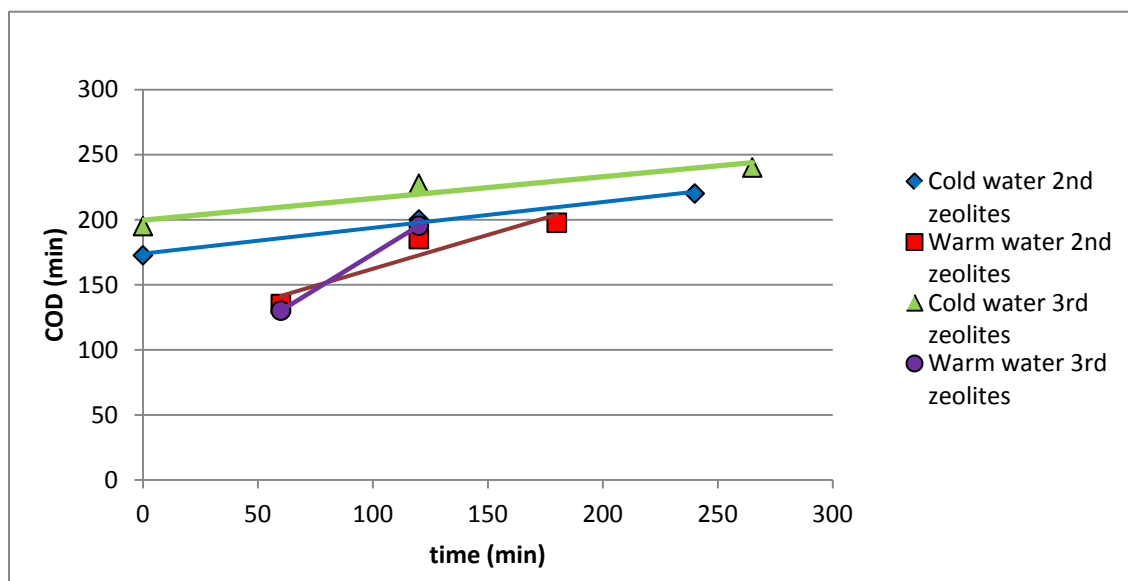
time (min)	COD (ppm)		
	1st zeolites	2nd zeolites	3rd zeolites
0	-	172,75	195,25
60	-	-	-
120	135,25	200,25	227,75
180	-	-	-
240	165,25	220,25	-
265	-	-	240,25

As it was expected as longer as the photoreduction is higher COD value appears. The zeolites which can convert more CO₂ into COD are the third ones (240,25 ppm of COD) , and the ones that can convert less amount are the first ones (165.25 ppm of COD).

It was also studied the relation between the temperature and the COD values. Several photoreduction were performed (0,15 g of zeolites, 20 min bubbling), changing the temperatures (cold and warm water), changing the zeolites and taking samples from time to time.

Table 6.10: Data of the COD with different temperature for the 2nd and 3rd zeolites

time (min)	2nd zeolites				3rd zeolites			
	cold water		warm water		cold water		warm water	
	T(°C)	COD (ppm)	T(°C)	COD (ppm)	T(°C)	COD (ppm)	T(°C)	COD (ppm)
0	9,5	172,75	29	135,25	12	195,25		
60							29	130,25
120	14,2	200,25	30	185,25	15,5	227,75	30	195,5
240	18	220,25	31	197,75	21	240,25		

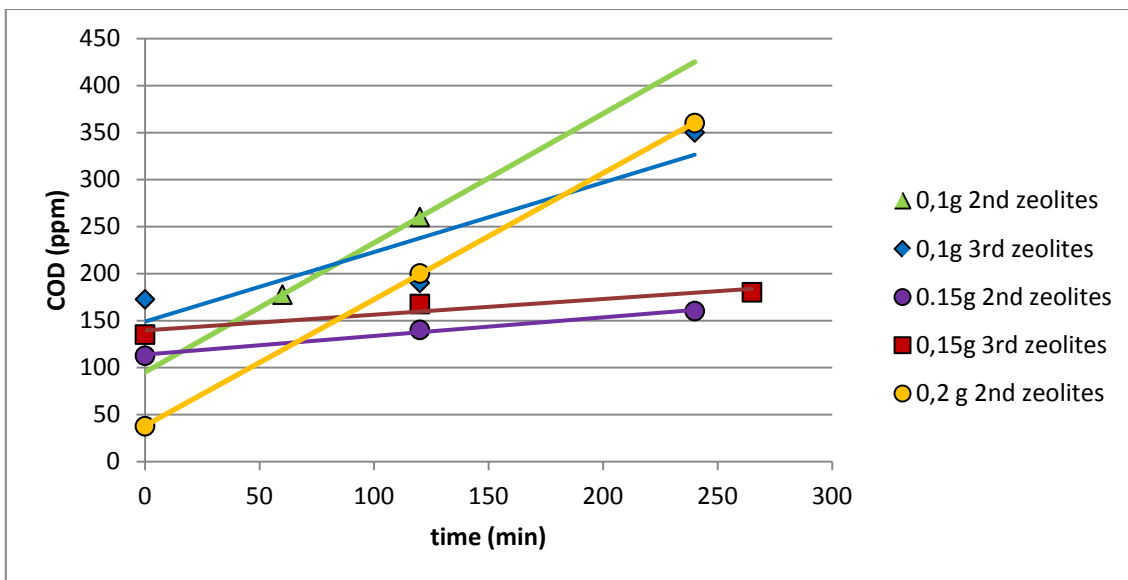


Graph 6.10: Plots of the COD curves for different temperatures and different time

According to the obtained results, the best conditions in order to obtain the biggest amount of COD are with the third zeolites and cold water, but it is not something determining because also the first value of COD of this experiment was higher than the others, it is something logic because as graph 6.4 shows the third zeolites are the ones which can absorb more CO₂ in 20min.

COD curves for cold water have less slope than the ones with warm water, it mean that the experiments with warm water are able to convert more CO₂ into organic matter faster than with cold water.

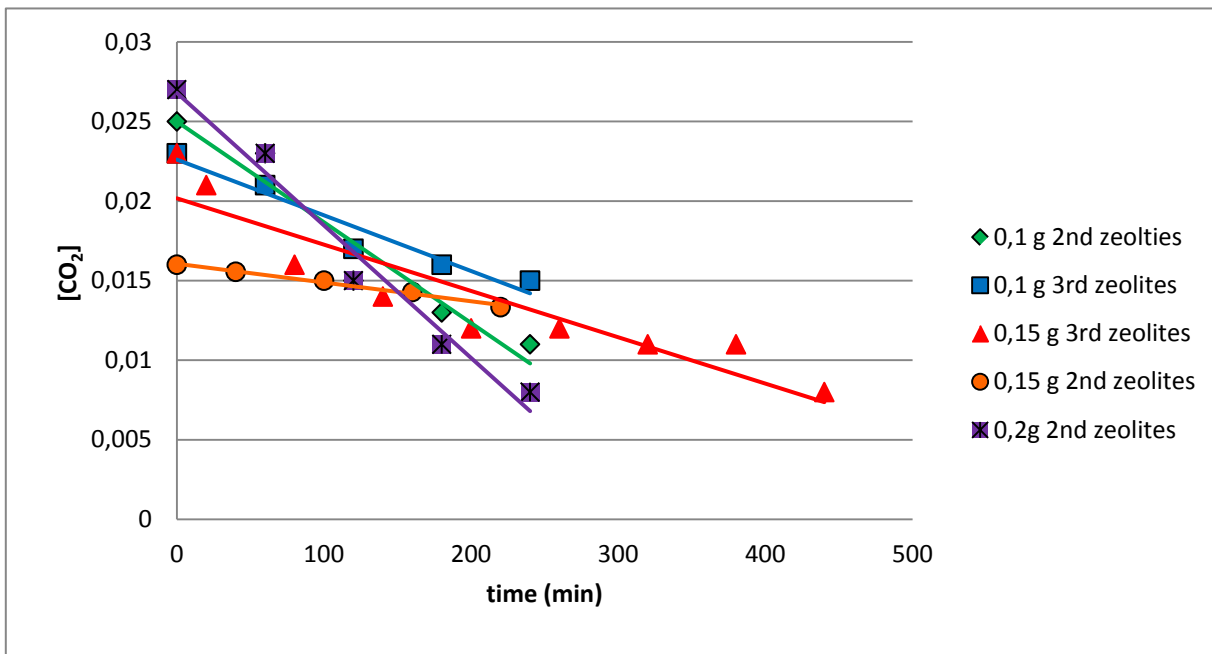
The amount of COD and the amount of zeolites for the catalysis were also considered an interesting relation to study. Several experiments were performed, the second and the third zeolites were tested with 0,1 g, 0,15 g and 0,2 g of zeolites with warm water and the COD was measured after the photoreduction.



Graph 6.11: Relation between the amount of zeolites and the COD

Table 6.11: Data of the experiments with 0,1 g, 0,15 g and 0,2 g of the second and third zeolites

Time (min)	COD (ppm)			COD (ppm)	
	2nd zeolites			3rd zeolites	
	0,1g	0,15g	0,2g	0,1g	0,15g
0		112,75	37,75	232,75	
60	177,75				130,25
120	260,25	140,25	200,25	250,25	195,5
180					
240		160,25	360,25	410,25	



6.12: Graph of the concentration of CO₂ during photoreduction with different zeolites

Table 6.12: Results for the concentration of CO₂ while photoreduction is occurring

Time (min)	[CO ₂]				
	0,1 g 2nd zeo.	0,15 g 2nd zeo.	0,2g 2nd zeo.	0,1 g 3rd zeo.	0,15g 3rd zeo.
0	0,025	0,016	0,027	0,1012	0,023
40		0,015556			0,021
60	0,023		0,023	0,07946	
100		0,015			0,016
120	0,015		0,015	0,05685	
160		0,014286			0,014
180	0,013		0,011	0,04365	
220		0,013333			0,012
240	0,011		0,008	0,03432	
280		0,02			0,012
340		0,02			0,011
400					0,011
460					0,008

Graph 6.11 shows that photoreduction with 0,1 g of zeolites achieve higher COD values. On graph 6.12 can be seen that also CO₂ concentration is decreasing. It can be seen the relation between both graphs, because the curves with more slope in the graph of COD are the ones with more negatives slope in the graph of CO₂ concentration. It means that zeolites really are converting this CO₂ into organic matter.

The zeolites which achieve more COD value are the second ones, with 0,15 g of them and they are also the ones which have more slope, so faster. The ones which reach less amount of COD are the 2nd and the 3rd ones with 0,15 g.

To know sure that the reaction was occurring, 0,15 g of zeolites with water were placed into a dark atmosphere and they were let it there 24 hours. After that time the COD was measured and it was 0,024 nm, exactly the same amount of absorbance than the blank. So it means that without light the reaction is not working.

It was made an experiment to know if the experiment was working or not. It consisted in place 0,15 g of the second zeolites into 100 ml of water in totally darkness for 24 hours. After that the absorbance was measured and COD calculated. The concentration was 0,024 ppm, the same of the blank, so it can be said that photoreduction is working.

6.3.2.3. Pseudo order of the reaction

It was done also some experiments according the procedure explained in 6.2.7 in order to know the kinetics of the reaction. It is going to detail the data of the first experiment as a representative example, the other ones were the same but changing the zeolites, the temperature or the amount of zeolites. Later is going to be detailed a table with all the experiments performed and the results obtained (table 6.12).

It has to be said that V flask is the total volume left in the flask every time a sample was taken, the sample was 0,01l but also every hour samples of 0.004 l were taken for the COD measurement. In all the experiments the bubbling time was 20 min.

Table 6.13: Data for calculate the pseudo order of the reaction (with 0,15g of the second zeolites)

				PSEUDO ORDER OF THE REACTION			
				0	1	2	
time PC (min)	T(°C)	V _{NaOH} (ml)	V flask (l)	[CO ₂]	ln([CO ₂₀]/[CO ₂])	1/[CO ₂]	
	24	-	-	-	-	-	
0	24,5	1,6	0,1	0,016	0	62,5	
40	28	1,4	0,09	0,0155	-0,028170877	64,2857	
80	30	1,2	0,08	0,0155	-0,064538521	66,6667	
120	31	1	0,07	0,0143	-0,113328685	70	
160	31,5	0,8	0,06	0,0133	-0,182321557	75	
200	31,7	1	0,05	0,002	0,223143551	50	
240	31	0,8	0,04	0,002	0,223143551	50	
				k:	0,00002 ²	0,0011 ³	0,0384 ⁴
				R ²	0,9775	0,969	0,9592

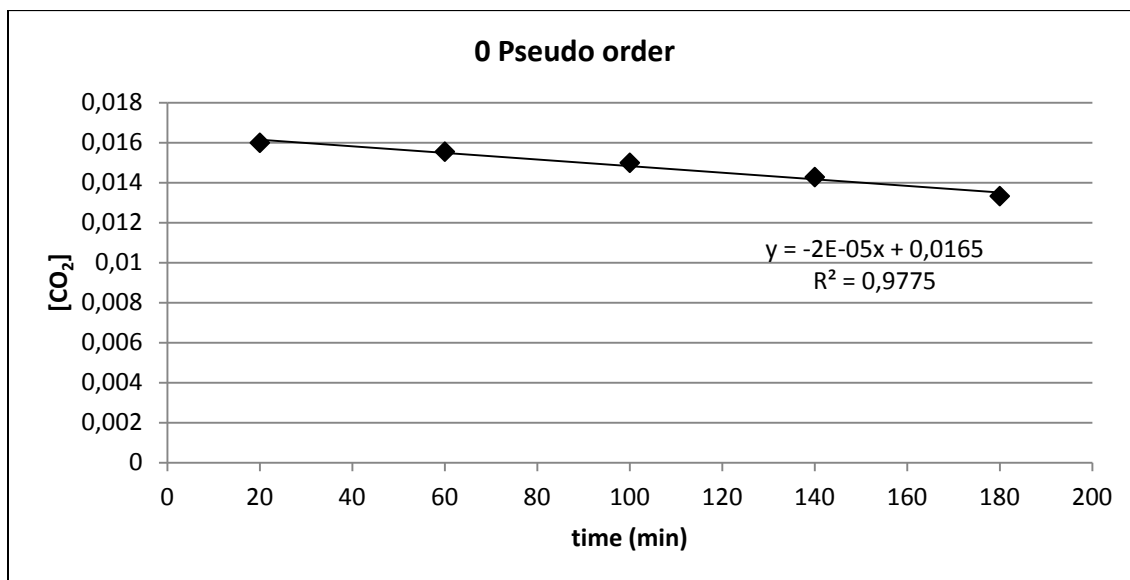
It was considered to omit some experimental points because they were very far of the other points, and they were considered as an anomaly.

It has to be said that as the equation of the second order reaction said (fig.6.19) the slope of the calibration for this order has to be divided by two in order to know the kinetic constant.

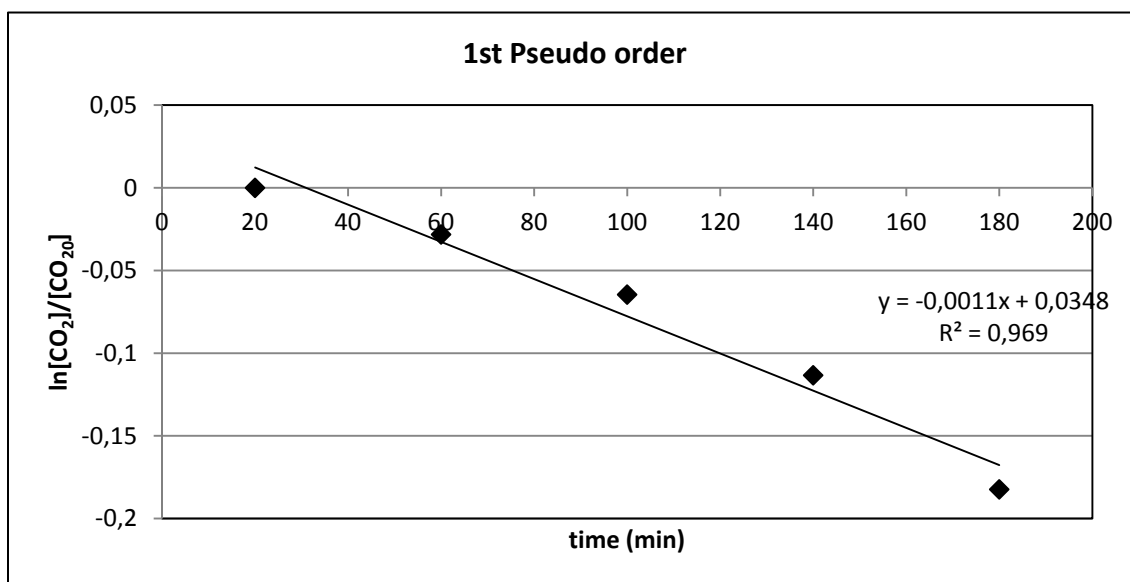
² Units: min⁻¹

³ Units: mol·l⁻¹·min⁻¹

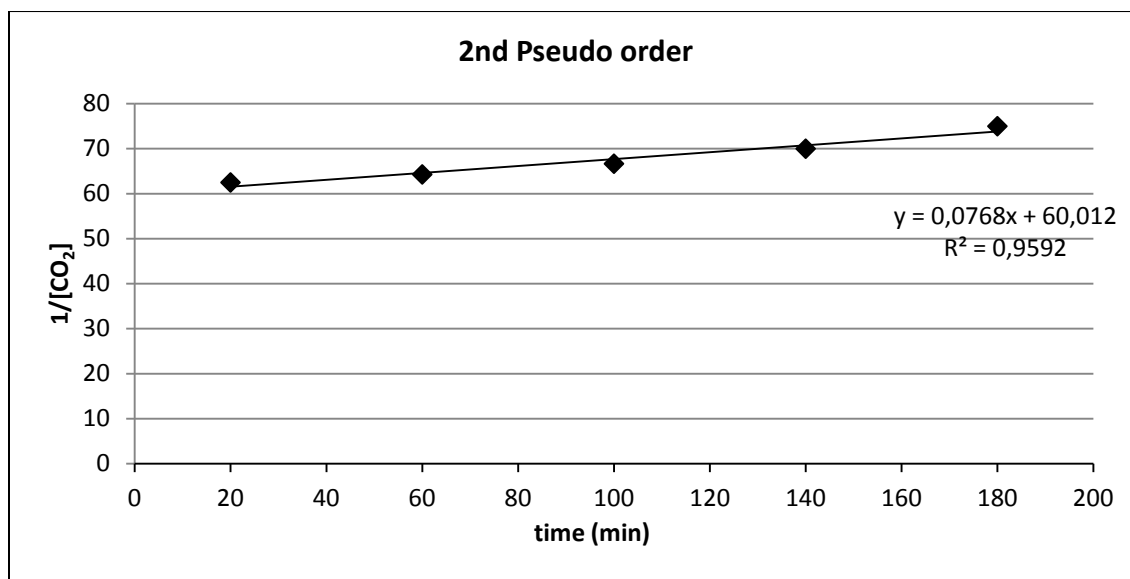
⁴ Units: l·mol⁻¹·min⁻¹



Graph 6.13: First experiment calibration curve for pseudo order 0



Graph 6.14: First experiment calibration curve for pseudo order 1



Graph 6.15: First experiment calibration curve for pseudo order 2

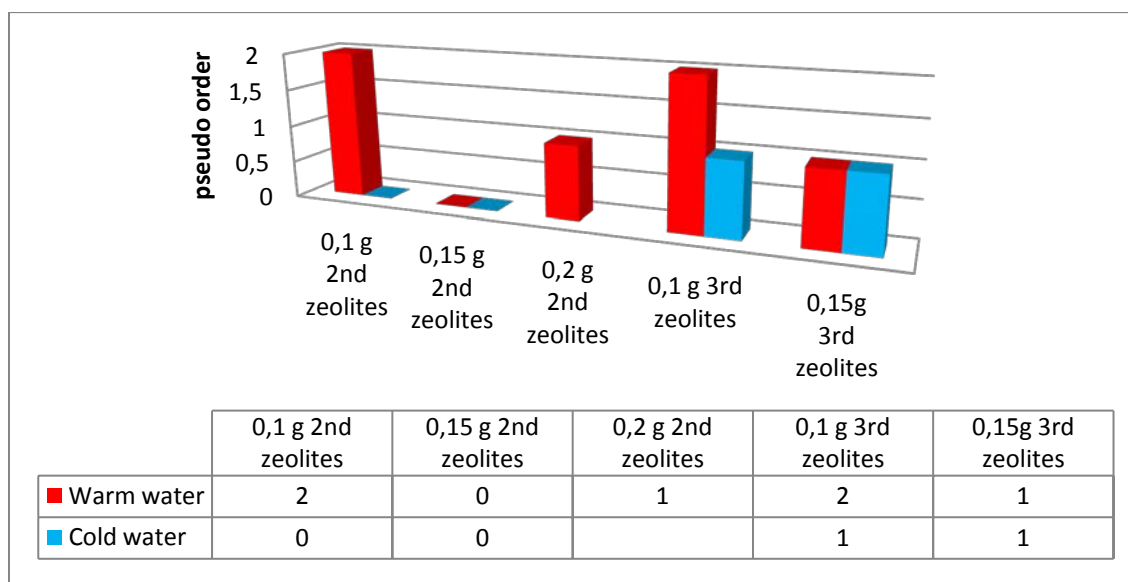
It can be seen in graph 6.12 and table 6.9 that the curve with better R^2 coefficient is the one for zero-pseudo order. With a R^2 of 0,9775.

Table 6.14: Results of all the experiments

	Zeolites	Water temperature ⁵	Pseudo order	k ⁶	R ²
1	0,15 g second zeolites	Warm water (around 29°C)	0	0,00002	0,9775
2	0,15 g third zeolites	Warm water (around 30°C)	1	0,0035	0,9173
3	0,1 g third zeolites	Warm water (around 27°C)	2	0,051	0,96
4	0,15 g second zeolites	Cold water (around 12°C)	0	0,00001	0,9745
5	0,15g third zeolites	Cold water (around 15°C)	1	0,0036	0,9895
6	0,2 g second zeolites	Warm water (around 28°C)	1	0,049	0,9835
7	0,1 g third zeolites	Cold water (around 15°C)	1	0,0022	0,9738
8	0,1 g second zeolites	Warm water (around 26°C)	2	0,1127	0,9567

⁵ The temperature on the reaction was continuously changing so it was calculated the average of all the temperatures to give an approximate idea.

⁶ Every k in its corresponding units.



Graph 6.16: Results for the pseudo order of the reaction

As it can be seen in table 6.13, the values are very different in every experiment, but it can be seen similarities between the sorts of zeolites. In graph 6.15 it can be seen for the case of the second zeolites (0,15 g) both experiments have results for zero-pseudo order reaction, with a very similar kinetic constant and also similar R^2 , but in the case of 0,2 g of zeolite the pseudo order changes. For the second zeolites and 2 g of amount it can be seen pseudo order 1 and a kinetic constant far from the others.

For the third zeolites, for 0,15 g, both kinetic constants are almost the same ($0,0035 \text{ min}^{-1}$ and $0,0036 \text{ min}^{-1}$) and the pseudo order is also the same for both (first). But for the amount of 0,1 g with warm water the experimental data give results for second pseudo order also with the second zeolites, but with cold water for first pseudo order, with kinetic constants quite different. This could be due to the different reactions of photoreduction, perhaps with 0,1 g of zeolites some reactions and temperature become more favoured some other with more amount of zeolites.

Anyway the majority orders are 0 and 1, which suggest that data are quite according to the ones found in the bibliography (section 5.2.2.3) [34].

6.3.2.4. Activation energy of the reaction

To know the activation energy of the reaction it has been taken the first and the forth experiment for the second zeolites, because to calculate this parameter was needed a change of temperature. It was followed the procedure explained in section

For the third zeolites the results are detailed below:

Table 6.15: Results for the calculation of the activation energy for the third zeolites

	T (K)	k (mol·l ⁻¹ s ⁻¹)	1/T	lnk	Ea (J/mol)
k ₁	287,04	6,00E-03	0,00348384	-5,11599581	-74370,2815
k ₂	302,67	0,0012	0,00330391	-6,72543372	

The Ea was calculated with the eq. (X), because it weren't enough data for doing a regression. It is very important to have all the units expressed in the International System, the temperature in absolute value (K) and k in seconds.

It can be seen in table 6.13 that the value of Ea is -74370,28 J/mol. Negative activation energy means that the speed decreases with the temperature, which thing doesn't surprise because at less temperature more amount of CO₂ is dissolved and more CO₂ is converted into organic compounds. As it was found in the bibliographic research the activation energy is about few KJ, nothing was found to know if 74 KJ/mol is too much or not. So it is known that the result is not far from what was expected but it is also not know how close they are to real ones.

7. Conclusions and future work

7.1. Conclusions

The main objective was to know if it is possible to develop a photoreduction with natural zeolites which reducing the CO₂ level and increasing the organic compounds on it. After this research it can be said that is possible, although it is still unknown the compounds it is known that the CO₂ is converted into organic matter (Graph 6.16).

About the secondary, but not less important, goals here it is written a brief description of the achievement of the research:

7.1.1. Conclusion about solubility

- The amount of CO₂ dissolved in water has a relationship between the bubbling time. As longer as it is bubbled the more CO₂ is dissolved (see graph 6.2 and table 6.2).
- Experimentally it can be said that probably the solubility of the CO₂ in water is better with cold water (graph 6.3 and table 6.3), but it cannot be said anything sure because there are not data enough. The temperature of the experiments was no constant, so this could be the reason why the results are not determining.
- As it was seen in graph 6.4, the zeolites which ones absorb more are the second ones in 30 min of bubbling time, the amount of CO₂ absorbed is 1,2628 g. And the zeolites which ones absorb less amount of CO₂ are the second ones also but in 10 min of bubbling time, 0,6864g absorbed.
- Zeolites with cold water achieve better results about solubility, for instance 0,15 g of the second zeolites in 20 min bubbling are able to dissolve 1,2232 g of CO₂ per litre of cold water while in warm water the solubility decreases at 1,144 g. (Graph 6.5)
- The zeolites which can absorb more CO₂ in cold water are the first (1,4784 g/l) in 30 min bubbling, and the ones which can absorb less are the first ones and the second ones in 10 min of bubbling (0,8184 g/l for both).
- It can be seen in graph 6.6 that solubility of CO₂ increases significantly with zeolites, whereas without zeolites the solubility in 20 min of bubbling is 0,3344 g/l of water, with the first the second and the third zeolites the solubility is 0,968, 1,144

and 1,157 g/l of water with the same amount of time. So it can be said that with the zeolites we at least multiplying by three the amount of CO₂ dissolved.

- The pH was another variable of interest, but in this research it cannot be determinate anything (see graph 6.7), with the experiment done no special relationship is noticed.

7.1.2. Conclusions about photoreduction

- The temperature is increasing along the photoreduction is occurring (graph 6.8), perhaps this is because photoreduction is an exothermic reaction.
- The zeolite which riches higher amount of COD, it means organic matter, is the third one, while the first one is the one which achieve less COD. While the third zeolites in two hours are able to achieve up to 227,75 ppm of COD, the first ones in the same time can achieve 135,25ppm (see graph 6.9). So it can be said that the fist zeolites were modified wrong.
- In graph 6.10, the best condition for developing a photoreduction can be deduced. The most effective way in order to obtain higher amount of organic compounds is with cold water and with the third zeolites, but it also depends on what is wanted. The slopes of the curves show that the reaction with cold water is slower than with warm water.
- In graph 6.11 and 6.12 it can be seen that the photoreduction is working and it is converting the CO₂ into organic matter.
- The amount of zeolites for performing the photoreduction is another parameter which changes the yield. In graph 6.11 it can be noticed that with less amount 0,1 g of zeolite the conversion is more effective, more amount of CO₂ is converted. It is also effective 0,2 g of zeolite, but in this research it was only performed one experiment with this amount of zeolites, so it is not determining.
- About the order of the reaction, it is not clear with the results but the majority of the experiments give pseudo order 1, which result is according to the bibliographic search. But one conclusion is that the photoreduction is a complex general reaction because there are a lot of reaction and factors involved, so it cannot be calculated carefully the kinetics of the reaction simplifying the reaction as one (see table 6.13 and graph 6.16).

- Another kinetic parameter is the activation energy, for the same reason as the kinetic constants it cannot be calculated precisely by simplify the reaction of photoreduction that much.

7.2. Future work

- Could be interesting to monitor the pH evolution during the reaction, to know more about the equilibrium of the carbonic acid in water and understand more the reactions involved.
- Performing the photoreduction with constant temperature (cold and warm) could be also interesting to know if there are fluctuations of products.
- It would be interesting to find the compounds which ones are forming during the photoreduction. For example GCMS.
- To know more about kinetics, the reaction could be breakdown into the main reactions and calculate the constants for each one of them.

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