



Research Article

Andras Jozsef Toth*, Eniko Haaz, Botond Szilagyi, Tibor Nagy, Ariella Janka Tarjani, Daniel Fozer, Anita Andre, Nora Valentinyi, Szabolcs Solti, Peter Mizsey

COD reduction of process wastewater with vacuum evaporation

<https://doi.org/10.1515/wtr-2018-0001>

received ???; accepted ???

Abstract: Washing detergents in process wastewaters from fine chemical industry produce high Chemical Oxygen Demand (COD), which poses a serious environmental problem. Method has to be found, which follows the principles of circular economy so that the treated water can be recycled or reused. Heat pump vacuum evaporator is evaluated in order to reduce the Chemical Oxygen Demand of process wastewater with washing detergent content from initial 7500 mg O₂/L to a lower value below the effluent limit, which is 1000 mg O₂/L. Yield and COD rejection are determined for the evaluation of selected treatment. Experiments are investigated with LED Italia R150-v3 pilot apparatus. Different evaporation pressures were applied during measurements. It The highest removal or reduction of in the Chemical Oxygen Demand was reached certainly using the lowest possible pressure, which is 40 mbar.

Keywords: COD reduction, vacuum evaporation, process wastewater, washing detergent

1 Introduction

Fine chemical process wastewaters (PWWs) contain a wide range of in pollutants and their pH is usually not neutral, which is why such wastewaters must be treated. In many cases, the PWWs also contain catalyst materials, emulsifying materials and other components. It is already apparent that these process wastewaters are significantly different from the communal wastewaters and from other industrial wastewaters too, primarily because they contain more non-biodegradable components. The organic pollutants are often molecularly dispersed, which complicates the destabilization and flocculation [1]. The treatment of the PWWs has two main objectives. On one hand the amount of non-biodegradable pollutants entering into the process wastewaters must be minimized and these components must be removed with greater efficiency by physical or chemical treatment before the biological step. On the other hand greater the reduction in Chemical Oxygen Demand (COD) must be implemented with the biological treatment, even if there are quantitative and qualitative fluctuations in the composition of the process wastewater [1].

A number of physicochemical methods are suitable for treating PWWs and the primary focus of the treatment is to remove the organic solvents and reduce the COD [2]. Selection of the method to use depends the composition of the PWW, the chemical nature of the pollutant present in the wastewater, environmental legislation in a country, economic parameters and local conditions [1]. The main physicochemical methods are: ion exchange, adsorption, absorption, stripping, extraction, wet oxidation, distillation, membrane processes and evaporation.

Some of the solvents that contaminate the PWWs can be regenerated by different procedures. However, these regenerated solvents often do not meet the relevant pharmacopoeial standards and so their reuse and recycling are limited in the production of fine chemicals. In some cases, the multi-regenerated solvent can be reused in other industries. Yet in practice solvent transfer

*Corresponding author: **Andras Jozsef Toth**, Environmental and Process Engineering Research Group, Budapest University of Technology and Economics, H-1111, Hungary, Budapest, Műegyetem rkp. 3, E-mail: andras86@kkft.bme.hu

Eniko Haaz, Botond Szilagyi, Tibor Nagy, Ariella Janka Tarjani, Daniel Fozer, Anita Andre, Nora Valentinyi, Peter Mizsey, Environmental and Process Engineering Research Group, Budapest University of Technology and Economics, H-1111, Hungary, Budapest, Műegyetem rkp. 3.

Szabolcs Solti, Szelenca Kamionmosó, Ipartelep, H-2431, Szabade gyháza, Hungary

Peter Mizsey, Department of Fine Chemicals and Environmental Technology, University of Miskolc, H-3515, Hungary, Miskolc, Egyetemváros C/1 108.

is not typical between industries. The reason for this is that the regenerated and/or recycled materials have variable quality, due to the contaminating chemical compounds which are present in the solvents [1].

The most widely current and applied form of disposal of pharmaceutical wastewater and PWWs is incineration. The procedure is advantageous, because the wastewater is used as energy source in the incineration plants as the heat produced can be utilized. The possibility of incinerating waste solvents is determined by their halogen and sulphur content. Temperature of incineration also plays an important role in the incineration process design. If the solvent does not contain these components, the wastewaters can be burned without danger of corrosion. However, this is a rare occurrence, therefore separate facilities are built for the burning of waste solvents or already existing hazardous waste incinerators are used to avoid formation of dangerous by-products such as dioxins during the incineration. The halogen-free waste solvent's calorific value is equal to or close to the petroleum-based fossil fuel liquid waste's (30000 to 40000 kJ / kg). Such wastes can be used as auxiliary fuels in high-temperature industrial technologies (e. g. cement and ceramics production) or as auxiliary feeding flame in the hazardous waste incinerator and in the afterburner, ensuring the necessary temperature [3].

Nowadays volatilizing large part of water with evaporation is a realistic option, therefore only small amount of waste needs to be treated, for example incinerated. The increased costs and penalties make this method competitive [2, 4].

Evaporation of PWW is a distillation process, where water is the volatile substance, leaving the concentrate as bottom residue to be disposed of. The aim of this operation is to reduce the volume of PWW or to concentrate mother liquors. The volatile steam is collected in a condenser and the condensed water is, if needed recycled after subsequent treatment. Operating under vacuum decreases the boiling temperature and enables the recycling of substances that would otherwise decompose. Evaporators are usually operated in series, where the condensation heat of one stage heats the condensate of the preceding stage [5].

Proper maintenance of the heat exchangers is crucial. Encrustations, fouling and corrosion disturb the heat transfer to the liquid and decrease the energy efficiency. The concentration of contaminants, or surrogate parameters (TOC, pH, conductivity, etc.) must be continuously monitored in the condensate need to prevent the transfer of pollutants [5].

It can be concluded, the driving force for implementation of vacuum evaporator is the recovery of

materials from PWW streams and the minimisation of the waste volume sent for treatment [5].

Evaporation is unique different from other separation processes, in that the water is removed from the contaminants rather than the other way round. Before recent technological developments, the capital and energy requirements have made widespread industrial application of for evaporation processes limited in the wastewater treatment and recycling of the regenerated solvents. Evaporation was only used if all other treatment methods had failed or could not be applied. The heat pump vacuum evaporator offers reduced electrical energy consumption, and superior reliability for low to medium flow produced water treatment applications. Evaporation occurs under high vacuum conditions [4, 6-11].

The aim of this study is to examine the COD reduction of process wastewater from fine chemical industry with vacuum evaporation. The COD content must be reduced under the emission limit, which is 1000 mgO₂/L [12]. Objective function can be defined in order to find the appropriate separation technology: COD rejection and yield must be maximized, common optimization is necessary.

The COD rejection can be calculated by the following equation [1]:

$$COD_{Rejection} = \left(1 - \frac{COD_{Distillate}}{COD_{Feed}}\right) \times 100 \quad [\%] \quad (1)$$

Yield is calculated according to Eq. (2)

$$Y = \left(\frac{V_{Distillate}}{V_{Feed}}\right) \times 100 \quad [\%] \quad (2)$$

which is the ratio of the volume of the distillate (V_D) and the volume of the feed solution (V_F).

2 Material and methods

The average COD of the treated PWW is 7500 mgO₂/L. Chemical oxygen demand of feed and bottom product of distillation and permeate of membrane filtration are determined by the K₂Cr₂O₇ standard method. This method is fully corresponds to the International Standard ISO 6060:1991 [1]. The PWW contains nonionic detergents and its pH is 7.5.

LED Italia R150-v3 type vacuum evaporator is applied. The main parameters can be seen in Table 1 and in Table 2 [13].

The flowsheet of the pilot, heat pump evaporator can be seen in Figure 1.

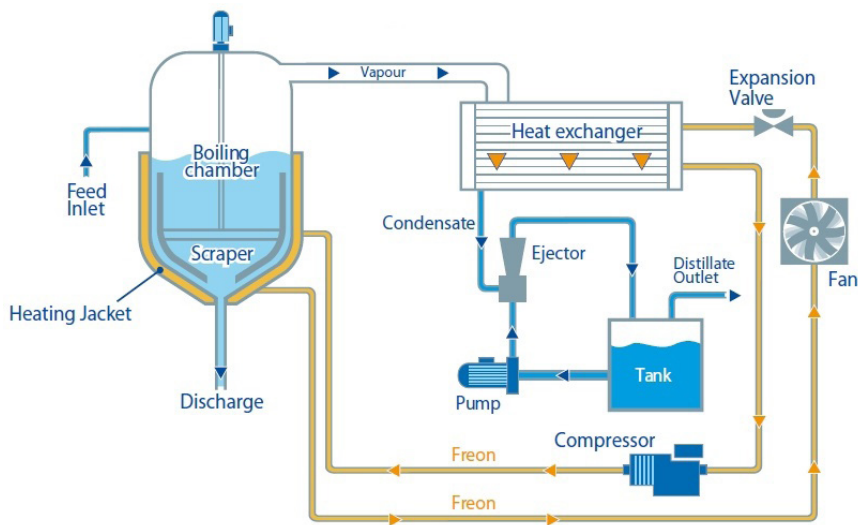
40 L initial process wastewater was pumped into the evaporator. Six different pressures were investigated. During the experiments, applied pressure and boiling

Table 1. Technical characteristics of LED Italia R150-v3 type vacuum evaporator [13]

Technical characteristics	
Nominal production of distillate with water	150 L/24h
Model	R 150v3 FF# ; Superduplex stainless steel
Electrical equipment	R 150v3--3 (400 [V] 50 [Hz] 3P)
Distillate heat exchanger	Internal coil
Primary heat exchanger	Heating jacket
Evaporation type	Vacuum with a scraped system
Evaporation pressure	Absolute pressure 40-50 mbar
Distillate temperature	33-35°C
Drops separator	Demister, grate type with packing elements
Technology of heating/cooling	Heat pump
Heat pump compressor	Reciprocating hermetic
Refrigeration fluid	R 134a (ozone friendly)
Cooling of refrigeration fluid	Air cooled finned heat exchanger
Vacuum system	Liquid ejector
Electrical cabinet rating	IP 54
Noise	< 80 dB(A)

Table 2. Nominal performance of LED Italia R150-v3 type vacuum evaporator [13]

Nominal performance	
Electrical feed	230 V ; 50 Hz ; 1F
Maximum production of distillate with water	170 L/24h \pm 10%
Absorbed power	2.3 kW \pm 10%
Specific consumption	0.325 kWh/L \pm 10%
Produced heat	2.3 kW \pm 10%
Maximum air flow of finned heat exchanger	1000 Nm ³ /h \pm 10%

**Figure 1.** Process diagram of LED Italia R-150 heat pump evaporator [14]

temperatures were measured. The examination was carried out until the best available yield. After the experiments the COD of distillate was measured in order to define the rejection. Finally, mass balance was also calculated.

3 Results and discussion

Figure 2 shows the COD rejection as a function of the yield. It can be seen, the maximal $COD_{rejection}$ value was reached at the yield of 85% and it was 88.7%. They represent a monotonous growing correlation.

In Figure 3, the COD values can be seen in the function of Y_s , where the straight line means the emission limit. It can be concluded, 84.5% must be reached in order to reduce under the emission limit the COD of process wastewater.

Figure 4 and Figure 5 depict the yield as the function of boiling temperatures and the applied pressure. It can be seen that both graphs they are logically in good accordance with each other and the lowest pressure can result the best available yield.

It can be identified, the boiling temperature values with the corresponding pressure pairs are in acceptance accuracy with water phase [15, 16], see Figure 6.

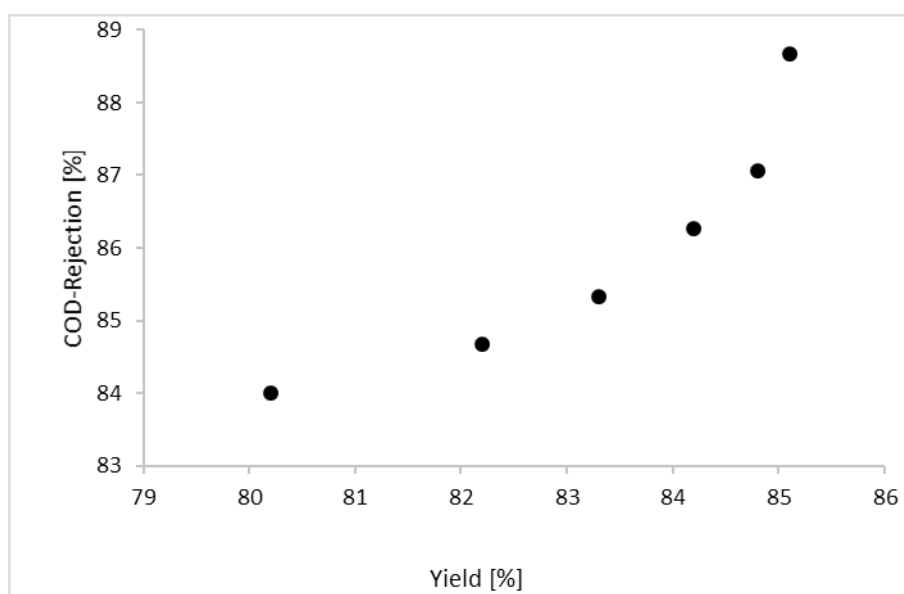


Figure 2. $COD_{rejection}$ as a function of Yield.

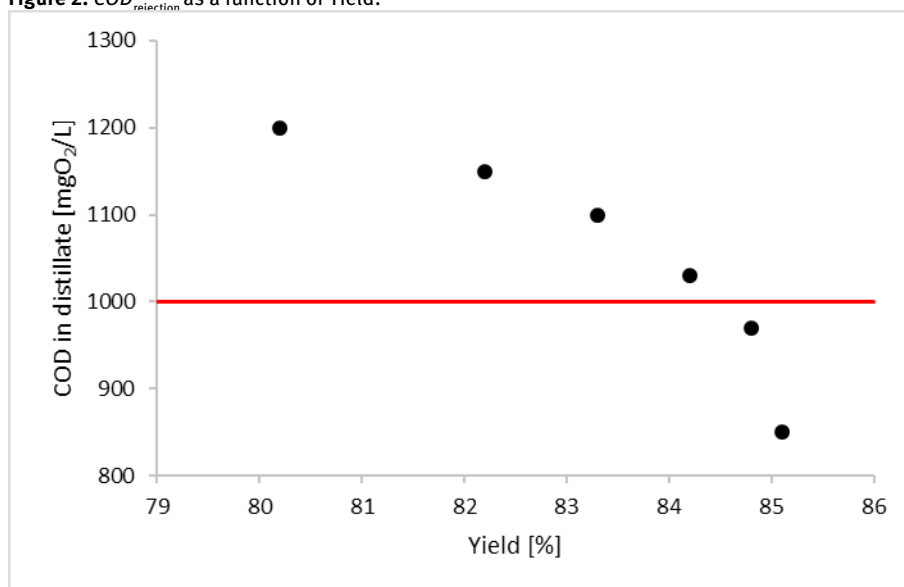


Figure 3. Yield results versus COD values in distillate (Line means the emission limit)

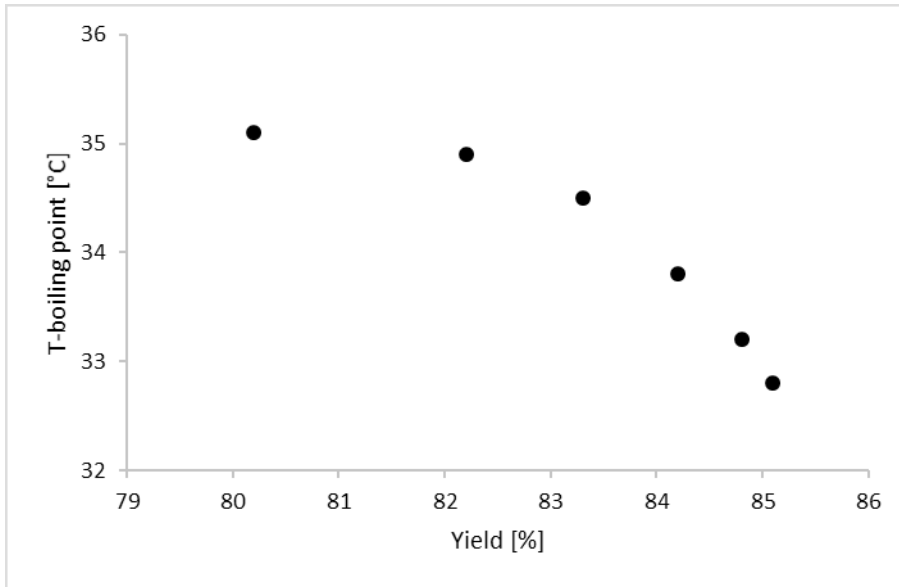


Figure 4. Yield results versus boiling temperatures

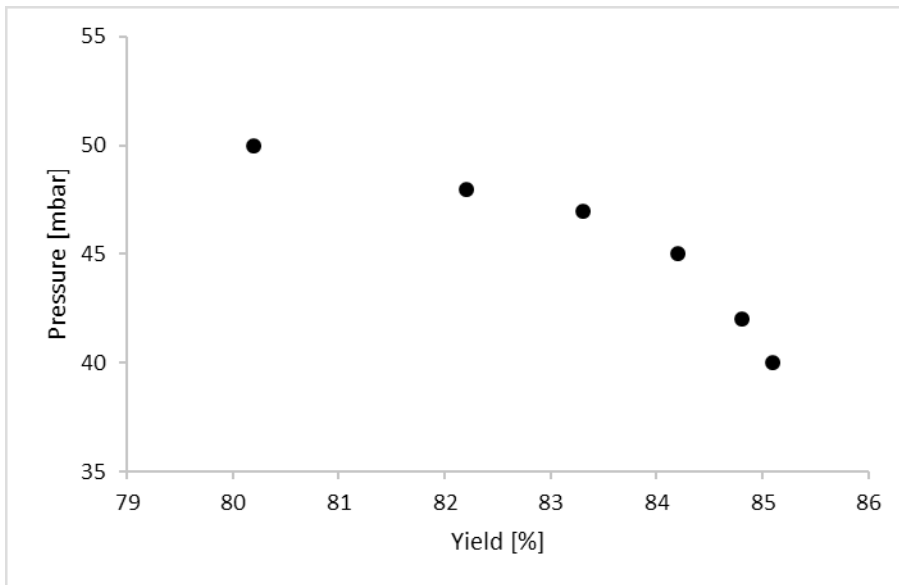


Figure 5. Yield results versus pressure values

Using this correlation, this figure can be applied for up-scaling the technology and for design evaporator in order to treat the process wastewater. Examination of yields, 15% material mass can be realized in the appropriate case, when COD can be reduced under the emission limit.

4 Conclusions

Vacuum evaporation of washing nonionic detergents at pilot-scale setup is investigated. Evaporation rates are influenced by operating pressure between 40 and 50 mbar. The highest yield can be achieved at 40 mbar,

where the boiling point is 32.8°C. The chemical oxygen demand is also the lowest using 40 mbar pressure: 850 mgO₂/L, which means 88.7% in COD rejection value. It can be concluded the COD value of process wastewater can be reduced under the effluent limit, so there is opportunity to recycle or reuse of this water.

Acknowledgement: The authors would like to acknowledge the financial support of János Bolyai Research Scholarship of the Hungarian Academy of Sciences and OTKA 112699 project. This research was supported by the European Union and the Hungarian State, co-financed by the European Regional Development

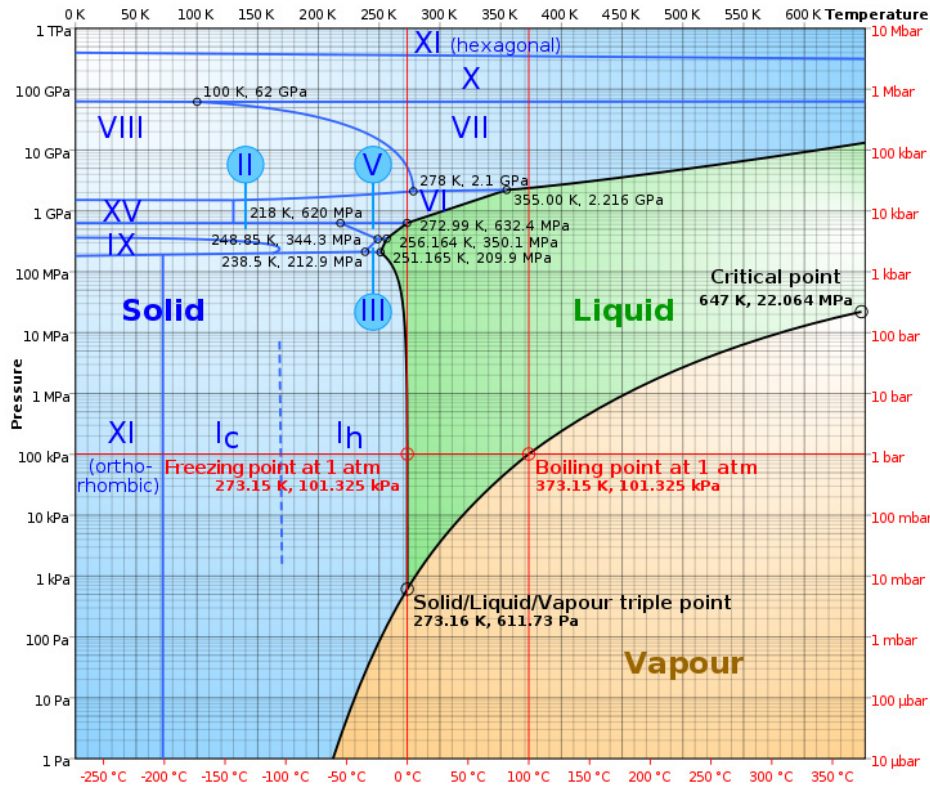


Figure 6 Water phase diagram [17]

Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, aimed to promote the cooperation between the higher education and the industry and the ÚNKP-17-3-I New National Excellence Program of the Ministry of Human Capacities.

Nomenclature

COD	Chemical oxygen demand	[mgO ₂ /L]
D	Distillate	[L]
F	Feed	[L]
PWW	Process wastewater	
T-bp	Boiling point	[°C]
V	Volume	[L]
Y	Yield	[%]

References

- [1] A.J. Toth, Liquid Waste Treatment with Physicochemical Tools for Environmental Protection, Budapest University of Technology and Economics, Budapest, 2015.
- [2] K. Koczka, P. Mizsey, New area for distillation: Wastewater treatment, Periodica Polytechnica: Chemical Engineering 54 (2010) 41-45.
- [3] I.E.T.C. (IETC), Global Waste Management Outlook (GWMO), International Solid Waste Association, Vienna, Austria, 2015.
- [4] G. Gutiérrez, J.M. Benito, J. Coca, C. Pazos, Vacuum evaporation of surfactant solutions and oil-in-water emulsions, Chemical Engineering Journal 162 (2010) 201-207.
- [5] T. Brinkmann, G.G. Santonja, H. Yükseler, S. Roudier, L.D. Sancho, Best Available Techniques (BAT) Reference Document for Common Waste water and Waste Gas Treatment/Management Systems in the Chemical Sector, 2016.
- [6] PRAB, Evaporation Technology for Industrial Wastewater Treatment, 2017. http://wastewater.prab.com/wp-content/uploads/2015/07/WWT2005-EVAPORATION_WASTEWATER_TREATMENT-TB-JUN2015.pdf
- [7] A.S. Nafey, H.E.S. Fath, A.A. Mabrouk, Thermoeconomic design of a multi-effect evaporation mechanical vapor compression (MEE-MVC) desalination process, Desalination 230 (2008) 1-15.
- [8] H. Rahman, M.N.A. Hawlader, A. Malek, An experiment with a single-effect submerged vertical tube evaporator in multi-effect desalination, Desalination 156 (2003) 91-100.
- [9] L. Di Palma, P. Ferrantelli, C. Merli, E. Petrucci, Treatment of industrial landfill leachate by means of evaporation and reverse osmosis, Waste Management 22 (2002) 951-955.
- [10] K. Jevons, M. Awe, Economic benefits of membrane technology vs. evaporator, Desalination 250 (2010) 961-963.
- [11] D. Gavril, K.R. Atta, G. Karaiskakis, Study of the evaporation of pollutant liquids under the influence of surfactants, AIChE Journal 52 (2006) 2381-2390.
- [12] 28/2004. (XII. 25.) Ministry of Environment Regulation. https://net.jogtar.hu/jr/gen/hjegy_doc.cgi?docid=A0400028.KVV
- [13] Veolia Water, Evaporator catalogue, 2017. http://www.evaled.com/wp-content/uploads/2016/09/mobile-catalogue_R150.pdf

- [14] EVALED, Vacuum heat pump evaporators, 2017. http://www.veoliawaterst.it/vwst-italia/ressources/files/1/18920,VWS-Italia_EVALED-PC_eng_LR_04_201.pdf
- [15] Creative Commons Attribution, Water Structure and Science, 2017. http://www1.lsbu.ac.uk/water/water_phase_diagram.html
- [16] Water structure and behavior, The Phase Diagram of Water, 2017. <http://ergodic.ugr.es/termo/lecciones/water1.html>
- [17] X. Zhang, P. Sun, T. Yan, Y. Huang, Z. Ma, B. Zou, W. Zheng, J. Zhou, Y. Gong, C.Q. Sun, Water's phase diagram: From the notion of thermodynamics to hydrogen-bond cooperativity, *Progress in Solid State Chemistry* 43 (2015) 71-81.