SIWI STOCKHOLM JUNIOR WATER PRIZE

Lycée André Theuriet Civray

académie Poitiers

# Washing With Degassed Water

High School André Theuriet of Civray
Mathylde SENTIS - Nils DONK - Lucie MALPEYRE - Clément CADIER
Maëlle ANASTASI - Adrien HERMAN - Floriane CAILLIERET
Professor: Vincent CARRIER

# Summary

Detergents are a scourge for society, both in terms of public health and of environment. We have conducted research to find washing methods without detergents. We have tested an original idea based on a recent discovery showing that hydroxide ions, naturally present in the water, may serve as surfactant, but only if water is degassed. In this experimental study,we show that we can wash dirty laundry, simply with water, degassed with a vacuum pump ; degassing playing the double fonction of mechanical desorption and emulsion stabilization.

# Detergents : a scourge for our society

Today, on an average year, a french family does 220 washings which represents a consomption of 26 litres of detergent. Those substances are harmful for environment, because, rejected in seas with wastewater, they destroy planktons, marine flora or even inshore vegetation. Today, we even consider that the levels of surfactants is so important that it starts to threaten drinkable water resources. Washing powders are dangerous because of their components. Indeed, surfactants are present in detergents, that is, for example, the case of the LAS, which is forbidden in Sweden because of its toxicity for aquatic life. We also see the bleaching agents, which turn out to be powerful oxidants, which destroy organic matter. Detergents act especially on animal metabolism but could also be the cause of spermatogenesis decrease in humans. Detergents contain also softeners and organic complexes like phosphonate, responsible for water's eutrophication and for polycarboxylates. The NTA is one of those and is also prejudicial for health : it's carcinogenic like the formaldehyde, a preservative. Detergents are also composed of solvent (phenol, ...) which are toxic. Some producers add perfumes containing for most of them musks which represent a real danger for environment. Furthermore, brighteners are also present and can let chemical residues on skin potentially allergenic and irritating. Regarding the harmful impact of detergents on humans and ecosystems, it's essential to find an alternative to detergents to preserve the planet and to facilitate millions people life who don't tolerate traditional detergents. [1] [2]

# Contents

# Introduction

And if... it could be possible to wash without detergents ?

It would be a real progress and the ending of many difficulties for the people suffering of allergies, who, according to the INSERM [3], represent twenty-five to thirty percents of population, and who don't generally tolerate traditional detergents, but also concerning environment protection, which is a big society issue.

This is why we ask ourselves : "Is it possible to wash laundry without surfactants ?"

Some Japanese researchers, aware of amelioration to bring to this topic, already created washing machines without detergents, working with ultrasounds. They had got reduced results, ultrasounds penetrating badly fabrics. So we tried to find an other way to wash laundry without using detergents in view of a more environmentally friendly alternative that may be suitable for the majority of people.

Our project was born on September 2017, thanks to our physics teacher who allowed us to develop our appetence for scientific researches. 5 at the beginning of the project, Adrien HERMAN and Clément CADIER joined us this year while Lucie MALPEYRE and Maëlle ANASTASI started a new project. So we are still 5 but only 4 of us, Mathylde SENTIS, Nils DONK, Adrien HERMAN and Floriane CAILLIERET represent today the project. For almost two years, we conducted our research, every wednesday afternoon.

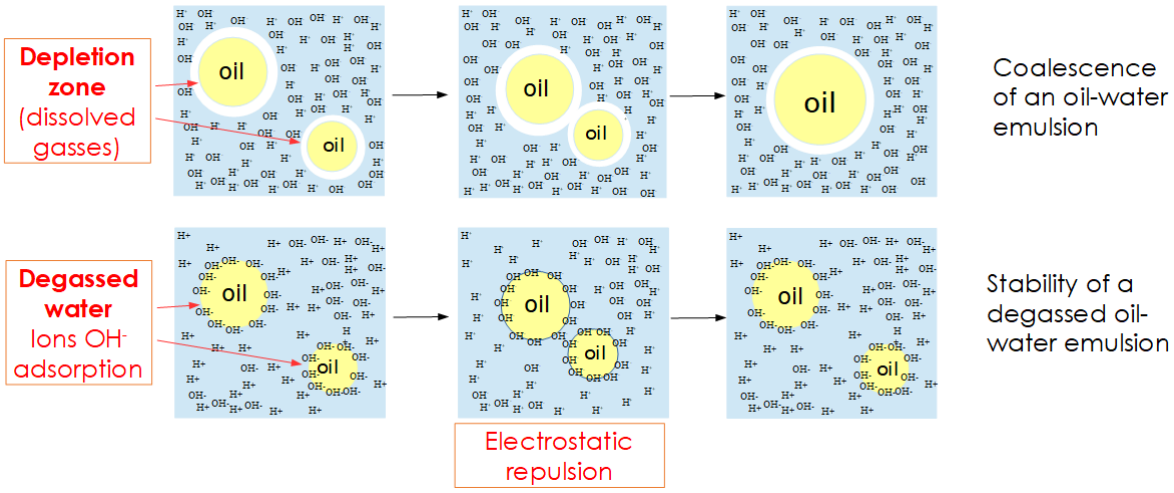
Moreover this problematic is important to us because some of us have washing powders allergies, so, this project seems to us to have a direct application and need in-depth research. Our idea would therefore be to develop a surfactant-free washing medium. So, we ask ourselves if it could be possible to use Pashley's recent discovery to wash laudry.

# Part I
# Theoretical principle

## 1 A surprising discovery...

In 2003, Pashley [4] discovers that it's possible to emulsify oil in water without amphiphilic molecules just by degassing.

Emulsions formed are stable even in contact with air. Stabilization of drops comes from the adsorption of the hydroxide ions to the surface, creating an electrostatic repulsive force between the drops, stabilizing the latter. Indeed, in non-degassed water, dissolved gases concentrate on the surface of hydrophobic particles, preventing hydroxide ions to reach it.




## 2 ... A complicated protocol

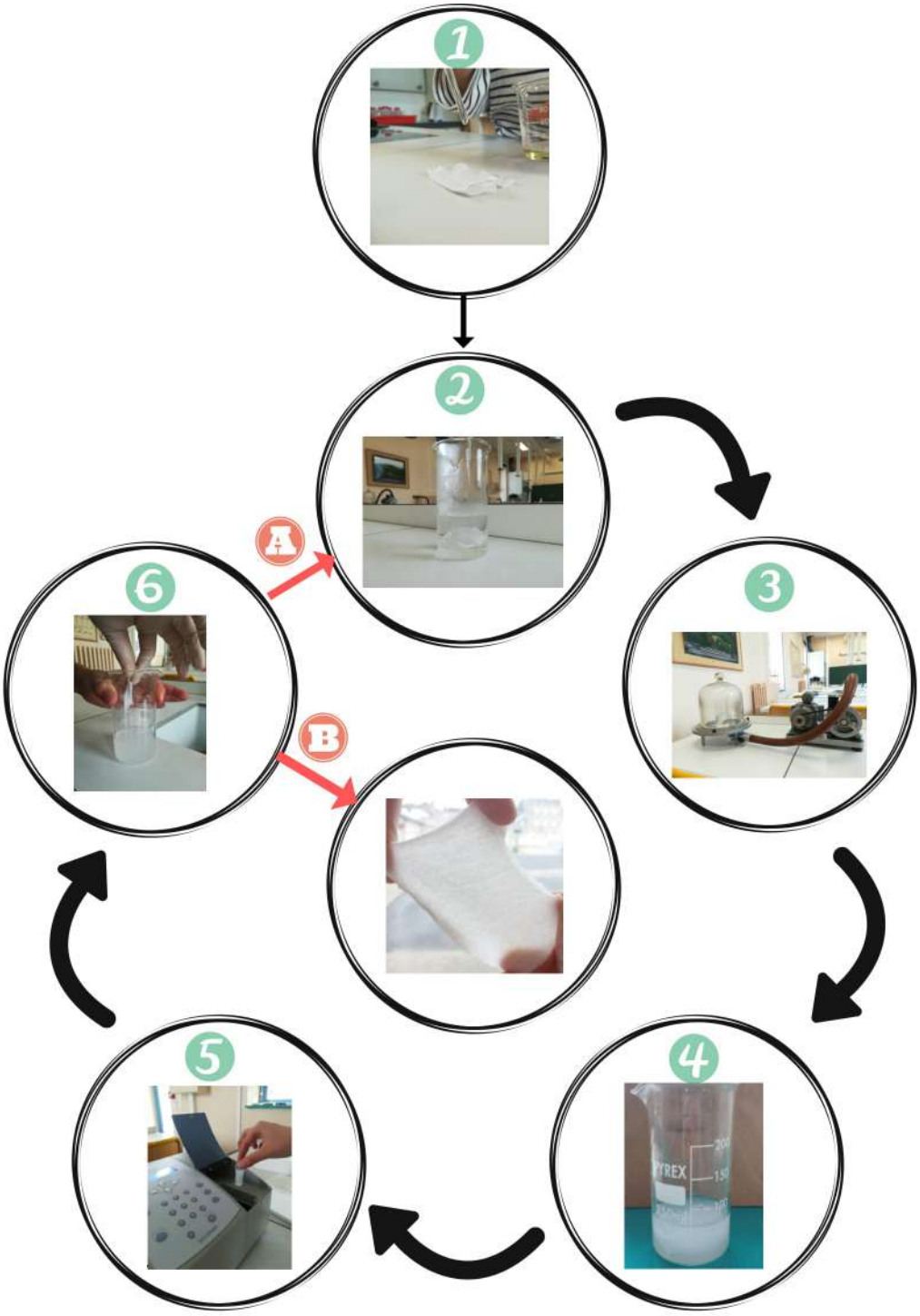
In his experimental protocol, Pashley is degassing water by repeating a three-step cycle (called Freeze-Pump-Thaw or F-P-T) :

- Water's solidification
- Vacuum pumping
- Meltdown by bringing the sample back to room temperature

This cycle is repeated several times. It does emulsify without surfactant, but it's a complicated protocol.

# Part II
# Method

## 1 Protocol



## 2 Protocol's explanation

**Steps :**

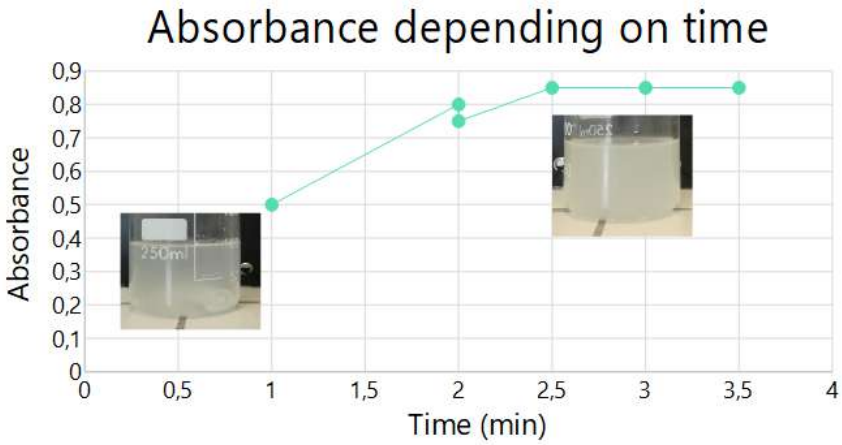
1. On a piece of fabric (cotton) clean washed with acetone and dried up, we put 3 drops of sunflower oil.
2. This fabric is placed in a beaker containing 100,0 ml of fresh distilled water at 80 degrees Celsius.
3. We place this beaker under the vacuum bell jar. We turn on vacuum pumping during 2min30.
4. At the end of the draw, a portion of oil is emulsified in water, that's why water has a whitish aspect.
5. We want to quantify the effectiveness of our washing by measuring the turbidity of the solution thanks to the absorbance at 450, 600 and 750 nanometer .
6. The fabric is extracted from the washing water and depending on the color of our solution, we have two possibilities :
   - Possibility A : if the wash water is turbid, that is to say a high absorbance, we start a new washing cycle for the same fabric. That means : take the same fabric and put it in a new beaker containing 100,0 ml of fresh distilled water at 80°C and repeat the same steps.
   - Possibility B : if the wash water is not turbid, we stop the washing cycle, because this means that either all oil has been removed from the fabric, or either we can not remove more.

For our experiment, we based ourselves on the absorbance measurement to have a quantitative result of the effectiveness of our washing. The higher the absorbance, the greater the emulsification of the oil in the water, so the more efficient our washing is. We averaged the absorbances at 450, 600 and 750 nanometers. In most cases, several experiments have been made to estimate a repeatability uncertainty that is represented by an uncertainty bar on the graphs.

# Part III
# Results

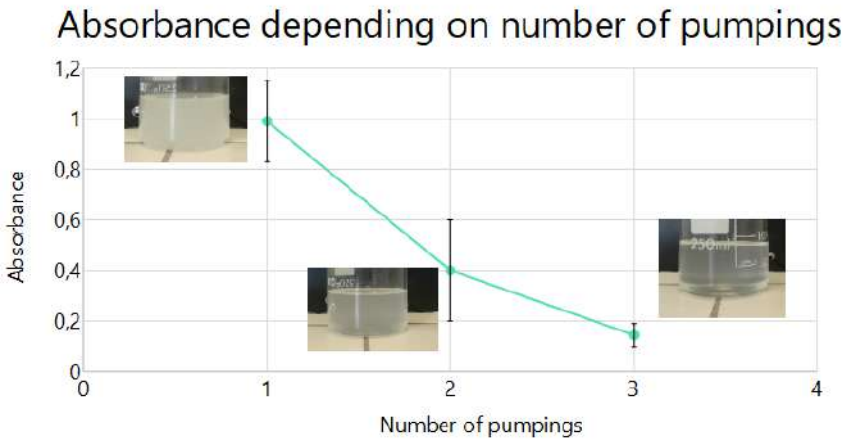
With our protocol, we managed to quantify the variation of the efficiency of the washing program depending on various parameters.

## 1 Variation of emulsification depending on running time



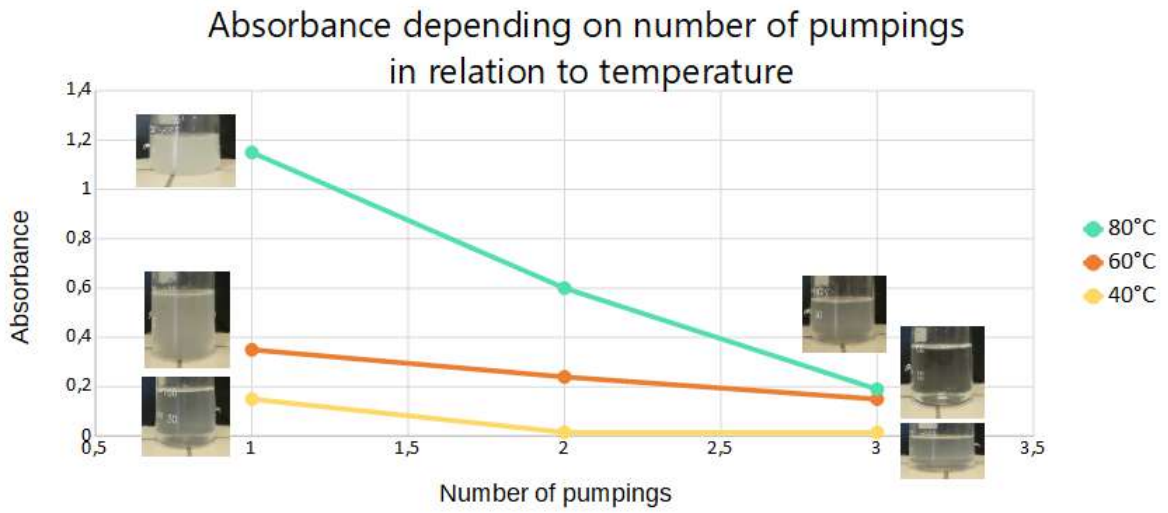

To begin with, we studied variations of the absorbance depending of the pumping time. We can clearly observe that the best results were obtained after 2'30 of under-vacuum washing. Even if we increase this duration, we obtain some similar results, and this is how we deduced that after 2'30 of pumping, we reach a step, a level from which we can't emulsify more oil in distilled water. That is why we decided to use a 2'30 time as a reference, because it represents the best time/absorbance ratio.

## 2 Study of washing efficiency according to the number of successive runs



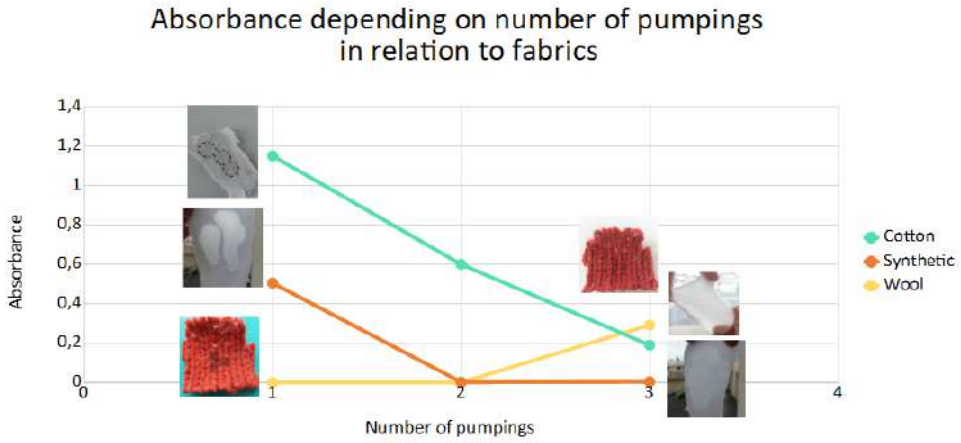
Secondly, we studied the evolution of absorbance depending on the number of successive washes. After the first one, the emulsion is turbid, which means that a very large part of the oil of the sample has been emulsified in water, that's why we note an absorbance up to 0.99. About the other washes, the sample is replaced in a clean water pot and, washes after washes, the absorbance decreases down to 0.145. We thus conclude, from the weak absorbance at the last wash, that the main part of the oil has been taken off the sample at the previous washes, a conclusion even confirmed by the visual analysis of the sample himself on which there's no more clue of any stain.

## 3 Temperature effects




Then, we tried to quantify the absorbance keeping the criteria of the number of washes but adding another one, the influence of water temperature. At 80°C, absorbance is high at the first wash (up to 1.15), and decreases a lot (down to 0.19) until the last wash; it seems to witness the quality of this washing program. However, it is relevant to note that for lower temperatures, the absorbance is way lower (only 0.35 at 60°C and 0.15 at 40°C). We can explain this phenomen on saying that the high temperature of the water allows the ebullition nucleated on the fibres to be way stronger which in turn increases the quantity of oil taken off the sample. Those results encourage us to dig deeper into our research about weak temperatures : some types of clothes can't handle high temperatures...

# 4 Fabric's nature




To complete, we changed the type of fabric (cotton, synthetic, wool). Experiences with wool, and synthetic have been conducted at 40°C because they can not withstand temperatures of 80°C contrarily to cotton. With cotton, used for previous experiments, the results show that our protocol is efficient for this type of fabric, because absorbance is small for the last draw and we don't see the stain. Concerning wool, oil is impregnated more, and we can see that the washing is efficient from the third draw. Wool would therefore require more washing, or a prior time when the fabric would be in the solution to moisten the stitches and make it easier to desorb oil from fabric. This can be explained by the washing machines : indeed the wool cycle already includes a time of humidification of the meshes before the beginning of washing. For the synthetic, on which the oil is apparent, we can see that at the last draw the absorbance is equal to zero, but there is oil on the fabric, we can see it to the naked eye. Thus, for the synthetic, it would be wise to consider another technique, to facilitate the desorption of the oil of the fabric, which could also be used for the wool.

# 5 Temporary conclusion

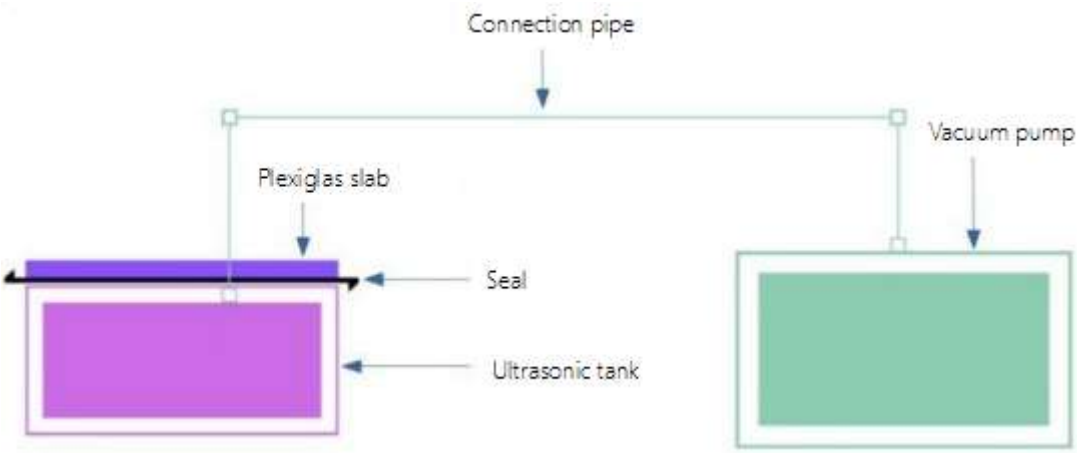
Washing a fabric consists of two steps:

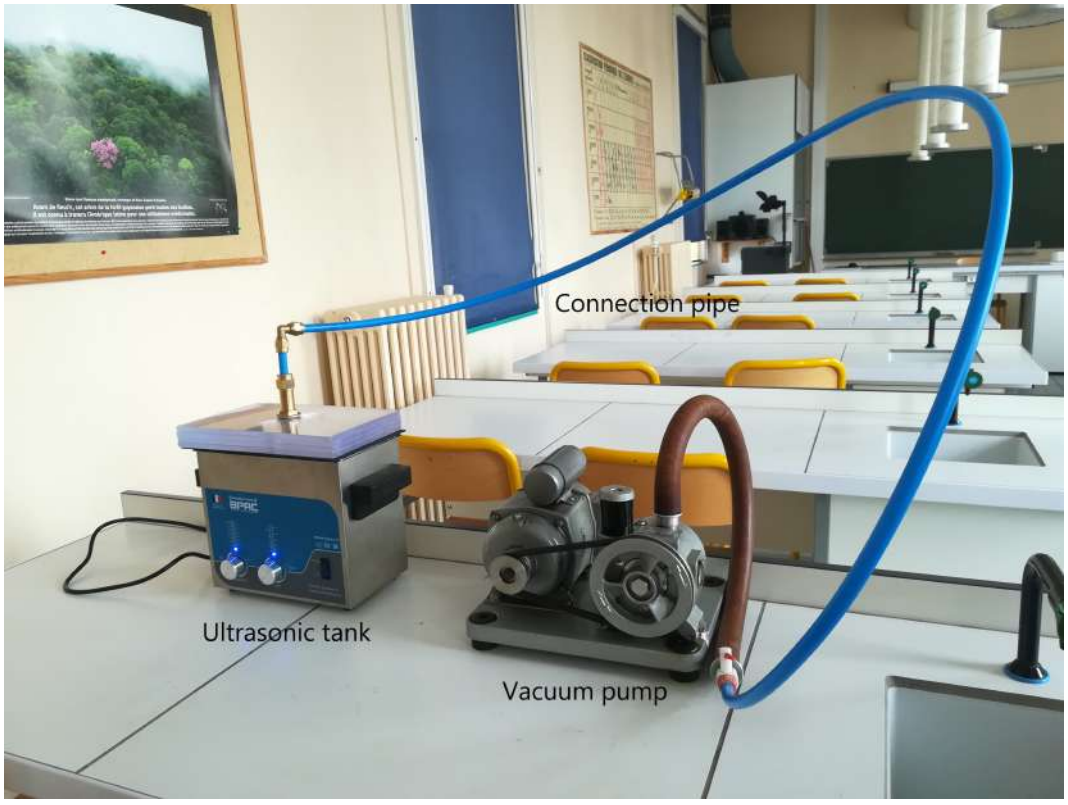
1. Desorbing the dirt from the fibers
2. Stabilize these impurities in the wash water

Previous experiments prove that without surfactant, we manage to stabilize the drops of oil in the wash water. The boiling which nucleates on the fibers of the fabrics, causes a mechanical agitation which desorbs the oil. However, this mechanical agitation is sufficiently efficient only at high temperatures. For fabric that do not tolerate temperatures above 40°C, boiling is less fervent, desorption is visibly insufficient. Based on this conclusion, we have tried to complete our technique with a second helping to desorb the impurities of the fabric.

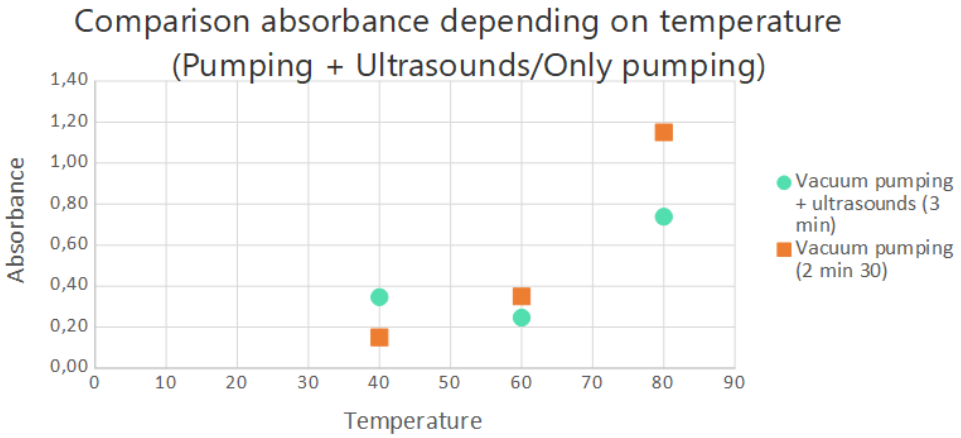
# Part IV
# Desorption aid

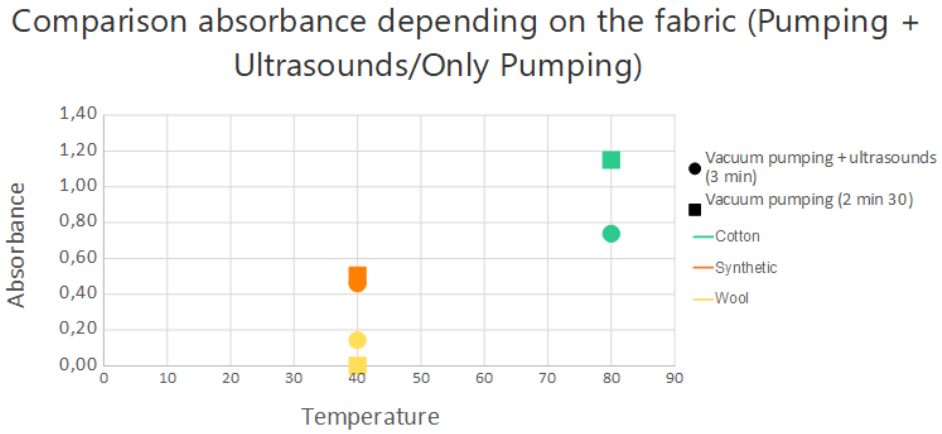
## 1 With ultrasounds




We connected our vacuum pump to an ultrasound tank. To do this, we had to build a plexiglass lid 3 centimeters thick. The ultrasounds were on at the same time as the pump and that is how we could bind our two ideas. For the rest, the precedent protocol was applied all the same.




The first graph shows different absorbances depending on the temperature and the presence of ultrasounds. We can observe that the washing program with vacuum at 80°C is more efficient without ultrasounds. So, at this temperature, it seems that ultrasounds aren't so benefic into the washing program. The same observation can be made at 60°C but when we go down to 40°C, ultrasounds seem to have a positive influence on the washing, even if it is not so strong and the results stay around what we observed without them.

Looking out for different types of clothes, we obtain best results without ultrasounds for cotton. About the synthetic cloth, it seems that washes are quite similar to each others, and for the wool, best numbers are reached with ultrasounds.

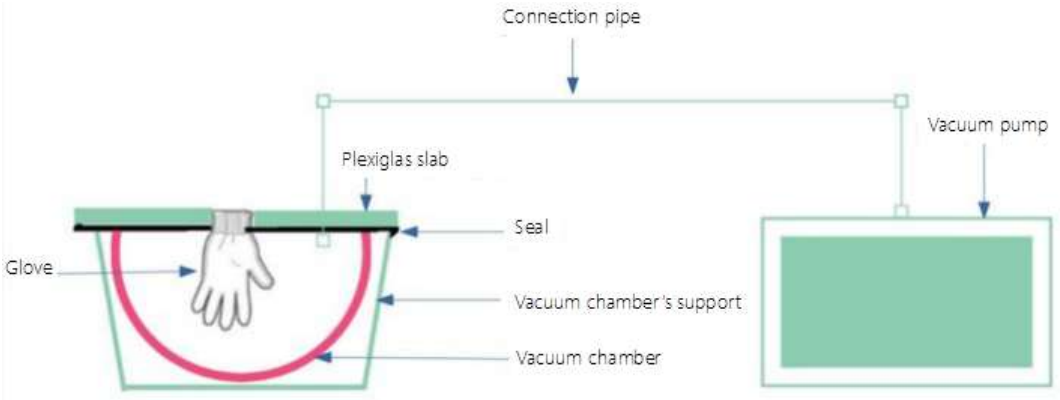
So it is quite tricky to reach a straight conclusion about the influence of ultrasounds on our washing protocol, but according to our experiments, it seems that ultrasounds aren't strong enough or cleverly used to increase the emulsification. Even for longer durations (+/-2hours), ultrasounds don't allow us to obtain satisfying results.

## 2 With mechanical stirring

Following our ultrasound researches, we looked for an other way to produce a mechanical agitation different from traditionnal washing machines to make the desorption of oil easier.

We met a lot of obstacles in this quest because creating a mechanical agitation under the vacuum bell came up as a difficult task.

After some numerous researches, we tried to setup a manual agitation during the vacuum extraction program as sketched below.




So, we made a protocol for this experiment :

| Protocol (Vacuum pumping without detergents) | Control experience (With detergents but without vacuum pumping) | Control experience (Without detergents and without vacuum pumping) |
|---|---|---|
| We have stained a little piece of fabric (cotton) and we placed it in a vacuum chamber which was filled by 40°C water. We pumped for 15 minutes, and during this time, the fabric was rubbed thanks to the glove which made a mechanicl agitation. | We have taken a piece of cotton with spots like the first protocol. We placed it in 40°C water with detergents and we rubbed the fabrics in the same conditions that the previous experiment during 15 minutes but without vacuum pumping. | We have taken a piece of cotton with spots like the first protocol. We placed it in 40°C water and we rubbed it like the previous experiment for 15 minutes but without detergents and vacuum pumping. |

However, the depression inside the vacuum bell was so strong that we could not agitate and scratch the fabric like we expected. So, at the end of the witness experiment (with laundry powder) we obtained a fabric that was almost clear of smudges, and the smudges got stomped on the experiment without laundry powder. The smudges also got stomped with the washing protocol we settled up.

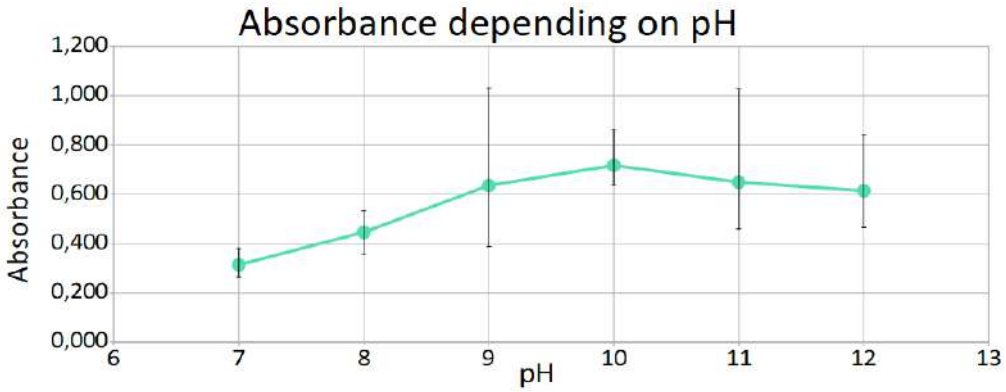
| | Under vacuum without detergents | With detergents without vacuum drawing | Without detergents without vacuum drawing |
|---|---|---|---|
| Before |  |  |  |
| After |  |  |  |

It is hard to take in count the up above results because we couldn't reproduce the same experimental conditions because it was impossible to scratch the cloth under vacuum. We are thus going to look for another way to create a mechanical agitation.

# Part V
# Improvement of the efficiency of our washing

## 1 pH effect

OH- ions allow us to emulsify oil in water. We were therefore interested in what could happen if the pH of the water was varied in a basic environment. For that, we dissolved sodium hydroxyde in water to do absorbance measurements between pH 7 and pH 12.




Results on this graphic show an optimum at pH 10. Indeed, from pH 7 to pH 10, absorbance grows to 0.717. At a higher pH, results are lower, so it seems that a pH 10 solution would be optimal for our washing protocol.

For our following experiences, we will use pH 10 solutions.

## 2 New stirring method

Following the problems met with our glove box to cause a mechanical agitation under the vacuum chamber for increasing the emulsification and so the efficiency of our washing, we decided to work differently to succeed to shake our emulsion.

**Steps :**

1. A fabric is stained with 3 oil drops.
2. The latter is placed in a jar (like the one on the picture) containing 100,0mL of a pH 10 solution at 80°C. A magnetic bar is added in the jar and then this one is close thanks to the lid and a rubber.
3. The jar is placed under the vacuum chamber for a 2 min 30 pumping.
4. At the end of the pumping, the jar is removed from under the vacuum chamber so that even once the jar removed, the emulsion inside be still under vacuum. Thereafter, the jar is placed on a magnetic agitator, where, thanks to the magnetic bar, we can create an agitation inside the jar and so, in the under vacuum emulsion.
5. We break the vacuum in the jar so we can open it and do our absorbance measures at 450, 600 and 750nm.

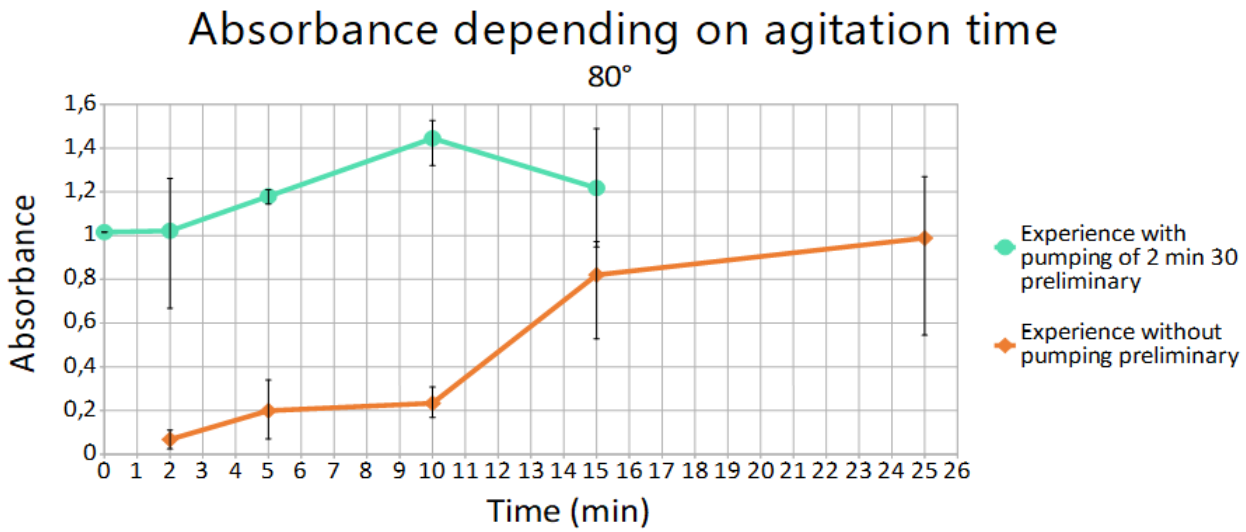
For information, the vacuum pump's base being in metal, it was impossible to use a magnetic bar under the vacuum chamber during the drawing, unless the bar would have been under the vacuum chamber too, which would have needed hard connections.

We also did a control experience containig the same steps than the previous experience except for the vacuum drawing


**Steps :**

1. A fabric is stained with 3 oil drops.
2. The latter is placed in a jar (like the one on the picture) containing 100,0mL of a pH 10 solution at 80°C. A magnetic bar is added in the jar and then this one is close thanks to the lid and a rubber.
3. The jar is shake for a given time.
4. Measure of absorbance.

## 2.1 80° experiments

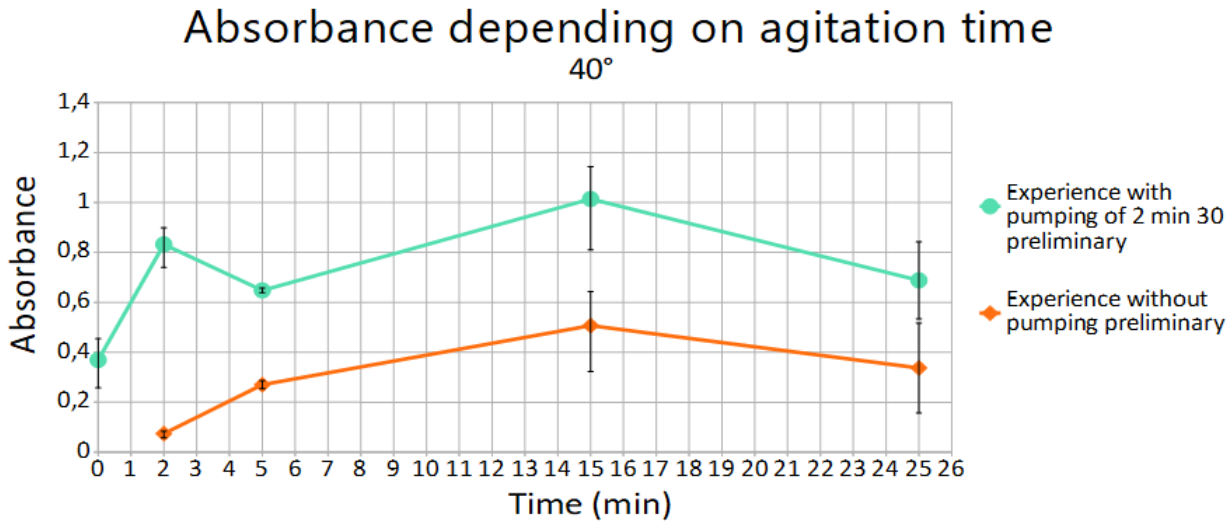



We sought to vary the stirring time and so to see the influence of this parameter on absorbance at 80°C.

On the graph are represented, in orange, the results got thanks to the control experience and, in green, the ones when the experience include a vacuum drawing.

This graph allows us to compare the absorbance with or without stirring. We can see that absorbance is clearly higher when there is a vacuum drawing. The absorbance is 1,022 for 2 minutes of stirring with the vacuum against 0,068 without the vacuum for the same time. We got a value of 0,98 without the vacuum for 25 minutes. So, it seems that the vacuum allows a better and a faster emulsification of oil in water. Furthermore, absorbance measurements obtained with vacuum shows that absorption is a key factor to optimise and improve our washing, because with 0 minute of stirring, absorbance is 1,016 against 1,445 with 10 minutes of stirring, time for which we obtain the higher absorbance values. So, the mechanical stirring would allowed us to increase washing performances at 80°C.

## 2.2 40° experiments




We reproduce the same experiences but for a temperature of 40°C where we had weak absorbance measures (0,38) with vacuum and so a very limited effeciency of our washing. On can see, as for 80°C, that the vacuum play an important role in emuslfication of oil in water.

This graph shows too the efficiency of the stirring, because after 15 minutes of stirring with preliminary vacuum, we obtained an absorbance superior to 1, which is twice the departure value without stirring (0,38). So, the stirring would allow us to wash, even at low temperature for fabrics which can't handle high temperature.

# Part VI
# Prospects

- During this project, we have researched the possibility to wash laundry using hydroxides ions instead of detergents. We have discovered that we can emulsify quickly oil in water without surfactants by impregnated the oil on clean fabrics. This technique could be an innovation in emulsions making without surfactants in the industry. For example, in the rolling mills, direct aqueous emulsions are used as lubricants, with normally from 1 to 10 percent of oil in water. The water allows, by its important calorific power, a good regulation of the heat. However, the surfactants make some little bubbles, which seriously damages the quality of the laminated steel surface. And in this case, the presence of anti-foam (microscopic silica particles for example) isn't recommended. So, we need emulsions which never foamed. An emulsion without surfactants will be ideal, in the condition that it will be stable over time. But, our emulsions without surfactants made by the method explained above are stable for at least 15 days. So this is maybe an innovation in the emulsions making without surfactants and it can maybe find an application in the rolling mill industry.
- So now, the purpose of the project is to make a prototype of washing machine without detergents. And next, if the prototype efficiency as well as the traditional detergent washing machines, we would like to contact the industry to make a washing machine for the general public, which uses the hydroxides ions.

# Conclusion

Our research allows us to show that now it is possible to wash laundry without detergents... and that was impossible before. Thanks to the hydroxide ions and a vacuum pump, we succeeded to stabilize very well oil in water, and thanks to our research about the mechanical agitation, we can desorb more easily impurities, and in a very short time. Preserving the environment and working to facilitate the life of millions of people suffering from allergies, we are convinced that this project is a major asset for our society. Those results made with little pieces of fabrics suggest a big alternative to the ultrasonic washing machines which work also without detergents.

Moreover, we have maybe found a new process of emulsification without surfactants, and it will maybe find application in the industry.

From now on, washing will no longer go with detergents ...!

## References

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[3] INSERM. Allergies, March 2016. www.inserm.fr/information-en-sante/dossiers-information/allergies.

[4] R. M. Pashley. Effect of degassing on the formation and stability of surfactant-free emulsions and fine teflon dispersions. *The Journal of Physical Chemistry B*, 107(7):1714–1720, January 2003.

# Thanks

We would like to thank :

- The Lycée Paul Guérin which lets compete one of their student,
- The Lycée André Theuriet's laboratory crew which was cooperating to facilitate our research
- Alain Pénicaud and Carlos Drummond from CRPP CNRS for their advice
- André Theuriet's management and especially Mister Ciret for his support
- Our parents without whom we could not have been able to participate.
- Julien Nicolai, university lecturer, who gave us valuable advice.
- Lucie Malpeyre et Maëlle Anastasi who worked on the project last year
- Very special thanks to our physics teacher who gave us a taste for research and brings forth in us vocations.

Special mention :

- For our charismatic leader who brings his touch of inventiveness
- For our intrepid vacuum pump which has never relinquished in front of adversity !