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Assessing the potential use of Water Treatment Sludge containing Activated Carbon for the removal of Emerging Pollutants

Dissertação para Obtenção do Grau de Mestre em
Engenharia do Ambiente, perfil de Engenharia Sanitária

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Dezembro de 2020

[Verso da Capa]

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“Mas o que é conhecido? O que é que tu conheces.

Para que chames desconhecido a qualquer coisa em especial?”

Álvaro de Campos

Acknowledgements

First of all, I would sincerely like to thank my thesis advisor Professor Rita Maurício for having accepted me in this project, for all the guidance, trust, motivation and support during the development of this thesis, especially considering the events of this atypical year.

To the researchers Maria Bernardo and Ines Matos for all the sympathy, monitoring and assistance in the laboratory processes, as well as, in clarifying various concepts about activated carbon. Your help was essential for the development of this project. I would also like to thank Professor Leonor Amaral for the support and friendliness during this work, but also throughout my academic career.

To my colleague Rita Dias for all the help, advices, and rides to the university. Our scientific discussions and share of knowledge were undoubtedly essential to me. I’m hopeful that we will be able to work together again. To Beatriz Oliveira for the support and all the conversation during this work.

I also wish to thank EPAL for this project and the financial support made. Especially to Eng. Pedro Fontes for the idea that served as the basis for this project. Thanks to all the team of EPAL’s laboratory. To D. Luísa, D. Adélia and D. Palminha for all the assistance and sympathy provided in the laboratory.

To my university partner, Vanessa. Thank you for taking part in this journey with me full of ups and downs from the first year to the last. I’m very appreciative of my university friends help, especially to Mariana and Carolina for dealing with my "burnout" during the last year of the course.

I would also like to thank all my close friends, especially Carlota, Teresa, Marta Ferreira, Beatriz, Bruna, Marta Ribeiro and Matilde for all the support and friendship.

And, last but not least to my family. For all the love, and the support through all my decisions. Thank you for the education and family values that allowed me to complete another stage of my life.

Resumo

A presença de poluentes emergentes (EP) nos cursos de água e os impactes destes no ambiente e na saúde humana é de extrema importância. Os estrogénios são um grupo de EP que possuem elevada prevalência no ambiente e toxicidade, mesmo a concentrações baixas, o que leva a ocorrência de impactes adversos tanto na vida selvagem com na humana. Neste grupo estão incluídos a estrona (E1), o 17β-estradiol (E2) e o 17α-etinilestradiol (EE2).

A descarga de águas residuais no ambiente é uma das principais causas responsáveis pela entrada destes compostos no ambiente. As estações de tratamento de águas residuais não foram projetadas e dimensionadas para a remoção dos EP. Por isso, torna-se importante estudar tratamentos complementares para a remoção destes compostos, especialmente com o aumento do incentivo à reutilização de águas residuais tratadas promovido nos Objetivos para o Desenvolvimento Sustentável das Nações Unidas.

Existem diversos tratamentos complementares que possibilitam a remoção de EP. O processo de adsorção é um dos mais comuns, uma vez que é de implementação e operação simples e, pelo que se conhece, não origina subprodutos tóxicos. Existem diversos tipos de materiais adsorventes, contudo, o mais utilizado é o carvão ativado (AC). O AC apresenta elevada capacidade de remoção de E1, E2 e EE2. Porém, a regeneração é um processo dispendioso e resulta num material com menor capacidade de adsorção. Por este motivo encontram-se em estudo alternativas, na procura de adsorventes mais económicos. A possibilidade de utilizar lamas de estações de tratamento de água (WTSs) que contêm AC como um adsorvente alternativo, poderá proporciona uma nova forma de gestão sustentável de recursos, alinhada com o conceito de economia circular e por outro lado irá contribuir para a descarbonização da industria de tratamento de água.

A presente dissertação teve como objetivo o estudo do potencial das WTS que contêm AC na remoção de E1, E2 e EE2. De forma a dar cumprimento ao objetivo proposto, foram estudadas duas WTS, enriquecidas com AC, de duas estações de tratamento de água, WTSs de Sta. Águeda e de Caldeirão. As duas demonstraram possuir potencial de adsorção, com eficiências de remoção de pelo menos 50%, sem diminuição da sua granulometria. Em relação à WTS de Caldeirão, as concentrações finais dos três estrogénios ficaram abaixo do limite de quantificação. Já em relação à WTS de Sta. Águeda, os resultados de remoção relativos a E1 e ao E2 foram semelhantes aos obtidos com a WTS de Caldeirão, contudo, em relação ao EE2 a eficiência de remoção foi inferior. Estes resultados evidenciam uma nova abordagem na gestão deste outrora resíduo e na remoção de EP.

Palavras-chave: Poluentes Emergentes; Estrogénios; Lamas de Estações de Tratamento De Água; Processo de Adsorção; Economia Circular.

Abstract

The presence of emerging pollutants (EP) in water bodies and its impacts on the environment and human health is of the utmost importance. Estrogens are a group of EP, that have a high prevalence in the environment and toxicity even at low concentrations, which leads to adverse impact in both wild and human life's. This group include compounds such as estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2).

The discharge of wastewater into the environment is one of the main causes for the release of these compounds in the environment. Wastewater treatment plants are not designed to remove EP. Therefore, it is important to add complementary treatments to remove these compounds, especially with the increasing of the incentive of the reuse of treated wastewater, promoted by the United Nations (UN) Sustainable Development Goals.

There are several additional treatments to accomplish EP removal. The adsorption process is one of the commonly used since it is simple to design and operate and does not generate toxic by-products. There are many kinds of adsorbent materials, however, the most used is activated carbon (AC). AC shows high removal capacity for the removal of E1, E2 and EE2. However, AC's regeneration is an expensive process and result in a material with low adsorption capacity. As a result, efforts are being raised to find low-cost adsorbents. The use of water treatment sludges (WTSs) containing AC as an alternative adsorbent provides a new way of sustainable resources management, lining up with circular economy proposals and on another hand will contribute to the decarbonization of the water treatment industry.

This work studied the potential of WTS containing AC for the removal of E1, E2 and EE2. For this purpose, WTS from two water treatment plants (WTP), St. Águeda WTS and Caldeirão WTS were characterised and tested as adsorbents. Both WTSs showed adsorption potential with efficiencies removal results above 50 %, without a significant decrease in their granulometry. For Caldeirão WTS final concentration for all the three EP were lower than the limit of quantification. As for St. Águeda WTS, the results for E1 and E2 removal were similar to Caldeirão WTS removal performance. However, for EE2 the removal efficiency was lower than the obtained with Caldeirão WTS. These results lead to a new approach in the management of this erstwhile reside and removal of EP.

Keywords: Emerging Pollutants; Estrogens; Water Treatment Sludges; Adsorption Processes; Circular Economy.

List of Abbreviations and Symbols

AC	Activated Carbon
b	Langmuir Isotherm Constant
BET	Brunauer-Emmett-Teller
C_0	Adsorbate Initial Concentration
C_{BET}	BET Constant Adsorption Isotherm
C_e	Adsorbate Equilibrium Concentration
CH_3OH	Methanol
C_s	Adsorbate Monolayer Saturation Concentration
C_t	Adsorbate Concentration After a Residence Time
DOM	Dissolved Organic Matter
E1	Estrone
E2	17β-estradiol
EDC	Endocrine Disrupting Chemicals
EE2	17α-ethinylestradiol
EP	Emerging Pollutants
EQSD	Environmental Quality Standards Directive
EU	European Union
FCT	Faculdade de Ciências e Tecnologia
GAC	Granular Activated Carbon
GC-MS	Gas Chromatography-Mass Spectrometry
HCl	Hydrochloric Acid

HPLC-MS-MS	High-Performance Liquid Chromatography Tandem Mass Spectrometry
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectrometry
IUPAC	International Union of Pure and Applied Chemistry
k_1	Rate Constant of the Pseudo-First Order Model
k_2	Rate Constant of the Pseudo-Second Order Model
K_F	Freundlich Isotherm Constant
k_{id}	Intraparticle Diffusion Rate Constant
K_{ow}	Octanol-Water Partition Coefficient
LC-MS-MS	Liquid Chromatography Triple Quadrupole Mass Spectrometry
LOQ	Limit of Quantification
$m_{Ash+crucible}$	Weight of the Crucible Containing WTS's Ash
MB^+	Methylene Blue
$m_{crucible}$	Weight of the Crucible
$m_{WTS+crucible}$	Weight of the Crucible Containing WTS
n	Adsorption Intensity
NaCl	Sodium Chloride
NaOH	Sodium hydroxide
PAC	Powdered Activated Carbon
pH_{pzc}	pH of the Point of Zero Charge
pKa	Acid Dissociation Constants
q	Adsorption Capacity
Q_0	Maximum Monolayer Coverage Capacities
q_e	Theoretical Adsorption Capacity at Equilibrium
q_s	Theoretical Isotherm Saturation Capacity
q_t	Adsorption Capacity at Time t
SDG	Sustainable Development Goals
SPE	Solid-phase extraction
t	Residence Time
TGA	Thermogravimetric Analysis
UN	United Nations
UNL	Universidade Nova de Lisboa

USA	United States of America
V	Solution Volume
WFD	Water Framework Directive
wt.%	Weight Percent
WTP	Water Treatment Plants
WTS	Water Treatment Sludge
WWTP	Wastewater Treatment Plants

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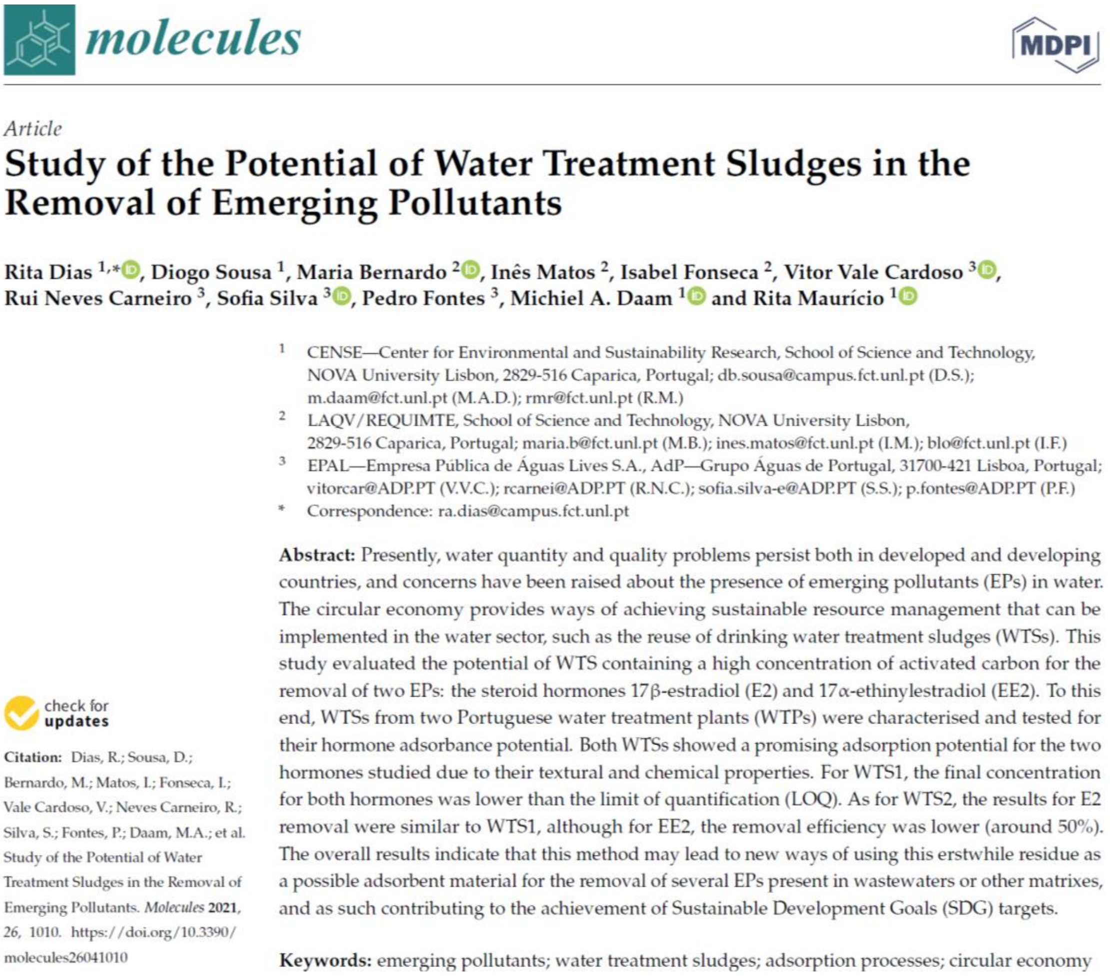
1 Published Work

In this chapter, it is possible to find the scientific article published in the Journal Molecules. The article has the following sections: Abstract, Introduction, Results and Discussion, Materials and Methods, Conclusions, Author Contributions, Acknowledgements and Funding, Conflicts of Interest, and References.



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Article

Study of the Potential of Water Treatment Sludges in the Removal of Emerging Pollutants

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Abstract: Presently, water quantity and quality problems persist both in developed and developing countries, and concerns have been raised about the presence of emerging pollutants (EPs) in water. The circular economy provides ways of achieving sustainable resource management that can be implemented in the water sector, such as the reuse of drinking water treatment sludges (WTSs). This study evaluated the potential of WTS containing a high concentration of activated carbon for the removal of two EPs: the steroid hormones 17β-estradiol (E2) and 17α-ethinylestradiol (EE2). To this end, WTSs from two Portuguese water treatment plants (WTPs) were characterised and tested for their hormone adsorbance potential. Both WTSs showed a promising adsorption potential for the two hormones studied due to their textural and chemical properties. For WTS1, the final concentration for both hormones was lower than the limit of quantification (LOQ). As for WTS2, the results for E2 removal were similar to WTS1, although for EE2, the removal efficiency was lower (around 50%). The overall results indicate that this method may lead to new ways of using this erstwhile residue as a possible adsorbent material for the removal of several EPs present in wastewaters or other matrixes, and as such contributing to the achievement of Sustainable Development Goals (SDG) targets.

Keywords: emerging pollutants; water treatment sludges; adsorption processes; circular economy

Citation: Dias, R.; Sousa, D.; Bernardo, M.; Matos, I.; Fonseca, I.; Vale Cardoso, V.; Neves Carneiro, R.; Silva, S.; Fontes, P.; Daam, M.A.; et al. Study of the Potential of Water Treatment Sludges in the Removal of Emerging Pollutants. *Molecules* **2021**, *26*, 1010. https://doi.org/10.3390/molecules26041010

Academic Editor: T. Jean Daou

Received: 13 January 2021
Accepted: 10 February 2021
Published: 14 February 2021

1. Introduction

One of the most prominent problems affecting the world's population is insufficient access to clean water and sanitation. According to Sustainable Development Goal (SDG) 6 "clean water and sanitation" of the Synthesis Report on Water and Sanitation [1], over two billion people are living in countries that are experiencing high water stress conditions. This situation is a result of an overuse of water resources with significant impacts on their sustainability. Concurrently, water quality problems persist in water bodies of both developed and developing countries, such as the loss of the pristine quality conditions, changes in hydromorphological characteristics and an increase in concentrations of emerging pollutants (EPs) [1]. The clearest link between water and the circular economy is to consider drinking water and wastewater treatment plants as resource recovery installations, stimulating the recovery and valorisation of treated water and wastewater materials [2]. The circular economy concept provides ways of advancing towards sustainable water resource management that can be implemented in the water sector to achieve circularity between drinking water and wastewater resources [3].

Conventional wastewater treatment plants (WWTPs) are not entirely effective in the removal of EPs from wastewater (WW) since they were conceptually designed for the removal of macropollutants such as nutrients, suspended solids, pathogenic microorganisms

Molecules **2021**, *26*, 1010. https://doi.org/10.3390/molecules26041010 https://www.mdpi.com/journal/molecules

and trace elements. Therefore, EPs such as pharmaceuticals and endocrine disrupting compounds (EDCs) may go through the treatment system unchanged or are only partially removed, leading to their detection in WW-receiving water bodies and WWTP discharges in concentrations ranging from ng/L to mg/L [4–8]. EDCs may lead to the modification of the natural function of the endocrine system in wildlife by (i) blocking or copying the normal effect of hormones; (ii) affecting their synthesis or metabolism; and (iii) changing hormone receptor levels [8–11]. Among EDCs, estrogens such as 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) have often been indicated as particularly problematic compounds with high associated risks [12–14]. E2 is a natural steroid hormone, which is secreted by humans and animals. The synthetic steroid hormone EE2 is based on the natural estrogen E2, which is used in oral contraceptives and hormone replacement therapies. These estrogens are largely excreted by humans and animals through urine and faeces and end up in the environment mainly through the discharge of WWTP effluents and the disposal of animal waste [10,15,16]. Secondary treatment is not effective in the removal of both of these compounds, especially for EE2 due to its recalcitrant nature. As such, it is known that WWTP final discharges are the main source of both E2 and EE2 in the aquatic environment. These chemicals have the potential to bioaccumulate and enter the food chain, posing ecotoxicity to aquatic organisms and implying risks to aquatic ecosystems. Several studies have reported the impact of E2 and EE2 on fish life, such as feminising male fish, reducing testicle size, reducing reproductive fitness, lowering sperm count, inducing the reproduction of vitellogenin, altering other reproductive characteristics and causing behavioural changes [9,17,18]. The uptake by fish and the presence of these compounds in the raw water that is used to produce drinking water to supply human communities also have impacts on human life and have previously been reported. The consumption of these compounds at concentrations above the safety thresholds can increase the risk of cancer and induce cardiovascular diseases [9,16,17].

Several technical solutions for EP removal have previously been developed that allow for their integration with existing treatment processes in an expedient way [7,19]. However, most of the methods are not techno-economically viable for large-scale implementation, and thus, comprehensive research is necessary to develop suitable, low cost, eco-friendly and efficient technologies to remove different kinds of EPs from WW [8,19–22]. The adsorption process with activated carbon (AC) is considered by many authors to be one of the most promising treatment processes with high EP removal capacity, mainly because (i) it is simple to design and operate; (ii) it has a low investment cost; (iii) it allows reuse and regeneration; and (iv) it does not generate toxic by-products [8,19,21–24]. Several studies have also already demonstrated that pure AC is able to effectively remove and lower the toxicity of E2 and EE2 in distilled water, drinking water and WW [25–35]. For example, Gökçe and Arayici [33] obtained a removal rate for E2 of 88% with AC produced from sewage sludge. In this referred work [33], the sludges were modified and submitted to several procedures in order to obtain sludge-based adsorbents.

Sludge-based adsorbents have been reported in the literature for the removal of several pollutants from water treatment plants (WTPs) and WWTPs [36,37]. Research efforts, however, have focused on their removal efficacy for compounds like heavy metals [38–43], dyes [44–46], phenols [47,48], phosphorus and phosphate [49–52] and antibiotics [53]. Consequently, the adsorbent potential of sludge for compounds like E2 and EE2 remains unknown. Clara et al. [54] tested the capacity of sludge from WWTP (without AC content) to adsorb E2 and EE2 in the mg/L range and noted a high adsorption potential of the tested sludge.

Drinking water treatment plant sludges (WTSs) have been recycled as aggregates, soil improvement agents and environmental remediation materials. The use of WTSs as an adsorbent in WW treatment is related to their high concentration of amorphous aluminium and ferric ions. These ions have a high affinity to phosphors and heavy metals through ion-exchange and complexation mechanisms [55–58]. The first report indicating the potential use of WTS containing AC was made by Lee et al. [58]. They evaluated the

possibility of regenerating the AC and coagulants present in WTS via pyrolysis to produce multifunctional remediation material for the removal of pollutants present in WW.

Considering (i) the capacity of AC to remove EPs in an adsorbent process and (ii) the possibility to reuse WTS for several applications, it is envisaged that there is a potential use of WTS containing AC for the removal of EPs. As detailed above, however, current knowledge in this field remains limited. The main goal of this study was therefore to evaluate the potential of two unmodified WTSs with high content of activated carbon, without reactivation, as an adsorbent for the removal of two selected EPs, namely, E2 and EE2. No additional AC was incorporated in the sludges used nor was any kind of sludge treatment/modification made (including an AC reactivation step). Consequently, the AC content in the test sludges only had its origin from the conventional liquid treatment phase in the drinking WTP process. The elemental and mineral composition, ash content, pH at the point of zero charge (pHpzc), thermogravimetric analysis and textural characterisation of the sludges were determined. The removal potential of the two hormones by the sludges was also assessed, allowing an evaluation of the circularity of this residue and thus the possibility of transforming it into a new adsorbent material.

2. Results and Discussion

2.1. Water Treatment Sludge Characterisation

The elemental analysis, ash content, pHpzc and textural parameters of the two WTSs are presented in Table 1. WTS samples presented high ash contents: 42.9% for WTS1 and 30.9% for WTS2, which was expected given their origin. Nevertheless, these values are slightly lower than those observed by Lee et al. [58], who reported an ash content of around 51.0% for sludge obtained in South Korea. The variation between the ash content of these WTSs could be explained by the different reagents used in the treatment line and therefore the different mineral content. In fact, the presence of some mineral elements could be important because they may promote the formation of strong interactions with organic pollutants and as such promote their removal from water [58–60].

Table 1. Elemental analysis, ash content, pH at the point of zero charge (pHpzc) and textural parameters of the selected drinking water treatment sludges (WTSs). The values presented for the ash content correspond to the mean of duplicates ($\overline{X} \pm \sigma$, $n = 2$).

Parameter	WTS1	WTS2
C (*w*/*w*%)	24.31	34.09
N (*w*/*w*%)	0.24	0.46
H (*w*/*w*%)	2.64	2.92
S (*w*/*w*%)	0.16	0.18
O (*w*/*w*%) *	29.78	31.49
Ash (*w*/*w*%)	42.9 ± 0.2	30.8 ± 0.8
Surface area (m^2/g)	127	318
Vtotal (cm^3/g)	0.065	0.161
pHpzc	11.29	7.46

* Obtained by difference (%O = 100 − %C − %H − %N − %S − %Ashes).

The higher content of carbon observed in WTS2 as compared to WTS1 indicates that WTS2 may have a higher incorporation of activated carbon in its composition. The higher carbon content is reflected in the lower ash content of WTS2 and consequently in a higher surface area and porosity (Table 1). On the other hand, since WTS1 presented a higher ash content, it has a lower surface area given that the ash may block the pores in the sludge [58,61]. The pHpzc is directly related to the ash content of the samples: WTS1 is the more alkaline sample because it presented the higher mineral content. WTS2, on other hand, had a more neutral pHpzc, which indicates that WTS2 is more similar to alum sludge [57,62]. According to these results, WTS1 and WTS2 surfaces were positively charged in water solutions with a pH of below 11.29 and 7.46, respectively (Table 1).

The results from the mineral analysis (Table 2) demonstrate that the elements present in higher concentrations in WTS2 were aluminium (Al; 5.4%) and phosphorous (P; 3.5%), followed by iron (Fe; 1%) and calcium (Ca; 0.6%), as visualised in Figure 1. For WTS1, the elements with the highest concentrations were calcium (Ca; 11.5%), followed by aluminium (Al; 5.3%), phosphorous (P; 3.4%) and iron (Fe; 0.7%) (Table 2; Figure 1).

Table 2. Mineral composition of drinking water treatment sludge (WTS) samples. The values presented correspond to the mean of replicates ($\overline{X} \pm \sigma$, $n = 2$)

Mineral Composition (mg/kg)	WTS1	WTS2
Al	53,000 ± 800	54,450 ± 5350
As	37.4 ± 0.9	65.6 ± 7.9
Ca	115,350 ± 1650	6429.54 ± 733.41
Cd	n.d.	n.d.
Cr	n.d.	n.d.
Cu	4.1 ± 0.4	10.5 ± 1.1
Fe	6890.5 ± 502.9	9442.5 ± 1328.5
Hg	n.d.	n.d.
K	275.8 ± 10.7	119.9 ± 13.0
Mg	5424.0 ± 112.0	2280.3 ± 458.7
Mn	468.6 ± 19.0	150.4 ± 14.1
Mo	5.3 ± 0.1	5.2 ± 0.6
Na	16.1 ± 0.3	5.4 ± 0.5
Ni	n.d.	n.d.
P	33,817.6 ± 588.5	34,947.3 ± 4242.3
Pb	13.1 ± 0.2	14.1 ± 2.6
Sb	37.0 ± 0.6	37.4 ± 3.8
Se	38.4 ± 0.2	41.3 ± 3.8
Zn	21.8 ± 1.4	15.5 ± 1.4

n.d.—not detected.

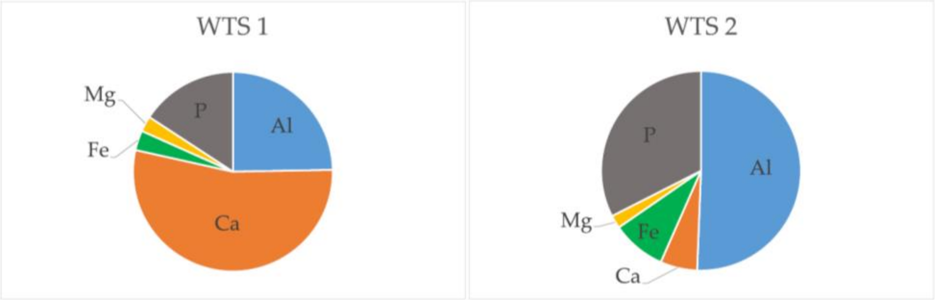

Figure 1. Mineral composition of drinking water treatment sludge (WTS) samples in *w*/*w*% for the major elements.

The main difference in mineral composition between the two WTSs was related to the calcium content (Table 2), which could be explained by the addition of insoluble limestone residues in the final stage of the sludge treatment of WTS1. To understand the thermal behaviour of WTS during an activation/regeneration process, it is fundamental to study their thermal decomposition through thermogravimetric analysis (TGA), which is presented in Figure 2.

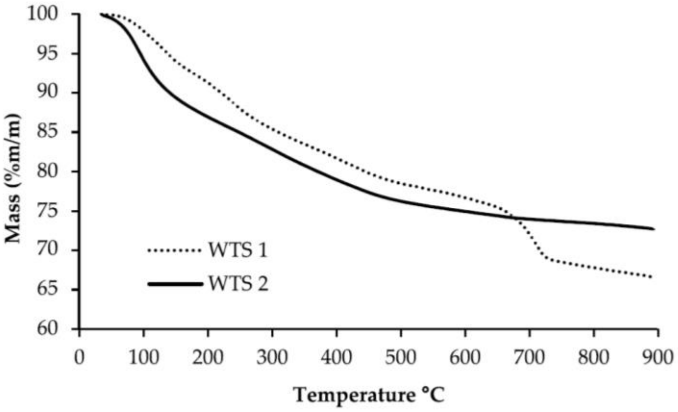

Figure 2. Thermogravimetric analysis (TGA) curves for the two water treatment sludges (WTSs) evaluated.

During the TGA analysis, the total mass loss was 34% and 27% for WTS1 and WTS2, respectively. These values may suggest that, through a regeneration/activation process, a significant mass was lost [61]. Both samples presented weight loss associated with water loss at 105 °C: WTS2 humidity was 6.5%, while for WTS1, this was 2.5%. WTS1 also presented a significant mass loss above 700 °C, which could be related to the decomposition of $CaCO_3$ [59,63]. In fact, WTS1 was enriched with calcium that was probably present as carbonates.

2.2. *Removal of Emerging Pollutants from Water*

The removal efficiency experiment of the adsorbates with the WTS adsorbents was performed by using a dosage of 5 g WTS/L. This dosage was based on the concentrations used by Lee et al. [58] in their adsorption experiment, which were 4, 5 and 20 g/L.

The overall removal efficiency for both hormones was above 50% in both WTSs (Table 3). These results are in line with the removal efficiencies reported in the studies by Yoon et al. [30], Fuerhacker et al. [31], Gökçe and Arayici [33] and Rowsell et al. [32]. It should be noted, however, that these previous studies were performed using pure AC, with higher surface areas and pore volumes. Thus, few studies have been conducted to date using raw (unmodified) WTS (with or without an activation process) for the removal of EPs, as done in the present study. Evidently, such studies would be useful to meet the SDG targets and circular economy commitments.

Table 3. Final concentrations of the emerging pollutants in the two water treatment sludges (WTSs) evaluated.

Compound	Initial Concentration (ng/L)	WTS1	WTS2
		Final Concentration (ng/L)	Final Concentration (ng/L)
E2	600 ± 200 (500 $^{(2)}$)	60 ± 20	<LOQ $^{(1)}$
	400 ± 100 (350 $^{(2)}$)	80 ± 30	<LOQ $^{(1)}$
	300 ± 100 (200 $^{(2)}$)	<LOQ $^{(1)}$	<LOQ $^{(1)}$
EE2	600 ± 200 (500 $^{(2)}$)	150 ± 60	<LOQ $^{(1)}$
	400 ± 100 (350 $^{(2)}$)	170 ± 70	<LOQ $^{(1)}$
	300 ± 100 (200 $^{(2)}$)	100 ± 40	<LOQ $^{(1)}$

(1) LOQ value—50 ng/L; (2) Initial target concentration.

The removal efficiency in WTS2 was over 90% (for both E2 and EE2) at any of the initial hormone concentrations tested (Table 3). This result is comparable to the one presented by Yoon et al. [30] using virgin powdered activated carbon (PAC), who achieved a removal efficacy of 99% for both E2 and EE2 with a contact time of 24 h. Ifelebuegu et al. [34] also achieved a 96% removal efficacy of EE2 with 0.1 g/L wood-based granular activated carbon (GAC). Regarding sludge-based carbons, Clara et al. [54] used activated and raw sludge from a WWTP to evaluate the adsorption capacity of E2 and EE2. These authors concluded that both compounds showed a high adsorption affinity to the adsorbent, and within a contact time of 24 h, no difference between activated and inactivated sludge was detected. Some authors have previously suggested that the octanol/water partition coefficient (Log Kow) values for estrogenic compounds, which vary between 2.5 and 4.0, can roughly predict the sorption behaviour. E2 and EE2 are often cited as moderately hydrophobic and to have a tendency to adsorb to the solid phase [9,30,32]. These properties could thus indicate an easy interaction with the adsorbent [35]. The pH value of the test matrix is also an important factor that affects the adsorption capacity of sludge as an adsorbent [37]. In this preliminary study, the pH of the solution with distilled water and hormones was around 3. Previous studies have demonstrated that adsorption is higher at acidic pH and that the highest adsorption of E2 and EE2 occurs at neutral pH (6-7) [25]. Both E2 and EE2 are protonated (with pKa 10.4 and 10.7, respectively), while, according to the WTS pHpzc values, WTS surfaces are positively charged, which may support a positive interaction (no electrostatic repulsion) between adsorbent and adsorbate. Besides the influence of the AC properties on its adsorption capacity, the presence of other elements could also have influenced the adsorption performance of the sludges tested. For example, the high aluminium content of the sludges (Table 2) may have influenced the adsorption process, although there appears little consensus in the literature on this influence [36,38,51,62]. On the one hand, aluminium has been indicated to improve the adsorption capacity of WTS (e.g., Lee et al. [58]). On the other hand, other studies have concluded that aluminium as a coagulant [64,65] in WTS has only a minimal impact on the removal efficacy of steroid compounds [66]. Therefore, it is of utmost importance that further research is conducted to assess the role of aluminium on the adsorption capacity of WTSs containing AC for these hormones.

WTS2 had a higher removal efficiency when compared with WTS1 since the final concentration was lower than the limit of quantification (LOQ) (Table 3), which could be related to a number of factors. The most evident reason is the higher surface area and pore volume of WTS2 as compared to WTS1, which logically also increases the number of available adsorption sites of the former [34]. The better performance of WTS2 may also suggest that a greater portion of AC was available in this sludge for adsorption, and that therefore the reactivation processes may not even be necessary. However, other adsorption mechanisms not evaluated in the present study could also be responsible for the differential interactions between the EPs and the two WTSs evaluated, such as π–π interactions, hydrogen bonding or electrostatic interactions, and this should be explored in future studies [67]. Short-term future prospects for this research are to complete the full characterisation of WTS, including complete textural characterisation and surface chemistry evaluation to identify surface functional groups by Fourier-transform infrared (FT-IR) and X-ray diffraction (XRD) analysis, and also to perform kinetic and equilibrium assays to elucidate the adsorption mechanisms. The pH and temperature dependence of the adsorption process will also be assessed, along with analysis of the stability of the WTS to ensure the safe application of this material. Long-term prospects for this research will include WTS adsorbent capacity analysis by using a real wastewater matrix in order to analyse the removal efficiency of both E2 and EE2 with the aim of bringing the research closer to a real situation.

3. Materials and Methods

3.1. Raw Material

Two WTSs from different WTPs in Portugal were used to evaluate their adsorption potential of E2 and EE2: (i) Santa Águeda WTP in the Castelo Branco region (WTS1) and (ii) Caldeirão WTP in the Guarda region (WTS2). Both these WTPs use powdered AC in their water treatment process to remove flavour and odours from raw water. Therefore, the sludge produced in the sedimentation tanks of these WTPs will always contain AC. Sludges were collected from these WTPs after the final stage of dewatering by filter press, and the collected sludge was kept in the sun for one month to completely remove the remaining water. The obtained material was not subjected to a reactivation process, and the dried material was ground and sieved to obtain a particle size of 45/60 mesh (250–354 µm), between conventional PAC and GAC particle sizes [68–70].

3.2. Analytical Methods

3.2.1. WTS Characterisation

Elemental analyses (quantification of carbon, hydrogen, nitrogen and sulphur contents) were performed using an Elemental Thermo Finnigan Analyzer—CE Instruments, model Flash EA 1112 CHNS series (Waltham, MA, USA), based on sample combustion dynamics. The determination of the ash content followed the ASTM D 1762-84 guideline (750 °C) [71]. The pH at the point of zero charge (pHpzc) determination was performed according to the methodology presented by Bernardo et al. [59]. Thermogravimetric analysis (TGA) was performed with Setaram Labsys EVO equipment (Caluire, France) between room temperature and 900 °C with a heating rate of 5 °C/min under argon atmosphere. The mineral analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Horiba Jobin-Yvon equipment, Kyoto, Japan) after acidic digestion of the WTS samples for the quantification of the following elements: Al, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se and Zn. Textural parameters such as surface area and total pore volume (V_{total}) were evaluated from the adsorption of N_2 at 77 K (ASAP 2010 Micromeritics equipment, Atlanta, GA, USA) by using the single point method at the relative pressure of $p/p_0 = 0.3$.

3.2.2. Stock Solution and Determination of the Emerging Pollutants

Stock solutions for both 17β-estradiol (E2; Acros Organics, 98% purity, China) and 17α-ethinylestradiol (EE2; Dr. Ehrenstorfer, 97% purity, Germany) were prepared with a concentration of 500 µg/L for each hormone. The stock solutions were stored in a fridge at 4 °C. Each WTS was added to three separate solutions with different hormone concentrations (200, 350 and 500 ng/L) by using a solid/liquid ratio of 5 g/L. The solutions with WTS were submitted to agitation (200 rpm) in jar test equipment for 24 h. After mixing, the samples were filtered through glass microfibre filters (1.2 µm, GF/C—WATERS) under vacuum. The extraction and detection of the studied EPs were performed by solid-phase extraction (SPE) and high-performance liquid chromatography tandem mass spectrometry (HPLC-MS-MS), according to Gaffney et al. [72,73].

4. Conclusions

The results obtained indicate that the tested WTSs present high adsorption potential for both E2 and EE2. Without regeneration or any kind of modification, this adsorbent allowed the achievement of a considerably high, up to a complete, removal of these hormones. These promising results indicate the potential of WTS without addition or activation of AC (i.e., with only AC present from the regular WTP process) in the removal of EPs and may lead to new ways of transforming this erstwhile residue into a possible value-added product. Further studies should be conducted to fully characterise these adsorbent materials through a complete textural characterisation and surface chemistry evaluation to identify surface functional groups and also to perform kinetic and equilibrium assays to elucidate the adsorption mechanisms.

Author Contributions: Conceptualisation, R.M. and P.F.; methodology, R.D., D.S., M.B., V.V.C. and S.S.; validation, M.B., I.M., I.F., V.V.C., R.N.C., P.F., M.A.D. and R.M.; formal analysis, R.D., D.S., M.B., V.V.C. and S.S.; investigation, R.D. and D.S.; resources, R.M., V.V.C., P.F., M.B, I.M. and I.F.; writing—original draft preparation, R.D. and D.S.; writing—review and editing, R.D., R.M. and M.A.D.; visualization, R.D., R.M. and M.A.D.; supervision, R.M. and M.A.D.; funding acquisition, R.D., M.B., P.F., R.M. and M.A.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by CENSE through the Portuguese Foundation for Science and Technology (FCT; UIDB/04085/2020) and through a PhD grant for Rita Dias (SFRH/BD/148793/2019). The authors are also indebted to EPAL AdVT for their financial support to this project. This work was also supported by the Associate Laboratory for Green Chemistry—LAQV, which is financed by national funds from FCT/MCTES (UIDB/50006/2020). Maria Bernardo acknowledges Norma Transitória DL57/2016 Contract (FCT/MCTES).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors would like to thank to EPAL—Empresa Pública de Águas Lives S.A., AdP—Grupo Águas de Portugal for the technical support.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: MSamples of the compounds E2 and EE2 are available from the authors.

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2 Structure

This work is divide into nine chapters. In the first chapter, which presents the article under revision that was made based on this work. The current one presents the structure of this work. The third chapter, which presents the the state of the art and the objectives of this work. The fourth one, which presents the materials and the methods used during this work. The fifth chapter includes the results obtained and their discussion. The sixth one which includes the conclusion obtained through this study and the future developments. The seventh chapter presents the bibliography that sports this thesis and the last one, in which it is present the annexes.

3 State of the Art

3.1 Emerging Pollutants

Water quality is a key aspect in today's societies since it is intrinsically linked with the preservation of the ecosystem, food safety, human health, poverty reduction, economic growth, social development and many other factors. Consequently, the preservation of water quality is essential to achieve sustainable progress (Gorito et al., 2017). Water quality is so important for the sustainable progress that it makes part of the 17 United Nations (UN) Sustainable Development Goals (SDG). The SDG’s sixth goal is clean water and sanitation, that have seven targets. One of these targets intends to achieve the improvement of water quality by reducing pollution, eliminating dumping and the release of hazardous chemicals and materials (Gorito et al., 2017; UN, 2016).

In recent years, the concerns about the presence of "emerging pollutants" in water bodies and its impacts on the environment and human health have been raised and are in agreement with the targets of elimination of hazardous substances proposed by the UN. The term emerging pollutants (EP) has been applied to a variety of chemical compounds without regulatory status in the environment, that are continuously introduced into the aquatic environment through anthropogenic sources (Anjali & Shanthakumar, 2019; Elizalde-Velázquez et al., 2016; Grassi et al., 2013; Mailler et al., 2016).

Currently, the presence of these compounds in aquatic environments is the utmost important aspect of water quality, therefore, it is imperative to establish water quality targets (Johnson et al., 2020; Maurício et al., 2018). EP can be natural or synthetic substances such as pesticides, hormones and antibiotics that are characterized by being bioactive and poorly degradable molecules that persist in the environment at low concentrations, ranging from micrograms to nanograms per litre or even lower, picograms per litre (Benstoem et al., 2017; Krahnstöver & Wintgens, 2018; Maurício et al., 2018; Gorito et al., 2017). This study focuses on a group of emerging pollutants that are classified as estrogens.

3.2 Estrogens

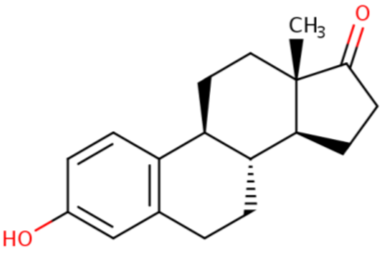
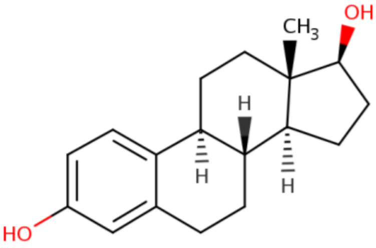
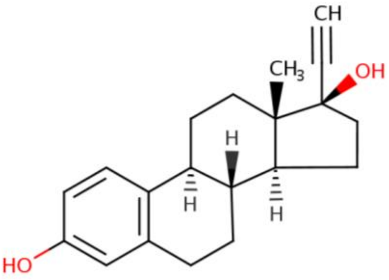
In recent years, the research for the presence of EP in the environment has been increasing, especially for estrogens such as estrone (E1), 17β-estradiol (E2), and 17α-ethinylestradiol (EE2) due to their high prevalence in the environment and their toxicity (Ashfaq et al., 2018; Bilal and Iqbal, 2019; Hamid and Eskicioglu, 2012). These EP are also classified as endocrine disrupting chemicals (EDC). EDCs are defined, according to the United States Environmental Protection Agency, as "exogenous agents that interfere with the synthesis, secretion, transport, binding, action or elimination of natural hormones that are essential for the maintenance of homeostasis, reproduction, development and behaviour" (Ben Fredj et al., 2015; Jung et al., 2015).

There are more than 100 compounds that are classified as potential endocrine disrupters, among them the main classes of EDC are androgens and estrogens, pharmaceuticals and drugs, pesticides, synthetically produced medicines, detergents and industrial chemicals (Gadupudi et al., 2019; Vilela et al., 2018). These compounds have a structure similar to the hormones present in the organism, that even at the range of concentration previously mentioned can cause adverse impact (Giulivo et al., 2016; Vilela et al., 2018).

The estrogens are hormones derived from cholesterol, that are released through the adrenal cortex, testes, ovary and placenta in both humans and animals. These hormones are the primary female sex hormones, that play an important role in reproductive and non-reproductive systems. The steroid estrogens are classified into natural, in which E1 and E2 are included, or synthetic hormones, in which EE2 is included. The hormones belonging to the class of natural steroid estrogens are produced by vertebrates and some insects and are also known as the C18 steroidal group. This group is characterized by sharing the same tetracyclic molecular framework comprising four rings, one phenolic group, two cyclohexane and one cyclo-pentane ring (Adeel et al., 2017; Aris et al., 2014; Bilal & Iqbal, 2019; Hamid & Eskicioglu, 2012).

The differences between the compounds belonging to the C18 group lies in the configuration of the D-ring at positions C16 and C17. For instance, E1 has a carbonyl group on C17 while E2 has a hydroxyl group on C17. The EE2, as mentioned, is a synthetic hormone derived from E2, sharing a very similar chemical structure. The difference between them lies in the additional ethynyl group on the C17 in the EE2. This synthetic hormone is used in almost all oral contraceptive pills and as medicine in menopausal and postmenopausal syndrome, physiological replacement therapy in deficiency states, treatment of prostatic cancer and breast cancer in postmenopausal women and osteoporosis. EE2 is also used in animals to promote their growth and to prevent and treat reproductive disorders. The EE2 binding affinity for the human's estrogen receptor is one to two times higher than E2, and up to five times in some fish species. Therefore EE2 can be more potent compared with the natural steroid estrogens regarding the eliciting of an estrogenic response (Adeel et al., 2017; Aris et al., 2014; Hamid and Eskicioglu, 2012). Table 3.1 shows the physicochemical properties of the studied compounds.

Table 3.1 – Physicochemical properties of the studied compounds.

E1	
CAS	53-16-7
Molecular formula	$C_{18}H_{22}O_2$
Molecular structure	
Peso Molecular (g/mol)	270.4(a)(b)(c)
Water solubility (mg/L)	30(a); 13(b)(c)
Log K_{ow}[1]	3.13(a)(b); 3.43(c)
pKa[2]	10.4(a)(b); 10.3(c)
Estrogenic potency	0.38(a)
E2	
CAS	50-28-2
Molecular formula	$C_{18}H_{24}O_2$
Molecular structure	
Peso Molecular (g/mol)	272.4(a)(b)(d)
Water solubility (mg/L)	3.6(a); 13(b)(d)
Log K_{ow}[1]	4.01(a)(b); 3.94(d)
pKa[2]	10.4(a)(b)(d)
Estrogenic potency	1(a)(d)
EE2	
CAS	57-63-6
Molecular formula	$C_{20}H_{24}O_2$
Molecular structure	
Peso Molecular (g/mol)	296.4(a)(b)(c)(d)
Water solubility (mg/L)	116(a); 4.8(b)(c)(d)
Log K_{ow}[1]	3.67(a)(b)(c); 4.15(d)
pKa[2]	10.46-10.7(a)(d); 10.4(b)(c) ; 10.24(d)
Estrogenic potency	1.19;1.5(a)(d); 1.62(d)

[1] Octanol-Water Partition Coefficient

[2] Acid Dissociation Constants

(a) (Hamid and Eskicioglu, 2012)

(b) (Rowsell et al., 2009)

(c) (Adeel et al., 2017)

(d) (Maurício et al., 2018)

The estrogens' physicochemical properties are vital to understanding the behaviour of these compounds in soil and water systems. The K_{ow} is defined as the ratio of a chemical's concentration in octanol phase to its concentration in the aqueous phase of a two-phase octanol-water system, which indicates the lipophilicity of a chemical. Therefore, the Log K_{ow} value can be used to approximately predict the compound's sorption behaviour. The estrogens can be classified as moderately hydrophobic compounds, due to their high Log K_{ow} values, which means that these compounds tend to be adsorbed onto a solid surface (Adeel et al., 2017; Hamid & Eskicioglu, 2012; Rowsell et al., 2009; Ting & Praveena, 2017).

Another parameter to highlight from the parameters present in the previous table is the estrogenic potency, that is obtained through a yeast-based in vitro bioassay. Comparing the values of the three hormones it is possible to see that EE2 has the highest estrogenic potency, followed by E2, while E1 has the lowest estrogenic potency. Among the EDC, EE2 and E2 are the ones with the highest estrogenic potency even at low concentration (e.g. ng/L), which leads to the adverse impacts of the presence of these compounds in the environment (Hamid and Eskicioglu, 2012; Maurício et al., 2018).

3.2.1 Estrogens Sources into the Environment

Figure 3.1 shows the sources and routes of estrogens in the environment. Among the sources of estrogens in the environment, the livestock and the domestic and hospital wastewater are the main responsible for the release of these compounds in the environment. The estrogens are used in livestock to ensure the cattle growth rates, feed efficiency and to procure lean muscle mass (Adeel et al., 2017). These hormones are excreted through metabolic processes and released by the faeces and urine into the environment, which leads to soil and water resources contamination (Adeel et al., 2017; Zhao et al., 2019).

Domestic and hospital wastewater are another point source of these EP in the environment. The presence of estrogens in wastewater is one of the most studied since conventional treatments used in wastewater treatment plants (WWTP) are not designed to remove estrogens from wastewater. Therefore, compounds such the E1, E2 and EE2 are not fully removed in the WWTP leading to their discharge in water bodies (Vilela et al., 2018).

The discharge of such compounds in water bodies can compromise human health once those water bodies may be the raw water used for producing drinking water (Wee et al., 2020). In other hand, in recent years there has been an increase in the incentive to reuse treated wastewater, lining up with the SDGs that also endorse this reuse as a target (UN, 2016). Consequently, there has been an increase of the use of treated wastewater for agriculture and potable purposes, which has led to an increment of concerns about the presence of these compounds in wastewater (Bai & Acharya, 2019).

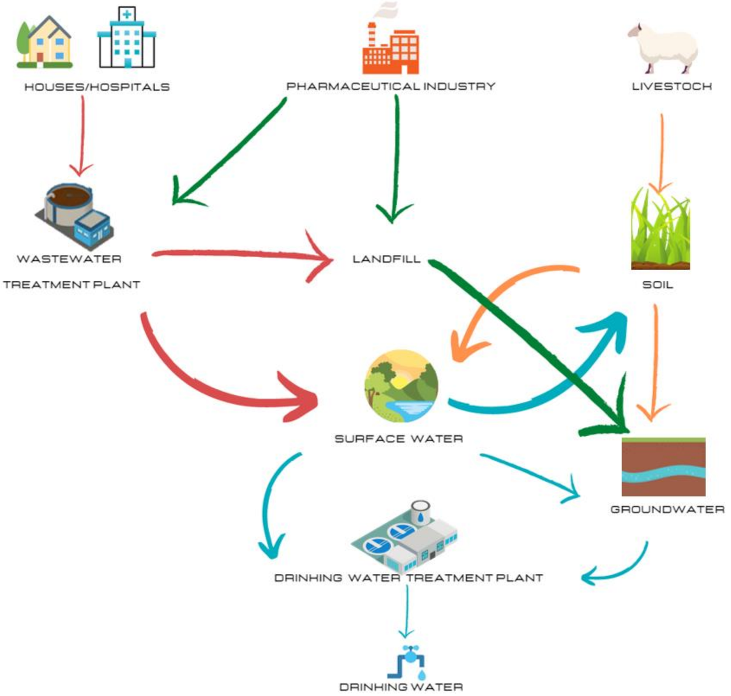


Figure 3.1 – Representative sources and routes of estrogens in the environment (adapted from Adeel et al., 2017; Barbosa et al., 2016)

The presence of these compounds in wastewater can be explained by the fact that they are excreted through the humane's urine and faeces. The estrogen hormones are excreted free and conjugated with glucuronide or sulfate forms, which can suffer biotransformation to their free forms. It is estimated that men excrete 3.9 and 1.6 μg per day of E1 and E2 respectively, while women excrete higher values of these hormones. The amount of hormones excreted by women varies throughout life, for instance, menstruating women excrete 8 and 3.5 μg per day of E1 and E2 respectively, while menopausal women excrete 4 μg per day of E1 and 2.3 μg per day of E2. The values excreted by pregnant women are 600 and 259 μg per day of E1 and E2 respectively. The daily excreted value of EE2, that is the synthetic hormone present in contraceptive pills, is 35 μg. According to the literature, from the total EE2 ingested, from 80 % which is excreted un-metabolized, 22-50 % is excreted through urine and 30 % through faeces (Ting and Praveena, 2017).

3.2.2 Estrogens Impacts

The presence of estrogens in the environment is a big concern due to their impact on living beings. Several studies reported the impact of natural and synthetic estrogens on fish life, such as feminizing male fish, reducing testes size, affecting reproductive fitness, lowering sperm count, inducing the reproduction of vitellogenin, altering other reproductive characteristics, and behavioural changes. For instance, the E2 even at concentrations as low as 100 ng/L is able to lead to changes in the manifestation of the urogenital papillae in male zebra-fish gonadal growth and sex ratio. Furthermore, EE2 has impacts in the fish life, at concentrations as low as 4.5 ng/L cause estrogenicity of male rainbow trout and stimulate the production of vitellogenin mRNA and protein for both male and female fathead minnows, trout and Japanese medaka. EE2 is also associated with the reduction of fish biomass (Adeel et al., 2017; Aris et al., 2014; Hamid & Eskicioglu, 2012; Zhao et al., 2019). The estrogens' impacts on the fish compromise the food chain, however, the fish are not the only animals that suffer the consequences of the presence of these compounds in the environment. For example, 10 ng/L of EE2 affects directly the heart function of bullfrog tadpoles and also can cause feminization and sex reversal of the males of various amphibian species such as the wood frog at concentrations as low as 1.8 ng/L (Adeel et al., 2017; Zhao et al., 2019).

Nonetheless, it is not only in the aquatic environment that the impacts occur. These compounds also have effects on the reproductive functions of mammals, birds and reptiles (Zhao et al., 2019). The uptake by fish and the presence of these compounds in the raw water supply that is used to produce drinking water to supply human communities, also have impacts in humans life. The impacts of the presence of estrogens in the drinking water and the food chain on humans are a debatable issue, however same impacts have been linked to these compounds. The consumption of these compounds, at concentrations above the safety levels, can increase the risk of cancer and induce cardiovascular diseases. Levels higher than the optimal have been linked with the increasing incidence of breast cancer in women and of prostate cancer in men. In addition to this, these compounds can also induce premature menopause, virilization in young women, a decline of sperm counts and men's reproductive health and feminization of men (Adeel et al., 2017; Hamid and Eskicioglu, 2012; Ting and Praveena, 2017). Therefore, the EP removal is more relevant than ever in the production of safe drinking water as well as in the responsible discharge of wastewater into the environment (Grassi et al., 2012).

3.2.3 Legislation

In past years, an effort it has been seen to establish new approaches and legislation to monitor and mitigate the estrogens’ impacts by countries, such as the United States of America (USA), Canada, Japan and European Union (EU). The regulations and approaches implemented by the countries above mentioned are present in Table 3.2.

Table 3.2 – Regulatory or approaches for estrogens *(Ting & Praveena, 2017)*.

Country	Regulatory/approaches	Field
EU	Directive 96/22/EC	Uses in agriculture and aquaculture
	Directive 2003/74/EC	Veterinary control
	Directive 2000/60/EC	Surface water and groundwater
	Directive 2008/105/EC	Surface water
	Directive 2013/39/EU	Surface water
	Decision 2015/495/EU	Surface water
	Decision 2018/840/EU	Surface water
	Decision 2020/1161/EU	Surface water

Country	Regulatory/approaches	Field
USA	Contaminant Candidate List (CCL_3)	Drinking water
	2-tier Endocrine Disruptor Screening Program (EDSP)	Pharmaceutical intake
Canada	Wastewater Systems Effluent Regulations	Wastewater
Japan	Strategic Program on Endocrine Disruptors (SPEED)	Environment and organisms

It can be seen from the table above that the EU is responsible for most of the legislation regarding estrogens. The Directive 96/22/EC intends to regulate the use of estrogenic compounds in agriculture and aquaculture, while the Directive 2003/74/EC focuses on animals, namely because it intends to reduce the circumstances in which E2 is administered. It can be administered under strict veterinary control for uses such as animal's uterus disease, uterus induction and treatment of fetus maceration while being forbidden as a hormone to promote the animals' growth (Ting & Praveena, 2017).

Despite the effort that has been made by the EU to improve the protection of the aquatic environment and human health, there are no legal discharge limits for these compounds yet. The Directive 2000/60/EC (Water Framework Directive, WFD) established an action plan in order to achieve a good ecological and chemical status of surface water, in which a strategy is established to define high-risk substances to be prioritized. Furthermore, EU established the need, by the Environmental Quality Standards Directive 2008/105/EC as amended by Directive 2013/39/EU (EQSD), for a new mechanism to accomplish high-quality monitoring information of forty-five priority substances and highlighting the demand to develop new water treatment solutions. In this last Directive, the first Watch List was proposed as a guideline of emerging aquatic pollutants, aimed at substances with insufficient available monitoring data or insufficient quality to identify the risk posed across the EU (Carvalho et al., 2015; Jaria et al., 2019; Sousa et al., 2019).

The first Watch List published in the Decision 2015/495/EU (2015), encompassed ten groups of substances, with a total of seventeen substances classified as EP and established the monitored matrices and the possible methods of analysis for each substance. This list includes the hormones E1, E2 and EE2, and substances such as antibiotics and pesticides, among others. The fact that the compounds mentioned are detected at residual levels in environmental samples, requires the use of selective and sensitive analytical techniques. The indicative analytical method proposed for EE2 was large-volume solid-phase extraction (SPE) and liquid chromatography triple quadrupole mass spectrometry (LC-MS-MS) associated with a maximum acceptable method detection limit of 0.035 ng/L. The indicative analytical method proposed for both E1 and E2 was SPE and LC-MS-MS associated with a maximum acceptable method detection limit of 0.4 ng/L (Barbosa et al., 2016; European Commission, 2015; Gorito et al., 2017; Sousa et al., 2019).

In 2018, the second Watch List has proposed by the Decision 2018/840/EU. In this update of the Watch List, five substances were removed from this list because it was considered that there were enough monitoring data. However, the estrogens present in the first list were maintained in this one. This Decision included three new substances, one pesticide and two antibiotics. In this Decision, the methods of analysis suggested in the previous decision remained, as well as the maximum acceptable method detection limit (Jurado et al., 2019; Pesqueira et al., 2020).

The last update of the Watch List was published in 2020 by the Decision 2020/1161/EU. In this last version, only three compounds from the previous Watch List remained. The E1, E2 and EE2 were removed from the Watch List because the Article 8b(2) of Directive 2013/39/EU establishes that a substance can only remain on the Watch List continuously for a period of four years, therefore the period of the compounds previous mentioned ceased in 2019 (European Commission, 2020).

The monitorization of these compounds in drinking water is also important in other to protect the human's health. The World Health Organization (2017) presented a benchmark value for E2 (0.001 µg/L). The purpose of this benchmark value is to determine if the surface water is impacted by the discharged of treated wastewater.

3.2.4 Estrogens in Wastewater Treatment Plants

According to several studies, WWTP discharges are the most important point sources of EP into water bodies, once many of these compounds pass through the WWTP process, lacking significant removal (Bai and Acharya, 2019; Benstoem et al., 2017; Hamid and Eskicioglu, 2012; Hu et al., 2016; Jaria et al., 2019). Compounds such hormones can be completely or partially metabolised by the human metabolism, consequently, the unchanged or partially metabolised compounds are excreted via urine and faeces, reaching the WWTP (Sousa et al., 2019; Ting and Praveena, 2017). Conventional wastewater treatment processes are designed to remove carbon sources, particles, nutrients and some pathogenic agents, but are insufficient to remove EP that are found at low concentrations in wastewater, which leads to their discharge into the aquatic environment (Guillossou et al., 2019; Krahnstöver & Wintgens, 2018).

In Table 3.3 are presented some the mean detected concentration of the studied compounds in the WWTP influent and their removal. The concentrations of these compounds in the WWTP influent vary in the literature, as the capacity WWTP for their removal. The E1 reported concentrations vary between 3.3 to 84.0 ng/L, and the removal capacity for this compound ranges between 34.5 to 92.0 %. The biggest removal capacity reported is associated with a treatment with conventional activated sludge followed by advanced treatment with ultraviolet radiation.

The E2 reported concentrations vary between 3.0 to 119.0 ng/L, and the removal capacity for this compound ranges between 0 to 97.1 %. The biggest removal capacity reported is associated with treatment with conventional activated sludge. The EE2 reported concentrations vary between 0.8 to 155.0 ng/L, and the removal capacity for this compound ranges between 17.0 to 100 %. The biggest removal capacity reported is associated with a treatment with conventional activated sludge, followed by advanced treatment with ultraviolet radiation. Like it is possible to verify, the higher removal capacities are normally associated with WWTP that have advanced treatments.

Table 3.3 – Mean detected concentration of the studied compounds in the WWTP influent and their removal.

Compound	Country	Type of WWTP	Mean Detected Concentration in the influent (ng/L)	Removal (%)	Reference
E1	Canada	Conventional activated sludge	29.5	80	(Lishman et al., 2006 in Ting and Praveena, 2017)
	China	Conventional activated sludge	10.2-34.9	49.5	(Zhang et al. 2011 in Ting and Praveena, 2017)
	Iran	Conventional activated sludge	11.4	71.8	(Mohagheghian et al., 2014 in Ting and Praveena, 2017)
	Italy	Conventional activated sludge	35.0	54.3	(Lagana et al., 2004 in Ting and Praveena, 2017)
	Korea	Conventional activated sludge	47.0	87.1	(Behera et al., 2011 in Ting and Praveena, 2017)
	Korea	Conventional activated sludge	29.0	34.5	(Sim et al., 2011 in Ting and Praveena, 2017)
	South Africa	Conventional activated sludge	84.0	72.6	(Manickum and John, 2014 in Ting and Praveena, 2017)
	Sweden	Conventional activated sludge with chemical treatment	3.3	78.0	(Zorita et al. 2009 in Barbosa et al., 2016)
	Turkey	Conventional activated sludge	27.0	74.0	(Komesli et al., 2015 in Couto et al., 2019)
	UK	Conventional activated sludge	15.0	80.0	(Koh et al., 2007 in Ting and Praveena, 2017)
	UK	Conventional activated sludge with ultraviolet	20-60	78-92	(Zhang and Zhou, 2008 in Ting and Praveena, 2017)
E2	China	Conventional activated sludge	85.0	73.0	(Cui et al., 2006 in Ting and Praveena, 2017)
	China	Conventional activated sludge	46.6-93.0	69.3	(Zhang et al. 2011 in Ting and Praveena, 2017)
	Iran	Conventional activated sludge	3.0	68.2	(Mohagheghian et al., 2014 in Ting and Praveena, 2017)
	Italy	Conventional activated sludge	8	37.5	(Palli et al., 2019)
	Italy	Conventional activated sludge	5	0.0	(Palli et al., 2019)
	Italy	Conventional activated sludge	8	37.5	(Palli et al., 2019)
	Italy	Conventional activated sludge	25.0	76.0	(Lagana et al., 2004 in Ting and Praveena, 2017)
	Korea	Conventional activated sludge	47.0	87.1	(Behera et al., 2011 in Ting and Praveena, 2017)
	South Africa	Conventional activated sludge	119.0	83.2	(Manickum and John, 2014 in Ting and Praveena, 2017)
	Sweden	Conventional activated sludge with chemical treatment	14.5	47.0	(Zorita et al. 2009 in Barbosa et al., 2016)
	UK	Conventional activated sludge	5.0	86.0	(Koh et al., 2007 in Ting and Praveena, 2017)

Compound	Country	Type of WWTP	Mean Detected Concentration in the influent (ng/L)	Removal (%)	Reference
EE2	China	Conventional activated sludge	155.0	67.0	(Cui et al., 2006 in Ting and Praveena, 2017)
	Iran	Conventional activated sludge	6.2	80.4	(Mohagheghian et al., 2014 in Ting and Praveena, 2017)
	South Africa	Conventional activated sludge	30.0	90.0	(Manickum and John, 2014 in Ting and Praveena, 2017)
	Spain	Conventional activated sludge	133.3	47.0	(Martin et al., 2012 in Ting and Praveena, 2017)
	UK	Conventional activated sludge	1.2	17.0	(Koh et al., 2007 in Ting and Praveena, 2017)
	UK	Conventional activated sludge with ultraviolet	0.8-10.0	77-100	(Zhang and Zhou, 2008 in Ting and Praveena, 2017)
	USA	Conventional activated sludge with microfiltration, granular activated carbon and ozonation	140.0	96.0	(Yang et al., 2011 in (Barbosa et al., 2016)

To reduce the negative impact of the discharge of these compounds in aquatic environments, it is imperative to add complementary treatments to improve the removal of EP effluent before disposal. The complementary treatments that are needed will minimize the concentration of EP in wastewater, ensuring the safety of the reuse that has become a priority nowadays (Grassi et al., 2013; Guillossou et al., 2019; Ho et al., 2011; Hu et al., 2016; Mailler et al., 2016).

There are several additional treatments to accomplish EP removal, such as ozonation, advanced oxidation, membrane filtration and adsorption (Grassi et al., 2013; Guillossou et al., 2019; Luján-Facundo et al., 2019). Most of the methods above mentioned are not techno-economically viable for large-scale implementation, namely due to their complex maintenance, high investment cost and operating costs, and toxic by-product generation (Luján-Facundo et al., 2019; Sophia A. & Lima, 2018).

On the contrary, the adsorption process is considered by some authors to be one of the most promising treatment processes with high EP removal capacity, namely because it is simple to design and operate, has a low investment cost, enables the reuse and regeneration and does not generate toxic by-products (Boehler et al., 2012; Grassi et al., 2013; Ifelebuegu, 2012; Luján-Facundo et al., 2019; Mailler et al., 2016; Sophia A. and Lima, 2018).

The adsorption process resides in a mass transference process in which accumulation of substance at the interface of two phases occurs. The two phases can be gas-liquid, gas-solid, or liquid-solid. The substance adsorbed is designated as adsorbate and the adsorbing material is called adsorbent. There are many kinds of adsorbent materials, however, the most used is activated carbon (AC) (Grassi et al., 2012; Marsh and Rodríguez-Reinoso, 2006).

3.3 Activated Carbon

AC is a term that covers a broad range of amorphous carbonaceous materials characterized by having a high degree of porosity sizes that vary from visible slits to molecular size pores, associated with a pore volume ranging between 0.7 to 1.8 cm^3/g. This high degree of porosity is responsible for the large specific surface, ranging between 800 to 1 500 m^2/g. AC is normally used as granular activated carbon (GAC), which has a diameter greater than 0.1 mm, or powdered activated carbon (PAC), which has a diameter of less than 200 mesh (Bansal & Goyal, 2005; Çeçen & Aktaş, 2011; Luján-Facundo et al., 2019; Metcalf & Eddy, 1995; Paredes et al., 2018).

ACs are composed by microcrystallites that consist of fused hexagonal rings of carbon atoms, similar to the structure of graphite. The AC surface is composed of basal planes, inorganic ash and superficial groups. The superficial groups are derived from the heterogeneous elements presents in the raw material. Among these heterogeneous group of elements, the most important constituent of AC is carbon, that is present to the extent of 85 to 95 %. AC also contains several other elements such as hydrogen, nitrogen, sulphur and oxygen depending on the raw material used or additional treatments used after activation. The ash content of ACs is normally beneath 15 % (Bansal & Goyal, 2005; Çeçen & Aktaş, 2011; Jeirani et al., 2017; Krahnstöver & Wintgens, 2018).

AC is prepared from various raw materials such as coal, sludge, wood char, carbon black coconut shells, etc, that are subject to an activation process (Jeirani et al., 2017; Metcalf & Eddy, 1995; Mohan & Pittman, 2006). The activation process can be physical or chemical. The physical activation is normally executed via a two-step process, the first consists of the pyrolyzed of the carbonaceous material at temperatures lower than 800 ºC in the absence of air, the second one comprises the activation of the obtained carbon under an oxidizing atmosphere, such as steam and carbon dioxide. However, these two steps have been integrated into a single-step process, in which the pyrolysis is carried out under a stream of an oxidizing gas, which leads to a reduction of the production cost (Bansal & Goyal, 2005; Hadi et al., 2015).

Chemical activation is based in a single-step process in which the carbonaceous matter is soaked in a dehydrating agent, like potassium hydroxide or phosphoric acid, and posteriorly activated at high temperatures under an inert atmosphere. The chemical activation offers some benefits such as a lower activation temperature and higher carbon yield, however, this process can be more expensive due to the high cost of the activating agents. It is also important to refer that it has been reported that the use of an oxidizing environment instead of an inert atmosphere is beneficial in terms of porosity and formation of surface functional groups (Bansal & Goyal, 2005; Hadi et al., 2015).

After activation, the inner surface is composed of microcrystalline ununiform graphite layers in basal planes. This activation process can be complemented by other treatments in order to modify the surface to promote the formation of oxygen and nitrogen containing functional groups (like hydroxyl, carboxyl, phenol, etc.), like acid treatment, oxidation, ammonization or thermal treatment. Therefore, the activation process provides a change in the characteristics of the raw material originating a material with the largest number of pores of several shapes and sizes, creating a material with an extended and extremely high surface area (Bansal & Goyal, 2005; Jeirani et al., 2017; Krahnstöver & Wintgens, 2018).

3.3.1 Adsorption onto Activated Carbon

The process of adsorption resides in the accumulation or concentration of substances at a surface or interface of two phases, and in the case of AC, the adsorbing phase is a solid. The adsorption process strongly depends on the hydrophobic character of the compounds, since the solubility of a dissolved substance is the most important factor for the intensity of the adsorption. Hydrophilic compounds tend to stay dissolved in the water, therefore they are less adsorbable on a solid phase, while on the contrary, hydrophobic compounds tend to be adsorbed. The affinity of the solute for the solid due to electrical attraction between these two is another factor from which the adsorption depends. This kind of affinity can occur due to van der Waals forces or chemical interactions with the AC. These two types of interactions result due to the high affinity of the adsorbate for the adsorbent, which promotes the adsorption process (Çeçen & Aktaş, 2011).

In a liquid-solid system, the transport mechanisms are associated firstly with the transport of the adsorbate from the bulk solution to the boundary layer of water surrounding the AC particle. This process can occur by diffusion in static water or through turbulence due to the mixing or the flow passage. When there is an additional resistance to the mass transport of the adsorbate to the AC surface, from the bulk solution across the stationary layer of water that involves the AC, the transport mechanism is called external diffusion (Çeçen & Aktaş, 2011).

In this mechanism, the mass transport through this layer occurs due to the difference of concentration, by molecular diffusion. The rate of this diffusion depends on the hydrodynamic properties of the system. Another transport mechanism is the intraparticle (internal) diffusion. This mechanism involves the transfer of the adsorbate from the surface of the AC to the sites within the particle and is independent of the hydrodynamic properties of the system but depends on the pore structure. This mechanism can occur by pore diffusion, that is the molecular diffusion of solutes in fluid-filled pores, or by surface diffusion, which is the diffusion of solutes along the adsorbent surface after adsorption takes place, and only occurs when the surfaces' forces are not strong enough to prevent the surface mobility of the molecules. These two intraparticle processes often act in parallel in the interior of the AC. After the adsorbate transport to an available site, an adsorption bond is formed (Çeçen & Aktaş, 2011).

The adsorption process can be defined as physisorption or chemisorption that depending on the conditions can both occur simultaneously or alternatively. The first one occurs when the interaction between the solid surface and the adsorbed molecules has a physical nature. The adsorbate is attached to the AC surface by relatively weak van der Waals forces, which results in a reversible process. The chemisorption occurs when the attraction forces between the adsorbed molecules and the solid surface are due to an exchange of electrons between the adsorbate molecule and AC surface sites, therefore becoming chemically bound. The chemisorption happens only as a monolayer, contrarily to the physisorption. On the other hand, this type of adsorption is associated with stronger forces which make it hard to remove substances chemisorbed (Çeçen & Aktaş, 2011; Grassi et al., 2012; Krahnstöver & Wintgens, 2018).

The removal of estrogens using AC has been studied over the past years, in both water and wastewater. Chang et al. (2004) studied the removal of E1 from the WWTP secondary effluent with PAC through flask adsorption experiments. This study used different concentrations of E1 (17.2 to 120.0 ng/L) and PAC (0.5 to 100.0 mg/L), to assess the impact of the E1 initial concentration and the impact of PAC dosage. They achieved the removal of 95 to 96 %, and the highest removal was associated with the highest PAC dose, in which the adsorption was limited by the exhaustion of removable estrone in the solution, while at low PAC doses the estrone competed for a limited number of surface sites, with other compounds present in the wastewater. Guillossou et al. (2020) also studied the removal of E1 from wastewater with micro-grain activated carbon, which had a particle size between 100 to 800 µm. They used nitrified wastewater containing 67.9 ng/L of E1 and a dose of 10 mg/L of micro-grain activated carbon with which it was obtained the removal of 42 % of E1.

Fuerhacker et al. (2001) assessed the adsorption of E2 from water with three types of GAC. In this study, they used five different concentration of E2 (0.5, 1, 10, 50 and 100 ng/L) to simulate a realistic range of concentration present in groundwater or surface water. In this study, they concluded that all the ACs can be used for the removal of E2, reducing the risk of the presence of this compound in drinking water. In the research made by Ifelebuegu et al. (2006), they assessed three types of GAC for the removal of EE2 from WWTP final effluent. In this study dosages of AC raising between 0.1 to 3.0 g/L were used to remove the EE2 present at a concentration of 18.40 ng/L. This adsorption study achieved removal efficiencies higher than 96 % for all the AC at the lowest dosage. Kovalova et al. (2013) also studied the removal of EE2 from wastewater using PAC, achieving a removal efficiency of 90 %.

Fukuhara et al. (2006) studied the adsorbability of E1 and E2 from water using AC with various pore-size distributions. In this study, they concluded that the E1's adsorbability is slightly higher than the E2, due to its higher hydrophobicity. Another conclusion of this study was that the efficiency of the adsorption is correlated with the pore diameter. Large pore diameter has a lower adsorption capacity than a small pore diameter. Gökçe & Arayici (2016) also studied the removal of E1 and E2 with AC, although the AC used was driven from WWTP sludge, achieving removal rates between 88 and 94 %.

In the study done by Ifelebuegu (2012), he studied the adsorption of E2 and EE2 from water onto AC, to understand the adsorption process of this compound, concluding that adsorption of E2 and EE2 occurs mainly due to chemisorption supported by some van der Waals forces. Yoon et al. (2003) also studied the removal of E2 and EE2 by AC. In this study, the potential use of PAC for the removal of E2 and EE2 in drinking water was assessed. To this end, they studied six types of PAC, and different dosages ranging between 1 to 50 mg/L. With the dosage of 15 mg/L, estrogens removal greater than 99 % was obtained for almost every type of PAC.

Polloni-Silva et al. (2017) also studied the PAC's capacity for removal of E2's and EE2's estrogenicity in milliQ-water and wastewater. For that, they used 500 mg/L of PAC. With this dosage, they achieved the estrogenicity removal in milliQ-water of 97.0% for E2 and 86.4 % for EE2, and in wastewater, the estrogenicity removal of E2 and EE2 was of 99.8 and 97.6 % respectively. Saha et al. (2010) also studied the removal of E2 and EE2 using four types of GAC with successful results. This study concluded that the adsorption capacity of AC was related to the surface and the microporosity. Another conclusion made was that the estrogens adsorption seems to be due to hydrophobic interactions. In this study, some differences in the adsorption of these two compounds were verified, according to Saha et al. (2010) EE2 was less adsorbed than E2 probably because of size exclusion.

In the study done by Nolasco et al. (2017), the removal of E1, E2 and EE2 with AC in deionized water was studied, having concluded that 50 mg/L of AC is the most effective concentration. Rowsell et al. (2009) also studied the removal of E1, E2 and EE2 with AC. In this study, the adsorption capacity of two types of GAC (a virgin and a reactivated AC) in both distilled water and wastewater was assessed. This study was made through a small-scale column test using three different bed volume and three estrogens concentrations (10, 25 and 50 µg/L). The results in distilled water showed removal efficiencies greater than 95 % for the biggest bed volume and greater than 55 % in the smallest bed volume. Comparing the two types of GAC, it was possible to see that the virgin AC had obtained removal efficiencies slightly higher than the ones obtained with the reactivated carbon. However, in wastewater, the removal efficiencies achieved by the reactivated GAC (81 %) were higher than the ones obtained with the virgin carbon (65 %).

3.3.2 Activated Carbon Characteristics

Many factors influence the EP removal efficiency of AC, however, the most important factors are their pores and chemical structure. AC’s pores structure consists in the space formed among the graphite layers, which is responsible for its unique adsorption properties (Alves, 2010; Bansal and Goyal, 2005; Hadi et al., 2015; Marsh and Rodríguez-Reinoso, 2006). This structure originates during the carbonization process. This process and the raw material will determine the structure of the pores and their size distribution. However, it is during the activation process that this structure is further developed, when the space among the elementary crystallites is cleared of carbonaceous material, increasing the volume and enlarging the diameters of the pores (Bansal and Goyal, 2005).

AC’s pores have many sizes and shapes, and the shape doesn’t influence the adsorption process. According to the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC), there are three groups of pores, and each one plays a specific role in the adsorption process:

- Micropores: pores with a diameter inferior to 2 nm. These pores have a pore volume of 0.15 to 0.70 cm^3/g, and their surface area represents about 95 % of the total surface area of the AC. Due to these characteristics, this group of pores is determinant to the adsorption capacity of ACs, unless the adsorbate molecules are not too large to enter into these pores. The adsorption in these pores essentially occurs through the pore-filling process, therefore the volume is the most important parameter to control the adsorption in micropores. The adsorption energy associated with these pores is much larger relative to the other pores or the nonporous surface, because of the overlapping of adsorption forces from the opposite walls of the micropores;
- Mesopores: pores with a diameter between 2 – 50 nm. These pores do not represent a significant contribution to the surface area of AC, since their surface

area does not exceed 5 % of the total surface area of the AC. Their pore volume range between 0.1 and 0.2 cm^3/g. On the surface of these group of pores mono and multilayer adsorption takes place. The adsorption occurs by capillary adsorbate condensation. The elementary parameters to characterise mesopores are the specific surface area, the pore volume and the pore size distribution;

- Macropores: pores with a diameter larger than 50 nm. These pores are associated with a small surface area (inferior to 0.5 m^2/g) and for this reason, they are not of considerable importance to the adsorption process. Their pore volume varies between 0.2 and 0.4 cm^3/g and they act as transport conduits for the adsorbate into the meso- and micropores (Alves, 2010; Bansal and Goyal, 2005; Çeçen and Aktaş, 2011).

As previously mentioned, the pore size has a high impact in the adsorption process, namely because as the pore width approaches the adsorbate dimensions, it leads to the development of multiple contact points between the adsorbate and the surface of the AC. This leads to an overlap of surface forces that result in stronger adsorption energy, which consequently increases the adsorption of adsorbate by the microporous. The more microporous there are in the AC the greater adsorption of low molecular weight will be, due to the high adsorption energy associated with the microporous. Despite macro- and mesopores adsorption being less relevant than the adsorption in micropores, these pores play an essential role in the transport of the adsorbate through the micropores (Çeçen and Aktaş, 2011; Jeirani et al., 2017).

As aforementioned the porous structure is responsible for the large specific surface area of ACs, which are the most important factors because the adsorption process is a surface process. The extent of adsorption is proportional to the specific surface area of the AC. The specific surface area can be defined as the amount of total surface area that is available for adsorption. The surface can be classified as external, when it involves protuberances or cavities with a width greater than their depth, or internal when it involves porous and cavities with a depth greater than their width. It is expected that ACs more finely divided and more pores, especially if they have many pores with molecular dimensions, would be associated with a higher adsorption per unit of their weight (Çeçen and Aktaş, 2011; Grassi et al., 2012; Krahnstöver and Wintgens, 2018).

The adsorption process is also strongly influenced by the chemical structure. The most important element of AC is carbon. Although as said before, ACs are constituted by several other elements that are part of the chemical structure, as a result of imperfect carbonization of the raw material used, or become chemically bonded to the surface of AC during the activation process or in additional treatments (Bansal & Goyal, 2005).

Besides these elements, carbons can adsorb some molecular species such as amines, nitrobenzene, phenols, and several other cationic species. These elements and molecular species give rise to carbon-oxygen, carbon-hydrogen, carbon-nitrogen, carbon-sulphur, and carbon-halogen surface compounds, known as surface groups or surface complexes. The presence of surface compounds or molecular species modifies the surface characteristics and properties of ACs (Bansal & Goyal, 2005).

The carbon-oxygen surface group is the most important. Despite being present in relatively small amounts, this group affects AC surface properties such as acidity, wettability, polarity or hydrophobicity, and surface charge (Bansal & Goyal, 2005; Çeçen & Aktaş, 2011). The increasing of oxygen surface groups increases the polarity of the AC surface, which leads to the increasing of AC affinity to water. (Çeçen & Aktaş, 2011).

The adsorption of water clusters can result in pore blockage. In other words, these water clusters can prevent the access of EP to hydrophobic regions on the AC surface, reducing the interactions energy between adsorbate and adsorbent, and the access to micropores. The action of these groups results in the decrease of the van der Waals forces, which are very important in the adsorption process. However, these oxygenated groups constituted by carbonyl groups improves the adsorption of aromatic compounds, such as phenol and naphthalene (Çeçen & Aktaş, 2011).

As previously mentioned, the activation process influences carbon chemical surface characteristics. For instance, the chemical activation leads to ACs less hydrophobic and more negatively charged. Chemical treatment increases the quantity of acidic surface groups, while physical treatment results in the decreasing of the number of acidic surface groups (Çeçen & Aktaş, 2011).

3.3.3 Factors Influencing the Adsorption Process

The adsorption process, as above mentioned, is strongly conditioned by the AC characteristics, however, the physical and chemical characteristics of the adsorbate, the environmental conditions, such as pH, temperature and the presence of other substances, and the operational conditions also influence the adsorption process (Grassi et al., 2012).

One of the factors that strongly affect the adsorption process is the physicochemical nature of the adsorbate, such as its hydrophilicity, molecular size and the solubility. The hydrophilicity can be assessed through the Kow, that is defined as the ratio of a chemical's concentration in octanol phase to its concentration in the aqueous phase of a two-phase octanol-water system, which indicates the lipophilicity of a chemical. Like already explain hydrophobic compounds (log Kow > 4) tends to be attracted to the ACs surface, therefore these compounds are easily adsorbed than hydrophilic compounds (Jeirani et al., 2017). E1 is a hydrophobic compound, which improves the adsorption of this compound onto AC (Guillossou et al., 2020). Yoon et al. (2003) reported a correlation between the removal of E2 and EE2 by PAC with the log Kow. The higher is the log Kow the higher is the removal of the compound, proving that the hydrophobicity of the compound influence the adsorption process. The Kow of EE2 suggested that this compound will be effectively adsorbed onto AC (Ifelebuegu et al., 2006).

The molecular size of the substance influences the rate of uptake through the porous of the adsorbent material, which is improved with the decrease of adsorbate molecule size if the rate is controlled by intraparticle transport (Grassi et al., 2012; Hadi et al., 2015; Ifelebuegu et al., 2006; Lladó et al., 2016).

The solubility is another important factor because there is an inverse relationship between the extent of the adsorption and the solubility of the compound in the solvent from which the adsorption takes place. The higher solubility is the stronger the solute-solvent bonds will be, reducing the adsorption onto AC (Çeçen & Aktaş, 2011).

The adsorbate concentration also influences the adsorption. The adsorption increases with the increasing of the initial concentration. This relation can be explained by the increase of the driving forces of the concentration gradient that overcome the mass transfer resistance of the adsorbate between the aqueous and solid phases. Furthermore, the increase of the initial concentration leads to the increasing of collisions between the molecules and the AC surface groups (Hadi et al., 2015).

The pKa and the pH solution influence the ionic state of the adsorbate, which influence the adsorption process (Jeirani et al., 2017). The solution pH plays a critical role in the adsorption process, because affects the ionization degree of the adsorbate, and can change the surface charge of the AC, which results in a variation of the extent of adsorption. The surface charge that can be modified due to the protonation or deprotonation of the surface groups, which strongly influence the chemisorption. Due to the pKa of E2 and EE2 (Table 3.1) at low and neutral pHs these compounds are neutral charged and exist in non-ionic molecular form, being easily adsorbed onto AC. At high pHs, the AC is negatively charged reducing the adsorption of these compounds by electrostatic repulsion (Ifelebuegu, 2012). The pH value associated with the zero net surface charge is defined as the pH of the point of zero charged (pH_{pzc}) and differs from carbon to carbon. Normally when the solution pH is lower than AC's pH_{pzc}, the AC surface is positively charged. On the contrary, when the solution pH is higher AC's pH_{pzc}, the AC's surface is negatively charged (Grassi et al., 2012; Guillossou, Le Roux, Mailler, Morlay, et al., 2020; Hadi et al., 2015; Marsh and Rodríguez-Reinoso, 2006).

Temperature is another factor that influences the adsorption process. Normally the adsorption is an exothermic process, due to this the decreasing of temperature usually increases the adsorption extent. However, the increase of temperature results in the increase of the rate of diffusion of the solute through the liquid to the adsorption sites, which eventually leads to an increase of the adsorption (Çeçen & Aktaş, 2011; Grassi et al., 2012).

The presence of dissolved organic matter (DOM), such as humic and fluvic acids, can also affect the adsorption process. The presence of these substances in the wastewater matrix can significantly reduce the adsorption of EP, due to pore blockage and competition for the adsorption sites (Guillossou et al., 2020; Krahnstöver & Wintgens, 2018). In the study done by Yoon et al. (2003) the presence of DOM reduced the surface area available for the adsorption of E2 and EE2, which consequently leads to the reduction in the adsorption of these compounds.

The AC dosage also influences the amount of EP adsorbed. Low dosages are associated with low levels of adsorption due to the quick occupation of the adsorption sites. To accomplish the EP removal efficiency is necessary to increase the amount of AC, although this increase will result in the incomplete occupation of the AC surface. Generally in wastewater treatment, the dosage of AC used varies between 10 and 20 mg/L, due to the complex matrix of those waters (Hadi et al., 2015; Krahnstöver & Wintgens, 2018).

There are many mechanisms by which the EP are adsorbed onto AC depending on the properties of the compounds and the AC characteristics. Normally, the adsorption of these compounds is influenced by different molecular features such as the hydrophobicity and the nature of the functional groups. The type of adsorption that occurs due to hydrophobic interactions happens when the adsorbate expels water molecules from the AC surface. This type of interactions between adsorbate and adsorbent is van der Waals interactions, which plays an important role in the adsorption of EP from water. However, the presence of polar functional groups in the adsorbate and the AC have a bigger influence in adsorption process than the hydrophobic interactions, because polar interactions are stronger than van der Waals interactions (Jeirani et al., 2017).

As previously mentioned, the nature of the functional groups plays an important role in the interactions between the adsorbate and the AC. There are three adsorption mechanism relatable with the nature of the functional groups that can occur simultaneously, the electron donor-acceptor complex formation, π-π dispersion interactions and hydrogen bonding formation. In the first one, the carbonyl oxygen groups of the AC acts as the electron donor while the aromatic compounds act as the acceptor. During this process, the carbonyl groups are oxidized to carboxyl groups, which reduced the rate of the formation of electron donor-acceptor complex, and consequently the rate of uptake (Jeirani et al., 2017).

When the carbonyl groups are exhausted the aromatic compounds form π-π dispersion interactions complexes with the rings of the AC basal plane. This type of interaction is strongly affected by the functionalization of AC. The presence of -NHR and -OH in the constitution of the groups adds an electron density to the aromatic ring, making the organic aromatic compound a π-donor. On the contrary, the presence of -Cl makes the aromatic molecule a π-acceptor. Normally, the AC is a π-donor surface due to the presence of -OH aromatic groups, responsible for the increase of the electron density of the AC graphitic planes. This means that the π-electron acceptor compound has more affinity for the AC than a donor compound (Jeirani et al., 2017). For instance, the presence of a phenolic ring in EE2 influences the attachment of molecules to the solid, since the phenols strongly bind to the carbon surface due the π -electrons interactions of the benzene ring with the partial positive charge of the carbonyl carbon atoms (Ifelebuegu, 2012).

The other mechanism is hydrogen bonding. In this mechanism, the O-H groups present in the AC surface form a hydrogen bond with the functional groups of the adsorbate. The intensity of the net interactions determines the extent of the adsorption (Jeirani et al., 2017).

3.3.4 Adsorption Kinetics, Adsorption Equilibrium and Isotherms

The selection of the adsorbent used for a specific treatment is based on the results of adsorption studies which intend to characterize the removal performance. Usually, the adsorption studies are made in stirred batch reactors, that contains a volume of fluid with a known adsorbate concentration and a given amount of adsorbent (Bonilla-Petriciolet et al., 2019; Çeçen & Aktaş, 2011). These studies are essential to determine the adsorption equilibrium, the isotherms and the kinetics. In the adsorption process, the amount of adsorbate on the solid-phase at given operating conditions is known as the adsorption capacity (q). The adsorption capacity is very important, since it provides the amount of the pollutant that has been loaded on the AC surface. This variable can be determined through a mass balance and is express in mass of adsorbate per mass of adsorbent (e.g. mg/g) (Bonilla-Petriciolet et al., 2019).

The adsorption kinetics is defined as the rate of adsorbate mass transference from the bulk solution to the adsorbent surface, and also the adsorbate accumulation via the binding interactions with the surface groups available. These criteria are used to define the adsorbent efficiency (Bonilla-Petriciolet et al., 2019; Delgado et al., 2019). The adsorption kinetics can be determined by tracing the adsorbed amount of pollutant on the adsorbent surface over time. This can be experimentally accomplished using a given adsorbent dosage at fixed state variables (e.g. pH and temperature), in a batch experience, on which the volume of solution and the adsorbent amount, are maintained constant during the assay (Bonilla-Petriciolet et al., 2019).

Through the quantification of the adsorbate concentration in solution, it is possible to determined q at time t with the Equation (1), where V is the solution volume (L), m is the adsorbent mass used (g), $\mathrm{C_0}$ is the adsorbate initial concentration (mg/L) and $\mathrm{C_t}$ is the adsorbate concentration after a residence time t (mg/L). The residence time is defined as the adsorbent-adsorbate contact time required to achieve the thermodynamic stability, in other words, is the time required to achieve the equilibrium that is achieved during the isotherms (Bonilla-Petriciolet et al., 2019; De Gisi et al., 2016).

$$\mathrm{q} = \frac{\mathrm{V} \times (\mathrm{C_0} - \mathrm{C_t})}{\mathrm{m}} \tag{1}$$

The kinetics studies are crucial to identify if the adsorption of a substance is regulated by a specific transport mechanism, the residence time required for completion of adsorption reaction, and to clarify the dependence of the surface properties of the adsorbent (Bonilla-Petriciolet et al., 2019; Qiu et al., 2009; Wang & Guo, 2020). There are several kinetic models with different mathematical complexity, Table 3.4 presents some of the most used models.

Table 3.4 – Kinetics models *(Bonilla-Petriciolet et al., 2019; Delgado et al., 2019; Montes-Atenas & Valenzuela, 2017)*.

Kinetic model	Linearized Equation	Description	Equation number
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - \mathrm{k_1} t$	$\mathrm{q_e}$ is the theoretical adsorption capacity at equilibrium, $\mathrm{k_1}$ is the rate constant ($\mathrm{h^{-1}}$) and q_t adsorption capacity at time t This model is applied when the adsorbate is originally dissolved in the aqueous phase and the adsorption and follows the first-order equation. This model has the following assumptions: 1) The adsorption is localised and there is not any interaction between adsorbed molecules; 2) The adsorption energy is independent of surface coverage; 3) The maximum q is equivalent to the monolayer formation; 4) The adsorbate concentration is the fluid phase is constant.	*(2)*
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$\mathrm{k_2}$ is the rate constant ($\mathrm{mg.g^{-1}.h^{-1}}$). In this model is assumed that the chemisorption it the rate determining step. These model assumptions are similar to the previous model, but in this case, the adsorption follows the second-order kinetics.	*(3)*

Kinetic model	Linearized Equation	Description	Equation number
Intraparticle discussion or Weber and Morris model	$q_t = k_{id}\sqrt{t} + I$	k_{id} is the intraparticle diffusion rate constant (mg.g^{-1}.h$^{-½}$) and I provides information about the thickness of the boundary layer if the plot of q_t vs $\sqrt{t}$ passes through the origin. If not, the overall adsorption mechanism is also controlled by the boundary layer, to some degree.	*(4)*

The analysis of adsorption equilibrium is very important to identify if the removal of a pollutant is possible in the tested operating conditions. When the AC has been in contact with the liquid for a sufficient time, adsorption equilibrium is achieved. After that, the residual adsorbate concentration in solution reaches a constant value. In other words, the adsorption equilibrium is established when the adsorption rate equals the desorption rate (Bonilla-Petriciolet et al., 2019; Çeçen & Aktaş, 2011).

This experimental adsorption data is usually represented in the form of adsorption isotherms. The adsorption isotherms represent the adsorbed adsorbate distribution between the adsorbent and the solution phase at equilibrium at a specific temperature. These isotherms can give important information about the adsorbate, the adsorbent and the adsorption process. These isotherms also help in the determination of the specific surface area, the volume pores and their distribution sizes, the heat of adsorption, and the relative absorbability an adsorbent (Bansal & Goyal, 2005; Çeçen & Aktaş, 2011).

Isotherm is a curve which describes the relationship between the q and the equilibrium concentration in the liquid phase. Any point of these curve gives the q at a given concentration. The q value increases with the increasing concentration but not in a direct proportion way. (Çeçen & Aktaş, 2011). This can be experimentally reproduced by keeping two of the three parameters (solution volume, adsorbent mass and adsorbate concentration) constant and one varying (Bonilla-Petriciolet et al., 2019). The most common adsorption isotherm models are the Langmuir, the Freundlich, the Brunauer-Emmett-Teller (BET), which are presented in Table 3.5 (Çeçen & Aktaş, 2011).

Table 3.5 – Adsorption isotherms models (Al-Ghouti & Da'ana, 2020; Foo & Hameed, 2010)

Isotherm model	Equation	Description	Equation number
Langmuir	$q_e = \frac{Q_0 b C_e}{1 + b C_e}$	Q_0 is the maximum monolayer coverage capacities (mg/g), b is the Langmuir isotherm constant (L/mg), and C_e is the adsorbate equilibrium concentration (mg/L). This model assumes monolayer adsorption, with a fixed number of the definite localized site where the adsorption can occur, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites.	*(5)*

Isotherm model	Equation	Description	Equation number
Freundlich	$q_e = K_F C_e^{1/n}$	K_F is the Freundlich isotherm constant((mg/g) (dm^3/g)^n), and n is the adsorption intensity. Describes a non-ideal and reversible adsorption, not restricted to the formation of a monolayer, that way can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface.	*(6)*
BET	$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e/C_s)}$	q_s is the theoretical isotherm saturation capacity (mg/g), C_{BET} is the BET constant adsorption isotherm relating to the energy surface interaction (L/mg), and C_s is the adsorbate monolayer saturation concentration (mg/L). This model assumes the same assumption of the Langmuir model and the following ones: same adsorption energy is found in the second, third and higher layers, this energy is equal to the fusion heat that is not directly affected by the adsorbate-adsorbent interactions.	(7)

The isotherms shape provides information about the affinity and the mode of interaction between the adsorbate and the adsorbent. The classification of liquid-solid adsorption isotherms proposed by Giles et al. (1960) describes a system and allows the diagnose the adsorption mechanism, giving information regarding the physical nature of the adsorbate and the adsorbent surface. In this classification, the isotherms are identified according to the initial slope into four classes (S, L, H and C curves), and into subclasses based on the shapes of the upper parts and slope changes (Piccin et al., 2017). Figure 3.2 shows the classification of liquid-solid adsorption isotherms.

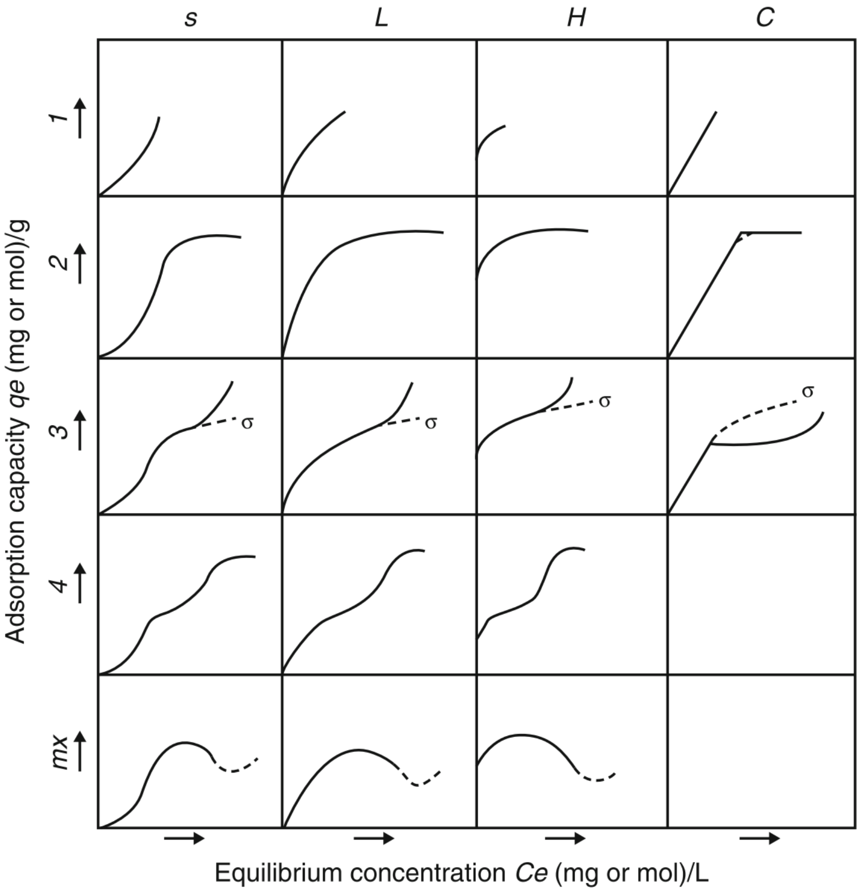


Figure 3.2 – Adsorption isotherm classification (Piccin et al., 2017)

As previously mentioned, there are three classes of liquid-solid adsorption isotherms:

- The *S curves* or vertical orientation isotherm has an inclined slope of the curve followed by a vertical orientation. In the beginning, when occurs the increase of the adsorbate concentration, there is a change of the adsorbate to find an available site to occupy, due to competition between solute molecules. Therefore, the adsorption capacity is limited, reaching a plateau. However, in this class of isotherms, this behaviour is opposed leading to the increasing of the curve slope, due to the vertical orientation tendency of the adsorbate molecules in a higher concentration, which promotes the occurrence of more sites available for adsorption. This type of curve occurs when three conditions are fulfilled: i) the adsorbate molecule is a monofunctional, ii) there is a moderate intermolecular attraction, leading to pack vertically in a regular array in the adsorbed layer, and iii) there is strong competition for substrate sites;
- The *L curves* or normal or "Langmuir" isotherms. This class is the most found in liquid-solid adsorption. The initial shape of the curve of this class of isotherms follows the premise that the higher the adsorbate concentration, the greater the adsorption capacity, however, this is limited to the number of available adsorption sites, occurring competition for them. This class of curve is indicative that the adsorbate molecules are adsorbed flat

on the surface or, sometimes, of vertically oriented adsorbed ions with strong intermolecular attraction. An isotherm of this class has one of the following characteristics: i) the adsorbed molecules are more likely to be adsorbed flat or ii) are systems with high polar solute and substrate. This class of isotherm indicates that the adsorption occurs due to relatively weak forces, such as van der Waals forces;

- *H curves* or high affinity isotherms. This curve differs from the previous class at the beginning of the curve. This class has an initial portion with a vertical orientation, and q_e value higher than zero, even when the adsorbate concentration is very close to zero. The adsorbed species associated with this class of isotherms are often large units, e.g. ionic micelles or polymeric molecules. However, these curves sometimes can be associated with the adsorption of simple ions, which exchange with others of much lower affinity with the adsorbent surface. This class of isotherms is associate with chemisorption and adsorption by electrostatic forces. This class is also known as irreversible isotherm because when the adsorption occurs at a high concentration, the reduction of the concentration does not affect the adsorption capacity;
- *C curves* or constant partition isotherm. This class is characterized by a linear behaviour of the equilibrium data at low concentrations of the adsorbent, following Henry's law for ideal gas equilibrium phases. This suggests that the adsorption capacity is proportional to the adsorbate concentration, until the maximum possible adsorption, when occurs an abrupt change to a horizontal plateau. This class of isotherms is obtained when the affinity of the solute by the solid is greater than the affinity for the solvent, or when the amount of available adsorption sites is sufficient for the adsorption of all adsorbate, but the bonding forces between the adsorbate and the solvent are weak and depend on the liquid phase concentration (Piccin et al., 2017).

As mentioned above, according to this classification, the isotherms are classified into subclasses:

- The *subclass 1* of S class indicates a complete vertical behaviour of the adsorption capacity, likely caused by surface precipitation of the adsorbate on the adsorbent surface. This subclass occurs when the adsorption sites were not fully occupied or did not occur a completely vertical orientation of the adsorbate molecules. The isotherms of this subclass are normally described the Freundlich model, in the case of the L and H class, or Henry's law, in the case of the C class;
- The *subclass 2* indicates that does not occur intermolecular interaction between the solute, forming a long plateau that indices the saturation of the adsorbent monolayer. In this case, the high energy barrier has to be overcome before the additional adsorption can occur on new sites after the surface has been saturated to the first degree. Thus, the solute has a high affinity for the solvent, but low affinity for the layer of adsorbed solute molecules. The equilibrium data of this subclass can be represented by the Langmuir model and the plateau is represented by the maximum adsorption capacity, in the case of L and H class;
- S*ubclass 3*. The short plateau of this subclass means that the adsorbed molecules expose a surface, which has nearly the same affinity for more solute than the original

surface possessed. This indicates that the adsorbate in the solution has some intermolecular interaction with the solute in the adsorbent surface, which leads to the formation of multilayers;

- The *subclass 4* is associated with the development of a fresh surface in which the adsorption can occur. This new layer can occur when i) a proportion of the original surface may be uncovered by reorientation of the molecules already adsorbed, due to the intermolecular interactions, ii) formation of new surfaces in crystalline solids, originating new adsorption site, or iii) exposed parts that allow the formation of two layers, e.g. due to the formation of micelles. The second plateau in this subclass of isotherms represents the saturation of the new layer;
- The *subclasss mx* occurs occasionally when occurs a fall in slope after the first inflexion. This occurs probably due to the association of the solutes in the solution, with the increasing of the concentration, the solute-solute attraction begins to increase faster than the adsorbent-solute attraction (Piccin et al., 2017).

3.4 Activated Carbon Reutilization

During the adsorption treatment, the pollutants are continually accumulated on the AC, which leads to the progressive reducing of its adsorption capacity and consequently the efficiency of the adsorption process. The period between the first use of a virgin AC until its exhaustion depends on the volume of substances adsorbed, but normally the exhaustion can be achieved within days or weeks. This implies a high annual request for AC if the spent one is not reused. The spent carbon has three disposal method: landfill, incineration, and reactivation. The most disposal method use varies with the type of AC. For instance, around 68 % of the spent GAC is regenerated, while 95 % of the spent PAC is forwarded to a landfill, because becomes more economical than regenerate this type of AC. Only 40 % of the spent AC is reused (Ma et al., 2017; Oladejo et al., 2020; Sophia A. & Lima, 2018).

The regeneration process increases the cost of this treatment due to energy consumptions and off-site transport. On the other hand, the regenerated AC is not as efficient as a virgin AC which leads to restricted use in wastewater treatment (De Gisi et al., 2016; Grassi et al., 2013; Sophia A. & Lima, 2018). The lack of PAC regeneration results in the recourse and waste management challenge, especially because this type of AC represented, in 2016, more than 55 % of the AC demand and has as the largest consumer the water treatment industry (Ma et al., 2017; Oladejo et al., 2020).

As a result, many studies are being made to propose alternative carbon source, producing ACs at lower costs, alternative regeneration process, and low-cost adsorbents such agriculture and industrial waste, such as water treatment sludge (WTS) (Babatunde & Zhao, 2007; De Gisi et al., 2016; Grassi et al., 2013; Kayranli, 2011; Sophia A. & Lima, 2018). WTS is a low-cost alternative to the commercial AC, with high potential as an adsorbent for the removal of various pollutants and metals in wastewater, such as heavy metals, fluoride and dyes (Babatunde & Zhao, 2007; Kayranli, 2011). The utilization of adsorbents such as WTS will contribute to the decarbonization of the water treatment industry.

3.4.1 Water Treatment Sludge

The WTS represents all wastes produced during the water treatment in the water treatment plant (WTP). According to the literature a typical WTP produces 100 000 ton/years of WTS. On a global scale, the daily production is estimated to be larger than 10 000 ton. These residues are normally placed in a landfill, which represents an environmental concern. The WTS constitution does not vary greatly from each other. However, their composition and quantity extremely depend on the characteristics of the raw water, the coagulant type and dosage applied during the water treatment, and from specific plant operating conditions. In the case of the treatment of groundwater with stable quality, the WTS produced quality and quantity does not fluctuate very much. On the contrary, the WTS produced during the treatment of surface water have visible variations in terms of quality and quantity. These variations can be explained due to the significant alteration of the raw water quality and/or by the variation of the dosage of the chemicals used in the WTP (Ahmad et al., 2016; Babatunde & Zhao, 2007).

WTS is typically composed of mineral, humic matters and microorganisms removed from the raw water and residues from the chemicals used during the treatments. The polydisperse suspension with a broad range of rough disperse or even colloidal particles, which are present in the raw water and that are agglomerated and settled down due to the action o coagulants, which contributes for the sludge production. The coagulants normally used in water treatment are aluminium salts, ferric ion salts and ferrous iron salts, which represent a considerable part of the WTS produced. WTS has many oxides in its constitution. In general, SiO_2 constitutes the major portion of the sludge followed by Al_2O_3 and Fe_2O_3, that are associated with the coagulant used. Other oxides might be present in a smaller percentage, such as CaO, MgO, Na_2O, K_2O, P_2O_5 and TiO_2 (Ahmad et al., 2016).

The excessive use of coagulants leads to the increasing of the WTSs production, as consequent the landfill space has become limited, which make extremely important to look for new alternatives (Lee et al., 2020). The disposal of WTS becomes a greater issue, especially nowadays with the increase of environmental concerns. Therefore, it is necessary to look for an alternative management strategy for this waste (Kulandaivelu et al., 2020).

The WTSs have been recycled as aggregates, soil improvement agents, environmental remediation materials, and as a coagulant in wastewater treatment. The use of WTS as an adsorbent in wastewater treatment has already been review in the literature since its adsorption capacity is related to the high concentration of amorphous aluminium and ferric ions (Ahmad et al., 2016; Babatunde & Zhao, 2007; Lee et al., 2020). WTS due to its properties can be used for the removal of heavy metals (Gibbons & Gagnon, 2010; Zhou & Haynes, 2012), dyes (Kayranli, 2011) and phosphorus (Mohammed & Rashid, 2012). Kulandaivelu et al. (2020) studied the removal of several micropollutants (e. g. pharmaceuticals) by adsorption onto aluminium-based and iron-based WTS, concluding that the use of iron-based sludge can lead to the removal of a significant number of micropollutants.

The adsorption process with AC in WTP was firstly used for the removal of substances that alter the colour and odour. However, with the degradation of the water quality, its use has become necessary for the removal of other compounds present in waters, such as heavy metals and emerging pollutants (Bonilla-Petriciolet et al., 2019). As previous mentioned, WTP are the biggest consumer of PAC, that is normally dosed temporarily or intermittently into the water, when occurs a deterioration of the raw water quality or for mitigation of short-term operational problems. The application of PAC can be made either into rapid mixing (coagulation), flocculation or in the filtration process (Çeçen & Aktaş, 2011).

After the contact between the PAC and the water, the AC is removed by a separation process becoming part of the WTS. The low hydraulic residence time associated with conventional treatments unit such as coagulation tanks does not enable the AC to reach the equilibrium conditions. Therefore, these systems are associated with limited elimination of the micropollutants. As a result, the WTP have to apply large doses of PAC, which leads to an additional sludge production (Çeçen & Aktaş, 2011).

The first report about the potential use of WTS containing AC was done by Lee et al., (2020). They analysed the possibility of regenerating the AC and coagulants present in WTS via pyrolysis to produce a multifunctional remediation material for the removal of pollutants present in wastewater. In this study, the influence of the temperature of the pyrolyzed process in the adsorption capacity of WTS containing AC for the removal of anions and cations was assessed. For that, they compared the adsorption capacity of the raw WTS with the pyrolyzed WTS at different temperatures (200-700 ^{o}C). The adsorption of PO_4^{3-} as an anion, and of the methylene blue (MB^+) as a cation, singly, and in simultaneal was studied, and it was verified that the adsorption in simultaneal was higher that adsorption without competition.

Relatively to the isolated adsorption experience, using to the raw WTS, the PAC had no interaction in the adsorption process. The PO_4^{3-} was adsorbed due to the presence of Al^{+3}, the MB^+ was adsorbed due to the presence of Al^{+3} and clay. When the pyrolyzed WTS was used the AC, that was negatively charged, influenced the adsorption of both compounds. The PO_4^{3-} had become also adsorbed to the Al^{+3} present in the AC pores, and the MB^+ was adsorbed onto the AC (Lee et al., 2020)

When the adsorption of both compounds was studied simultaneal, in the raw WTS it was verified a competition between them for the Al^{+3}.However, in the case of the pyrolyzed WTS, this competition was not verified. The PO_4^{3-} besides, being adsorbed by Al^{+3} within and without the AC pores was also adsorbed to the MB^+ adsorbed onto the AC. The MB^+ besides, being adsorbed onto the AC, clays and Al^{+3}, became also adsorbed to the PO_4^{3-} adsorbed in the Al^{+3}, which reduced the competition between the compounds. Therefore the pyrolyzed WTS can remove anions and cations simultaneously, which prove that this material can be used as a multifunctional remediation material in wastewater treatment (Lee et al., 2020).

4 Objectives

Nowadays, the importance of finding new uses for WTS is increasing due to environmental concerns, as well as the reuse AC and searching for alternative adsorbents materials. The use of WTS as an alternative adsorbent has been studied, however, most of the studies assed the WTS adsorption capacity based on its content in aluminium and ferric ions. Only one known assessed the potential use of WTS containing AC, in which it is concluded that these sludges are a multifunctional remediation material in wastewater treatment. Currently, studies regarding the use of WTS containing AC (with or without activation process) for the removal of estrogens are not known and could be useful concerning the SDG goals, the circular economy proposals and the decarbonization of the water treatment industry.

Therefore, the main goal of this work is to assess the remaining adsorption capacity of WTS containing AC, without reactivation for the removal of three EP (E1, E2 and EE2) using two different WTS. To achieve this goal a characterization of the WTS was made, which includes the ash content, the elemental composition, the pH_{pzc} determination, the thermogravimetric analysis, the mineral composition and the textural characterization. A preliminary test for the removal of these hormones was performed to understand the WTS's capacity for the removal of the studied hormones.

The main goal of this project was to apply WTS as an adsorbent for the removal of E1, E2 and EE2, as selected EP compounds. For such, it was intended to analyse the dose and contact time required to remove these compounds. Therefore, the optimal dose was assessed thought the removal efficiencies of different dosages.

5 Material and Methods

5.1 Material

5.1.1 Water Treatment Sludge

In this study, two WTS from two WTP in Portugal, Santa Águeda WTP and Caldeirão WTP were used. Figure 5.1 and Figure 5.2 presents the sequence of treatments used in these WTP’s, both for water and for the sludge produced, in which the reagent that contributes to the WTS composition and the respective places where they are dosed are presented. St. Águeda WTP in Castelo Branco region has a treatment capacity of 2 200 m^3/h, serving 63 000 inhabitants. Through Figure 5.1 is possible to understand that the produced WTSs are composed by the solid matter present in the raw water, milk lime used in the remineralisation, aluminium polyhydroxychlorosulfate used as a coagulant and PAC. The materials present in the water and the reagents used are removed in the sedimentation and/or filtration processes. After the aforementioned processes, the sludge is thickening in a gravity thickener and after that the sludge goes to the dewatering process through a filter press, to improve the efficiency of this process is added more polyelectrolyte and insoluble limestones resides produced during the preparation of the milk of lime and the lime water, that will be also part of WTS’s composition.

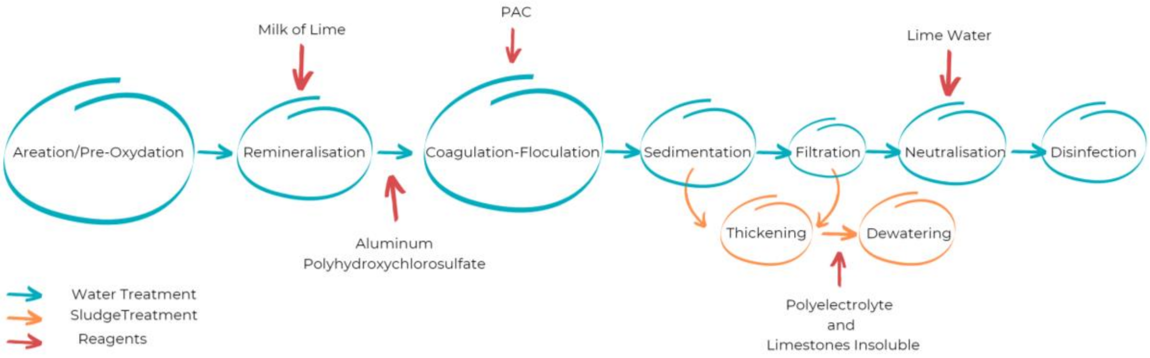


Figure 5.1 – Santa Águeda WTP treatment processes.

Caldeirão WTP is in Guarda region and has a treatment capacity of 1 000 m^3/h, serving 39 125 inhabitants. Based on Figure 5.2 the WTSs produced in this WTP are composed of solid matter present in the raw water, lime used in the remineralisation, aluminium polyhydroxychlorosulfate used as a coagulant and PAC. The materials present in the water and the reagents used are removed in the sedimentation and/or filtration processes. The sludge produced during the water treatment is thickening in a gravity thickener where it used polyelectrolyte to improve this process. After this process the WTS goes to the filter press where it is made the dewatering process, in this process, it is also used polyelectrolyte in other to accomplish a higher efficacy. The polyelectrolyte used during the thickening and the dewatering processes will be also part of the sludge constitution.

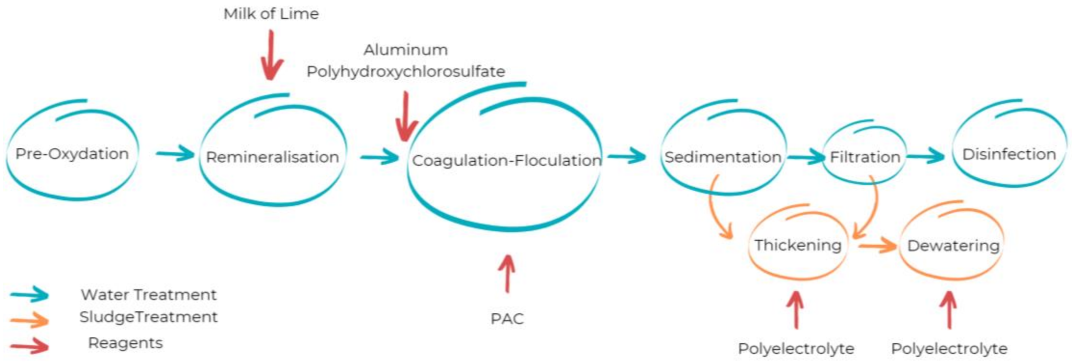


Figure 5.2 – WTP of Caldeirão treatment processes.

The samples of both WTSs were dry at the sun before proceeding to the characterization and the adsorption studies.

5.1.2 Emerging Pollutants

E1, from Sigma Aldrich, product code 46573 with 98 % of purity. For further information consult the product datasheet in Annex I.

E2, from Acros Organics, product code 436320050 with 98 % of purity. For further information consult the product datasheet in Annex II.

EE2, from Dr. Ehrenstorfer, product code DRE-C13245100 with 97.02 % of purity. For further information consult the product datasheet in Annex III.

5.1.3 Laboratory Material and Equipment

The material used during the laboratory test was the following one:

Compact shaker IKA LABORTECHNIK HS 501 digital.

Elemental analyser CHNS Analyzer – Thermo Finnigan CE Instruments Flash EA 1112 CHN.

Filters:

- Filter paper Whatman 40 ashless, diameter 11.0 cm, retention 8 µm;
- MFV3 Glass microfibre filters, Filter Lab, diameter 47 mm retention of 1.2 µm.

Gas Porosimeter – Micromeritics, ASAP2010

Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) ICP-AES Horiba Jobin-Yvon Ultima

Jar test equipment:

- G. Vittadini**;**
- VELP Scientific FC6S.

Magnetic stirrer VELPSCIENTIFICA Multi Magnetic St.

Muffle Lenton Furnaces AWF 12/5.

Orbital Shaker Lab-Line Instruments 4626 Variable Speed Orbital Shaker.

pH meter WTW inoLab ph/ION 735.

Scales:

- XS balance BL 303, Max. 300g, d=0,001g;
- Mettler Toledo A AG204, Max. 210g, d=0,001g.

Thermogravimetric Analizer Setaram Labsys EVO.

Vacuum pumps:

- ERT vacuum pump;
- KNF Neuberger GmbH vacuum pump, type N035 AN.18.

5.1.4 Reagents

The reagents used during the laboratory test was the following one:

- Sodium chloride (NaCl), from Honeywell™ Fluka™, CAS number 7647-14-5, 99.5 % of purity, molecular weight (g/mol) 58.66;
- Hydrochloric acid (HCl) 0.1 M;
- Hydrochloric acid (HCl) 1 M;
- Sodium hydroxide (NaOH) 0.1 M;
- Sodium hydroxide (NaOH) 1 M;
- Methanol (CH_3OH), from Honeywell – Riedel-de Häin; CAS number 67-68-5, molecular weight (g/mol) 32.04.

5.2 Methods

5.2.1 Ash Content

The determination of the ashes content was carried out according to the Standard Test Method for Chemical Analysis of Wood Charcoal (ASTM D 1762-84). For this procedure, approximately 1 g of WTS was put in a crucible that was previously weighed to eliminate errors duplicates were used. Then the crucible was placed in muffle Lenton Furnaces AWF 12/5 for 2 h in which the temperature will increase at a range of 5 ºC/min until reach the 750 ºC, after reaching this temperature the crucible remains in the muffle for more 6 h. After the this the crucible containing the WTS's ash was placed in the desiccator to cool and then it was weighed. The ash content was determined using the Equation (8), where $\mathrm{m_{crucible}}$ is the weight of the crucible (g), $\mathrm{m_{WTS+crucible}}$ is the weight of the crucible containing WTS before being in the muffle, and $\mathrm{m_{Ash+crucible}}$ is the weight of the crucible containing the WTS's ash.

$$Ash\ content\ (\%) = \left(\frac{m_{Ash+crucible} - m_{crucible}}{m_{WTS+crucible} - m_{crucible}}\right) \times 100 \tag{8}$$

5.2.2 Elemental Analysis

The elemental composition of the WTS aims to determine the content of hydrogen, carbon, nitrogen and sulphur. This analysis was performed with a CHNS Analyzer – Thermo Finnigan CE Instruments Flash EA 1112 CHN elemental analyser in the LAQV@REQIMTE's chemical analysis. Based on the results of this analysis and the ash content is possible to determine the oxygen content, using the Equation (9).

$$O\ (\%) = 100\% - (C + H + N + S + Ash) \tag{9}$$

5.2.3 Determination of the $\mathrm{pH_{pzc}}$

The determination of the $\mathrm{pH_{pzc}}$ was carried out through the preparation of portions of 20 mL of NaCl (0.1 M) solution in six different flasks. The pH of each flask was adjusted with the addition of 0.1 M HCl or NaOH and 1M HCl or NaOH in other to achieve a range of pH between 2 and 12. After the pH adjust, 0.1 g of the WTS was added in each vial, then the flasks were placed in agitation under an inert atmosphere for 24 h in other to reach the equilibrium. After agitation, the pH of the solution of each flask was filtered with filter paper (8 µm) and then it was measured the final pH of each solution using a pH meter WTW inoLab ph/ION 735 (Figure 5.3). The $\mathrm{pH_{pzc}}$ is defined as the point of the curve ΔpH (ΔpH = final pH - initial pH) versus initial pH, where ΔpH is equal to zero.

Figure 5.3 – Measured the pH

5.2.4 Thermogravimetric Analysis

The thermogravimetric analysis (TGA) allows inferring the viability of the WTS regeneration. The TGA was performed using a Thermogravimetric Analizer – Setaram Labsys EVO at the LAQV@REQIMTE's chemical analysis laboratory, under the following operational conditions: an atmosphere of argon, the temperature range between the room temperature and 900 ºC and with a heating rate of 5 ºC/min.

5.2.5 Mineral Analysis

The mineral analysis aims to determine the WTS's mineral composition. This analysis was performed at the LAQV@REQIMTE's chemical analysis laboratory, mineral's determination by ICP-AES using an ICP-AES Horiba Jobin-Yvon Ultima, after acidic digestion of the WTS samples. In this analysis, replicas of each WTS were made

5.2.6 Textural Characterization

The WTSs were submitted to a single point textural characterization, to determine the surface area and the total volume pores. This characterization was performed at analysis laboratory of the Chemistry Department of FCT-NOVA, through the adsorption of N_2 at 77K using a Gas Porosimeter – Micromeritics, ASAP2010 at the relative pressure of p/p0 = 0.3.

5.2.7 Stock Solution and Determination of the Estrogens

To simulate a closer situation to the environment condition, a stock solution with the three hormones was prepared. This stock solution was prepared with 1 L of distilled water in which the hormones previously dissolved in 10 mL of methanol were added, to obtain a concentration of 500 µg/L for each hormone. The stock solution was stored in a freezer at 4 ºC. To achieve the working concentrations, daily working solutions were prepared by dilution of the stock solution with distilled water. The determination of the study EP was made by SPE and high-performance liquid chromatography tandem mass spectrometry (HPLC-MS-MS) at the EPAL's laboratory. Under these analytical conditions, the limit of quantification (LOQ) of E1 was 60 ng/L, and the LOQ of E2 and EE2 was 50 ng/L.

5.2.8 Preliminary study

The preliminary study aims to determine if the WTSs might have the capacity to remove the estrogens. To this end, the adsorption capacity of each sludge was studied separately. Before the application of the WTS's, the sludges were grounded and sieved to obtain the particle size of 45/60 mesh. The preliminary study performed in 1 L beaker with 5 g/L of WTS, this concentration was based on concentrations used in other studies that range between 0.01 and 3.2 g/L(Guillossou et al., 2020; Ifelebuegu et al., 2006; Ifelebuegu, 2012; Yoon et al., 2003). However, since the adsorbent used in this study is a WTS containing spent AC with a carbon content lower than 50 % the AC typical carbon (Bansal & Goyal, 2005). The choice of concentration was made through a balance between the concentrations used in studies of hormones' removal with AC and the concentrations used by Lee et al., (2020), that was 20, 5 and 4 g/L.

Each WTS was added to three separate solutions, with different estrogens's concentrations (200, 350 and 500 ng/L), in a total of three beakers per WTS. The solutions with WTS were submitted to agitation (200 rpm) in a jar test equipment (Figure 5.4) for 24 h. In this study, three blanks were prepared, one for each estrogens's concentration, to verify the initial concentration of these compounds.

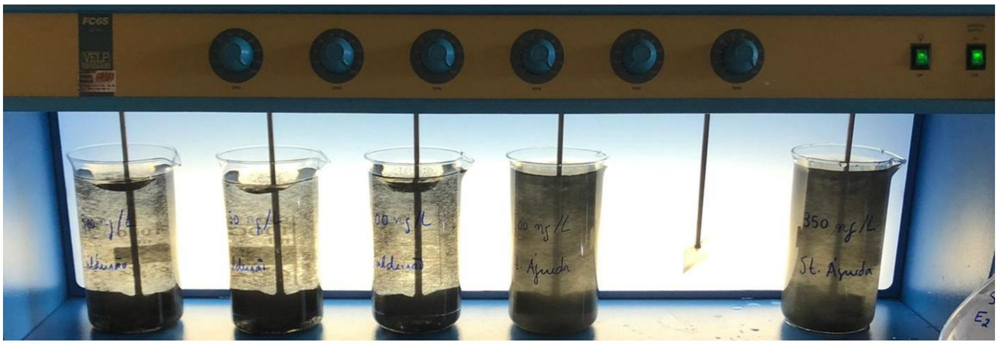


Figure 5.4 – Jar test equipment

After mixing, the samples were filtered with glass microfibre filters (1.2 µm) under vacuum to remove the WTS (Figure 5.5) and prepared for the determination of the concentration of the compounds, as well as the blanks of which EDC's concertation.

Figure 5.5 – Filtration system

In other to assed if the WTS granulometry decreased due to the intense agitation used in the preliminary study, the sludge of each WTP that had remained in the beakers (Figure 5.6) was collected and placed to dry in the sun. The dry sample of each WTS was weighed and then sieved. The sieving results in three samples of different particle size (>45 mesh, 45/60 mesh and <60 mesh) that were weighed.

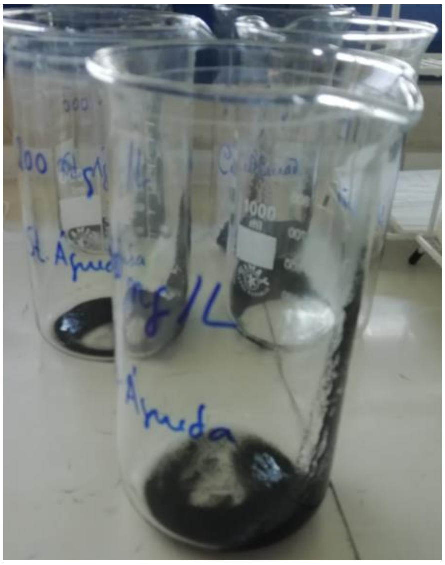


Figure 5.6 – Remained sludge

5.2.9 Dosage study

The dosage study aims to determine the concentration of Caldeirão WTS that achieves the greater EDC’s removal. This study focuses only on Caldeirão WTS since this sludge showed to had higher adsorption capacity than St. Águeda WTS. Since the preliminary results showed high removal capacity with 5 g/L, it was decided to reduce the dosage used. Therefore, five dosages (2.5, 1, 0.5 and 0.05 g/L) were selected, these dosages were selected based on the concentration used in the preliminary study and the literature previously mentioned.

The sample of Caldeirão WTS was grounded and sieved to obtain the particle size of 45/60 mesh. In this study, five concentrations of WTS were tested in triplicates and added to 250 mL flasks with an initial concentration of 500 ng/L of each hormone. In this study, a blank was also prepared to verify the initial concentration of the compounds. The solutions with WTS and the blank were submitted to agitation (270 rpm) in an orbital shaker for 24h at 20 ºC (Figure 5.7). After mixing, each sample was filtered with glass microfibre filters (1.2 µm) under vacuum, to remove the WTS, and prepared for the estrogens determination.

Figure 5.7 – Orbital shaker

6 Results and Discussion

6.1 Ash Content and Elemental Analysis

Table 6.1 lists the ash content and the elemental composition in weight percent (wt.%) of the two WTSs. Both sludges presented an ash content quite high, 30.81 % for Caldeirão WTS and 42.87 wt.% St. Águeda WTS, but smaller than observed by Lee et al., (2020), around 51.0 %. Both WTSs had an ash content much higher than the typical ash content of an AC, that is between 10 to 15 wt.%(Marsh & Rodríguez-Reinoso, 2006). The variations between the ash content of these WTS can be explained by the different reagent and amount of them used in the WTP. The ash content is associated with the mineral's content (Bansal & Goyal, 2005). Therefore, the mineral content of St. Águeda WTS is expected to be higher than the Caldeirão's mineral content. The presence of minerals is important because they may promote the formation of strong interaction with organic pollutants promoting their removal from the wastewater (Bernardo et al., 2020; Lee et al., 2020).

The carbon (C) content of a typical AC is 88 wt.% (Bansal & Goyal, 2005), a much higher value compared with the carbon content of the two WTSs used in this study, proximally 34 wt.% for the Caldeirão WTS and 24 wt.% for the St. Águeda WTS. However, the C content of these WTSs was slightly higher than the one observed in the research of Lee et al., (2020), that was 19 wt.%. Comparing the hydrogen (H) content of the WTSs with the content of this element in a typical AC, that is 0.5 wt.% (Bansal & Goyal, 2005) is possible to observe that the WTSs used in this study have a higher content of H, but smaller than the 3.7 wt.% obtained by Lee et al., (2020).

The nitrogen (N) and the sulphur (S) content of a typical AC are, respectively, 0.5 and 1 wt.% (Bansal & Goyal, 2005), the content of these elements in both WTSs were smaller compared with these values. The WTS's S content obtained by Lee et al., (2020), was also smaller than the normal content of an AC and the two WTSs used in this study. However, the N content obtained by Lee et al., (2020) was higher than the typical value associated with an AC and the value obtained in this study. According to Bansal and Goyal (2005), the oxygen (O) content value is typically between 6 to 7 wt.%, however, depending on the raw material of the AC, and its activation process this value can range between 1 to 20 wt.%. The WTS used by Lee et al., (2020) had an

O content proximally of 18 wt.%, being within the aforementioned range, however, the WTSs used in this study have a high O content.

Table 6.1 – Ash content and elemental composition of the WTSs ($\bar{X} \pm \sigma$, n=2)

WTS	Ash (wt.%^{1})	C (wt.% ^{1})	N (wt.% ^{1})	H (wt.% ^{1})	S (wt.% ^{1})	O (wt.% ^{1})
Caldeirão	30.81 ± 0.83	34.09	0.46	2.92	0.18	31.54
St. Águeda	42.87 ± 0.20	24.31	0.24	2.64	0.16	29.78

^{1} as-received the bases

Based on these results, it is possible to conclude that the two WTSs have a very similar elemental composition. The main difference in the elemental composition of the sludges is the C content. However, the difference between the C content does not allow to conclude which of the WTS has a higher AC content, since the C content can be correlated with the AC as well as the organic matter present in the WTS.

6.2 Determination of the pH_{pzc}

Table 6.2 presents the pH_{pzc} of the two WTSs. Based on these results it is possible to realize that St. Águeda had a very high pH_{pzc}, which means that this sludge is strongly alkaline, unlike Caldeirão WTS has a more neutral pH_{pzc}, similar to the typical value of an aluminium-based sludge (Muisa et al., 2020). The pH_{pzc} is directly related to the ash content of the WTS, St. Águeda WTS is more alkaline than Caldeirão WTS because it presented a higher mineral content.

Table 6.2 – pH_{pzc}

WTS	pH_{pzc}
Caldeirão	7.46
St. Águeda	11.29

According to these results, Caldeirão WTS and St. Águeda WTS are positively charged, respectively, at pH under 7.46 and 11.29. The studied compounds are neutrally charged at pH lower than the pKa of each compound (Ifelebuegu, 2012; Neale et al., 2009), which means that in the case of Caldeirão WTS only exist electrostatic repulsion at pH higher than the pKa of each compound, and in the case of St. Águeda WTS the electrostatic repulsion only occurs when the pH is higher than the pH_{pzc} of this sludge.

6.3 Thermogravimetric Analysis

Figure 6.1 presents the results of the TGA of the WTSs, which shows the degradation rates of the WTSs as a function of the temperature. The results of each WTS are found in the Annex IV and Annex VI. During this analysis, Caldeirão WTS total mass loss was 27.3 % and St. Águeda WTS total mass loss was 33.5 %. These results may suggest that during the WTS regeneration/reactivation process, a significant mass would be lost. In other hand, comparing the sludges results is also possible to conclude that the regeneration of St. Águeda WTS would be expected to be more efficient than the regeneration of Caldeirão WTS since greater mass losses are associated with higher regeneration efficiencies (Salvador et al., 2015).

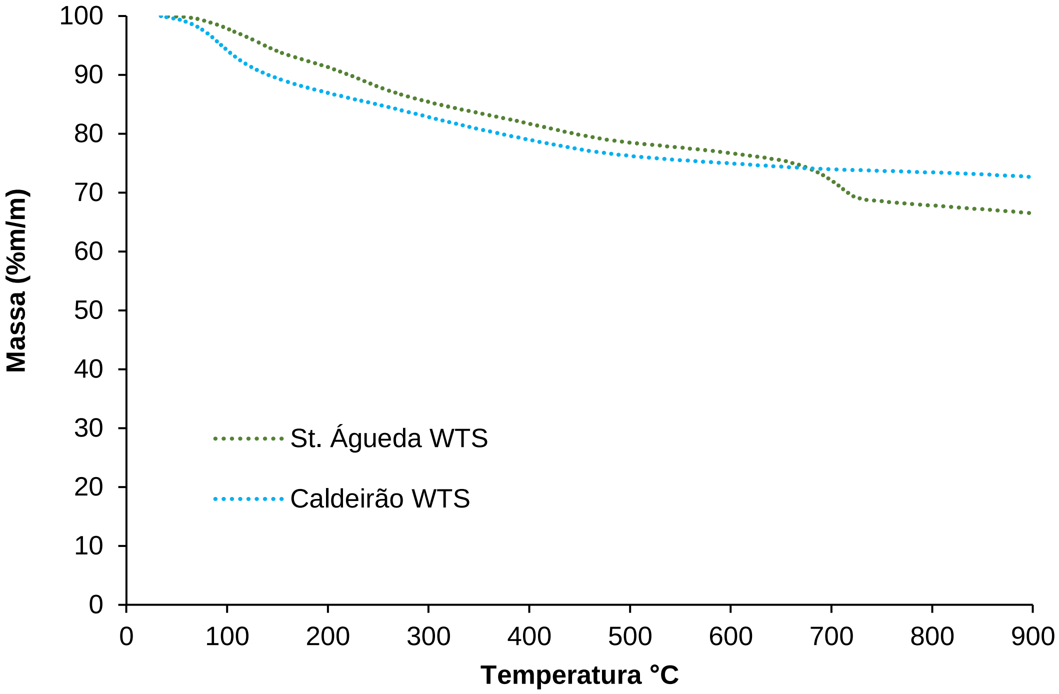


Figure 6.1 – Losing mass of the WTS during the Thermogravimetric Analysis

The greatest loss of Caldeirão mass occurs essentially around 100 ºC, so it is possible to conclude that this mass loss corresponds to the moisture present in the sample. On the other hand, the greatest loss St. Águeda WTS occurs around 700 ºC, according to Bernardo et al., (2020) this loss is related to the decomposition of some mineral compounds (e.g. $CaCO_3$). Based on the mass loss until the 105 ºC it was possible to determine the moisture of the samples of each WTS, Caldeirão WTS's moisture is 6.5 % while St. Águeda WTS's moisture is 2.5 %.

6.4 Mineral Analysis

Table 6.3 shows the average of the mineral composition results of the replicas of the two WTSs. Through them is possible to see some differences between the mineral composition of the two WTSs. The results showed that the mineral elements present in higher weight percentage in Caldeirão WTS were aluminium, Al (5.45 wt.%), followed by phosphorous, P (3.49 wt.%), iron, Fe, (0.94 wt.%) and calcium, Ca, (0.64 wt.%). As for St. Águeda WTS the elements with the highest weight percentage were Ca (11.54 wt.%), followed by Al (5.30 wt.%), P (3.49 wt.%) and Fe (0.69 wt.%).

Table 6.3 – Mineral analysis results ($\bar{X} \pm \sigma$, *n=2*)

Element	Chemical symbol	Sta. Águeda WTS (mg/kg WTS[1])	Caldeirão WTS (mg/kg WTS[1])
Aluminium	**Al**	53 000.0 ± 800.0	54 450.0 ± 5350.0
Arsenic	**As**	37.4 ± 0.9	65.6 ± 7.9
Calcium	**Ca**	115 350.0 ± 1650.0	6 429.5 ± 733.4
Cadmium	**Cd**	ND	ND
Chromium	**Cr**	ND	ND
Copper	**Cu**	4.1 ± 0.4	10.5 ± 1.1
Iron	**Fe**	6 890.5 ± 502.9	9 442.5 ± 1328.5
Mercury	**Hg**	ND	ND
Potassium	**K**	275.8 ± 10.7	119.9 ± 13.0
Magnesium	**Mg**	5 423.9 ± 111.9	2 280.3 ± 458.7
Manganese	**Mn**	468.6 ± 19.0	150.4 ± 14.1
Molybdenum	**Mo**	5.3 ± 0.1	5.2 ± 0.6
Sodium	**Na**	16.1 ± 0.3	5.4 ± 0.5
Nickel	**Ni**	ND	ND
Phosphorus	**P**	3 3816.6 ± 558.5	3 4947.3 ± 4242.3
Lead	**Pb**	13.1 ± 0.2	14.1 ± 2.6
Antimony	**Sb**	37.0 ± 0.6	37.4 ± 3.8
Selenium	**Se**	38.4 ±0.2	41.3 ± 3.8
Zinc	**Zn**	21.8 ± 1.4	15.5 ± 1.4
Total Mineral	**-**	215 398.7 ± 1 811.5	108 014.9 ± 12 161.8

ND - non detect

[1] as-received the base

Comparing the mineral composition of the WTS, it is possible to see that the main difference between them is the calcium content. This difference can be explained by the addition of limestones insoluble residues that are added in the final stage of the sludge treatment at the St. Águeda WTP, which result in the increasing of the calcium content. Except for this mineral, there are no significant differences between the WTS regarding the mineral composition. The high aluminium content reflects the type of coagulants used in both WTP (aluminium polyhydroxychlorosulfate). The presence of the other elements, such as phosphorus and iron may be related to the composition of the raw water, which are removed during the process treatment.

The total mineral content of each WTS (21.5 wt.% for St. Águeda WTS and 10.8 wt.% for Caldeirão WTS) was expected to be similar to the ash content (Table 6.1 in Chapter 6.1). However, the results show a difference of about 20 % in both WTSs. This difference might be due to the content of other elements that hadn't been completely solubilised in the acid digestion or even others that hadn't been quantified in the mineral analysis. An example of an element that hasn't been quantified is the silicon, that according to literature, in some cases, is significant (Ahmad et al., 2016; Babatunde & Zhao, 2007; Lee et al., 2020).

6.5 Textural Characterization

Table 6.4 presents the results of the WTSs' textural characterization. Caldeirão WTS's surface area was higher than St. Águeda WTS's surface area, therefore, is possible to assume that Caldeirão has a higher content of AC. The same conclusion can be made comparing the pore volume of the WTSs. The Caldeirão WTS's pore volume was relatively higher than St. Águeda WTS's pore volume. Despite the high surface area and pore volume of Caldeirão WTS, those values were far below the typical values for AC, according to the literature, AC's surface area range between 800 to 1 500 m^2/g, and the pore volume range between 0.7 to 2.8 cm^3/g. Comparing the results achieved with the ones obtained by Lee et al., (2020), namely a pore volume of 0.024 cm^3/g and a surface area of 6.547 m^2/g, is possible to verify that the WTS used in the study had a higher surface area and pore volume.

Table 6.4 – Textural characterization

WTS	Surface area (m^2/g)	Pore Volume (cm^3/g)
Caldeirão	318	0.161
St. Águeda	127	0.065

This result can be related to the ash content. Caldeirão WTS had a lower ash content but a higher surface area than St. Águeda, which means that there is less pore blockage (Lee et al., 2020; Salvador et al., 2015). Comparing these results, it is expected to be obtained higher removal efficiencies with Caldeirão WTS.

6.6 Preliminary Study

The results of the preliminary study showed that the use of WTS containing AC as an adsorbent for estrogens is a promising approach. Table 6.5 shows the results obtained with this assay, based on which were calculated the removal efficiency of hormones obtained for each sludge (Figure 6.2 and Annex VIII). The removal efficiency was calculated based on the final concentration which can be seen in Table 6.5. If the estrogens weren't detected in a sample, then the LOQ was used for this calculation, these removal efficiencies correspond to the minimum removal occurred. Blank concentrations, presented in Table 6.5, were considered as the initial concentration of the assay. However, it is possible to see that the E1's target concentration wasn't achieved, which can be explained by possible operation errors, therefore, the determined concentration was used. As for E2 and EE2, the target concentration was achieved (in the error range) therefore, for these compounds, the target concentration was considered the initial concentration.

Table 6.5 – Preliminary study results

Compund	**Initial Concentration (ng/L)**	**Target Concentration (ng/L)**	**Initial Concentration Considered (ng/L)**	**Final Concentration (ng/L)**	
				St. Águeda WTS	**Caldeirão WTS**
E1	1100 ± 400	500	1100	110 ± 40	< LOQ^1
	700 ± 200	350	700	140 ± 50	< LOQ^1
	400 ± 100	200	400	60 ± 20	< LOQ^1
E2	600 ± 200	500	500	60 ± 20	< LOQ^2
	400 ± 100	350	350	80 ± 30	< LOQ^2
	300 ± 100	200	200	< LOQ^2	< LOQ^2
EE2	600 ± 200	500	500	150 ± 60	< LOQ^2
	300 ± 100	350	350	170 ± 70	< LOQ^2
	300 ± 100	200	200	100 ± 40	< LOQ^2

LOQ^1= 60 ng/L
LOQ^2= 50 ng/L

Overall, the results show the removal of at least 50 % of the initial concentration of the compounds for both WTSs (Figure 6.2), indicating that the use of WTS containing AC for the removal of these compounds has high potential, even without reactivation or regeneration. The results achieved, especially the results obtain with Caldeirão WTS, are comparable with the results achieved in the studies using pure AC, namely the following studies Chang et al. (2004), Gökçe & Arayici (2016), Guillossou et al. (2020), Ifelebuegu et al. (2006), Kovalova et al. (2013), Rowsell et al. (2009) and Yoon et al. (2003), which corroborates the high potential of the use these erstwhile residues for the removal of estrogens.

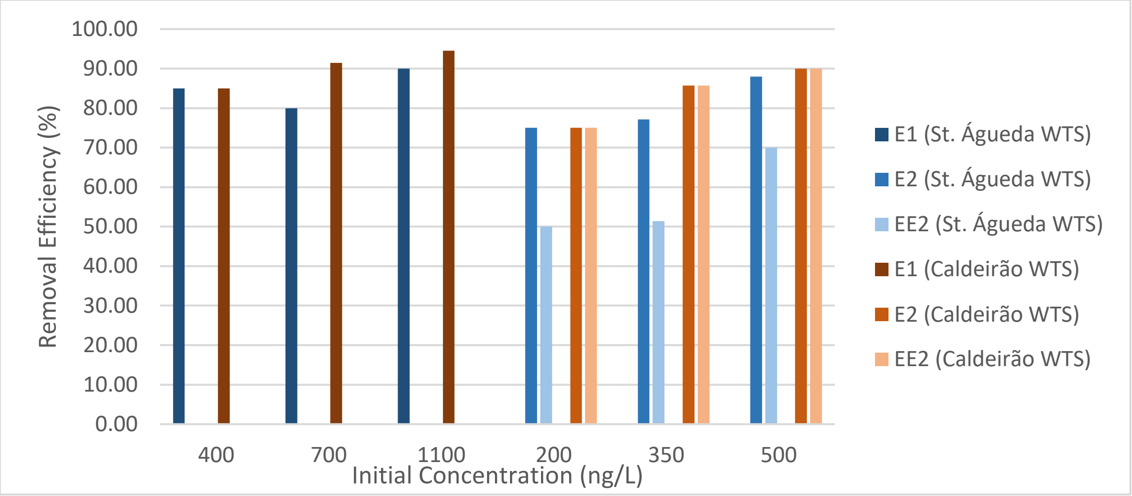


Figure 6.2 – Removal efficiency results

Comparing the results obtained for each WTS is possible to verify that Caldeirão WTS achieved higher removal rates than St. Águeda WTS, having been achieved the LOQ for all final concentrations when this sludge was used. Therefore the removal efficiencies for this sludge may be higher than calculated (Annex VIII). This difference can be explained because Caldeirão WTS had a higher surface area, which means a higher number of available sites which is a very important factor for the adsorption of this compounds (Ifelebuegu et al., 2006). The high removal efficiencies achieved by Caldeirão WTS may suggest that the AC present in this sludge still had adsorption capacity, which indicates that the reactivation process might not be necessary.

Another aspect correlated with the adsorption capacity that can be seen in the results achieved for E2 and EE2 in both WTS and E1 in Caldeirão WTS is the correlation between the adsorbate concentration and the removal performance (Figure 6.3). The highest removal efficiencies were achieved for the highest concentration of these compounds. As mention in the literature review, according to Hadi et al. (2015), this happens because the increase of the initial concentration leads to the increasing of the driving forces of the concentration gradient that overcome the mass transfer resistance of the compound between the aqueous and solid phases, in other hand the increase of the adsorbate concentration promotes an increase of collisions between the molecules compound and the surface groups of the adsorbent.

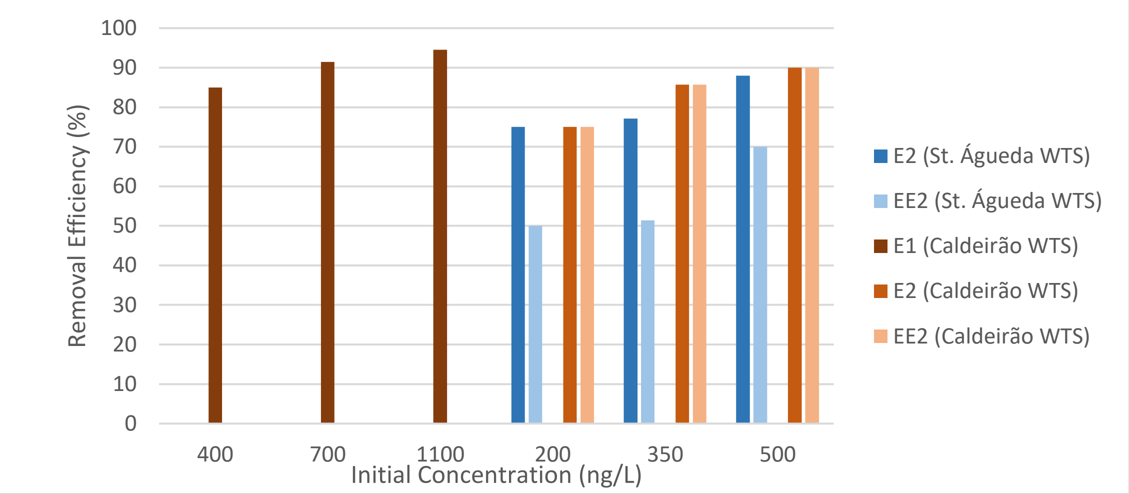


Figure 6.3 – Initial Concentration influence on the adsorption process

Looking at the results obtained with St. Águeda WTS (Figure 6.4) is possible to observe some difference between the adsorption of the studied compounds. Through the results of the adsorption onto this WTS it seems that the compounds can be ranked in terms of adsorbability as following way E2 > EE2. This difference, according to Saha et al. (2010) might be related to size exclusion. Another explanation might be the blockade of the formation of hydrogen bonding by the triple bond present in EE2. Although the results show higher removal efficiencies for E1 compared with the ones obtained for E2, is not possible to conclude that E1 have a higher adsorbability than E2 since the initial concentrations used were different. This difference can't be seen in the results obtained with Caldeirão WTS since the final concentration resulting were below the LOQ.

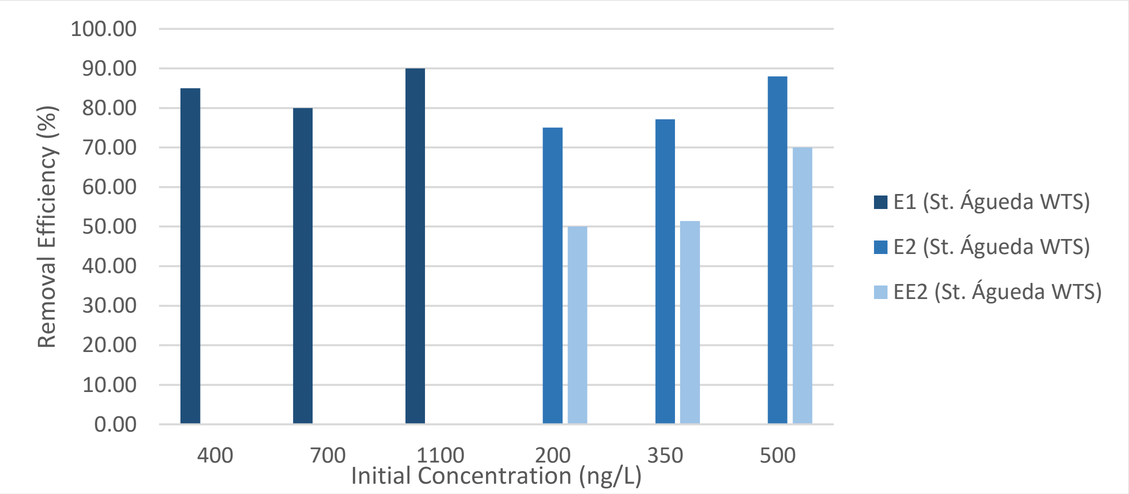


Figure 6.4 – St. Águeda WTS removal efficiency results

The pH is an important factor affecting the adsorption process. However, in this study, the influencing of this parameter in the adsorption was not assessed. Yet, it can be established some conclusion about the pH of this assay, that was 3.3. This pH might have favoured the adsorption process since according to Ifelebuegu (2012), the estrogens are easily adsorbed onto AC at low and neutral pHs, in other hand according to the WTS pH_{pzc} values (Table 6.2 in Chapter 6.2) the WTS's surfaces were positively charged at the pH of the assays which may support the inexistence of electrostatic repulsion between the adsorbent and the adsorbate, which happen when the adsorbent is negatively charged (Ifelebuegu, 2012).

In addition to the presence of AC with remaining adsorption capacity, the presence of other elements might also influence the adsorption performance of these sludges. The high content of aluminium gives to the WTS adsorbent properties even without activated carbon in their composition (Ahmad et al., 2016; Mohammed & Rashid, 2012; Yang et al., 2006; Zhou & Haynes, 2012). In other hand, when AC is present the aluminium can improve the adsorption capacity of the WTS as explain by Lee et al., (2020). However, many studied concluded that the user of aluminium as a coagulant (Auriol et al., 2006; Bodzek & Dudziak, 2006) or in the constitution of WTS as a minimal capacity to remove micropollutants (Kulandaivelu et al., 2020). Therefore, is important to study if the aluminium improves the adsorption capacity of the WTS containing AC.

Another aspect that might have influenced the adsorption onto the WTS is the fact that the studied compounds are classified as moderately hydrophobic (Guillossou et al., 2020; Hamid & Eskicioglu, 2012; Ifelebuegu et al., 2006; Rowsell et al., 2009; Yoon et al., 2003), this behaviour promotes the adsorption onto the sludge and therefore may also be responsible for the removal efficiencies achieved.

Figure 6.5 shows the particle size distribution of the remained WTS used during the preliminary study. Through these results, it is possible to see for both WTSs that most of the sludge did not decrease its granulometry. However, it is possible to verify that about 37 % of St. Águeda WTS sample has decreased its granulometry during the preliminary study, unlike Caleirão WTS that had less than half of that percentage of sludge which decreased its granulometry. Regarding the fraction of the sample with a particle size higher than 45 mesh, it might be related with some aggregation during the preliminary study or even during the drying, yet since this fraction represents around 1 % in both WTSs it is negligible.

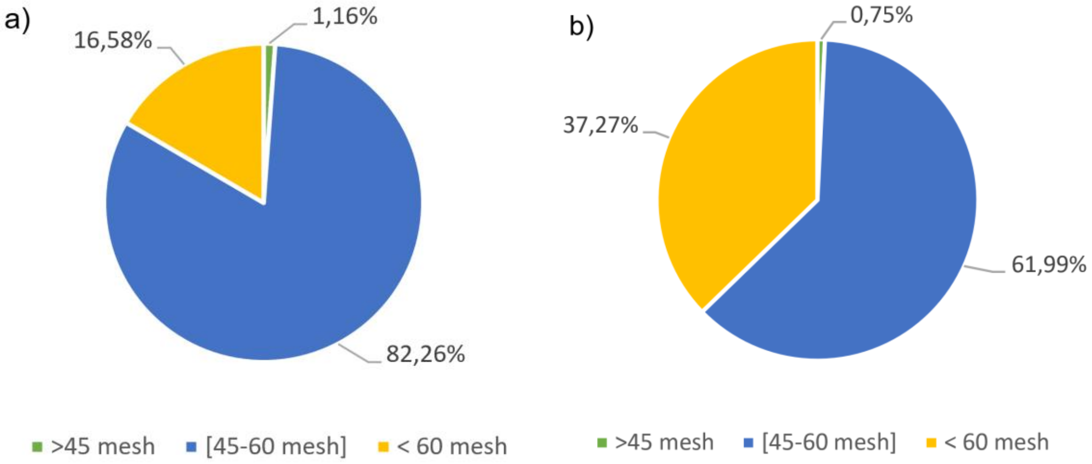


Figure 6.5 – Particle size distribution of the remaining sludge a) Caldeirão WTS b) St. Águeda WTS

6.7 Dosage study

The results of the estrogens determination of the samples of the dosage study have not been delivered until the submission of this master thesis.

7 Conclusion and Future Developments

The present work intends to give a contribution to the study of the application of WTS containing AC as a complementary treatment for the removal of EP in WWTP. The results of this work suggest that WTS containing AC presents adsorption potential, which leads to a new approach in the management of this erstwhile reside, lining up with the circular economy proposals. Considering the work developed and the results obtained throughout this study, the main conclusions were:

- Even without regeneration, the WTSs achieved very high or even total removal efficiencies for the studied estrogens, comparable to the results obtained with pure AC. Both WTSs showed adsorption potential with efficiencies removal of at least 50%;
- The results suggest that Caldeirão WTS had a higher content of AC than St. Águeda WTS. WTS with higher surface areas leads to higher removal efficiencies for the removal of the studied compounds;
- For Caldeirão WTS final concentration for all the three EP were lower than the limit of quantification. As for St. Águeda WTS, the results for E1 and E2 removal were similar to Caldeirão WTS, however, for EE2 the removal efficiency was lower;
- Apparently, the initial concentration might affect the adsorption results. Higher estrogens concentration could lead to the highest removal efficiencies.

This suggests a new and economic approach for the removal of these EP. It is also possible to conclude that during the mixing process most of the WTS did not decrease its granulometry, which is a positive factor in the application of these sludges in a large-scale.

Since the preliminary study shows high potential for the use of WTS as an adsorbent further study must be considered, such as:

- A complete textural characterization, in other to obtained information about the pores, and a surface chemistry evaluation, to identify surface functional groups;

- A dosage study to assed the WTS dosage that achieves the greater EDC’s removal;
- And kinetic and equilibrium assays to go insight the adsorption mechanisms;
- Evaluation of the impact of the presence of aluminium in the adsorption process;
- Study of the adsorption process in wastewater.

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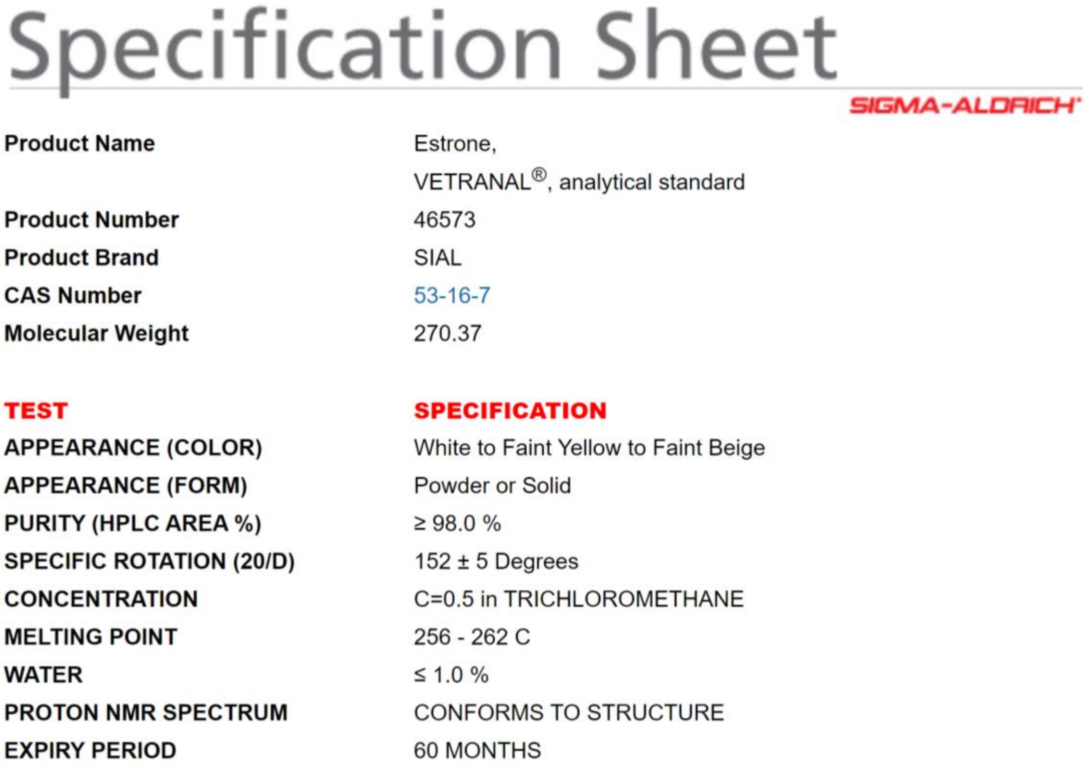
Annexs

Annex I – Estrone Product Datasheet



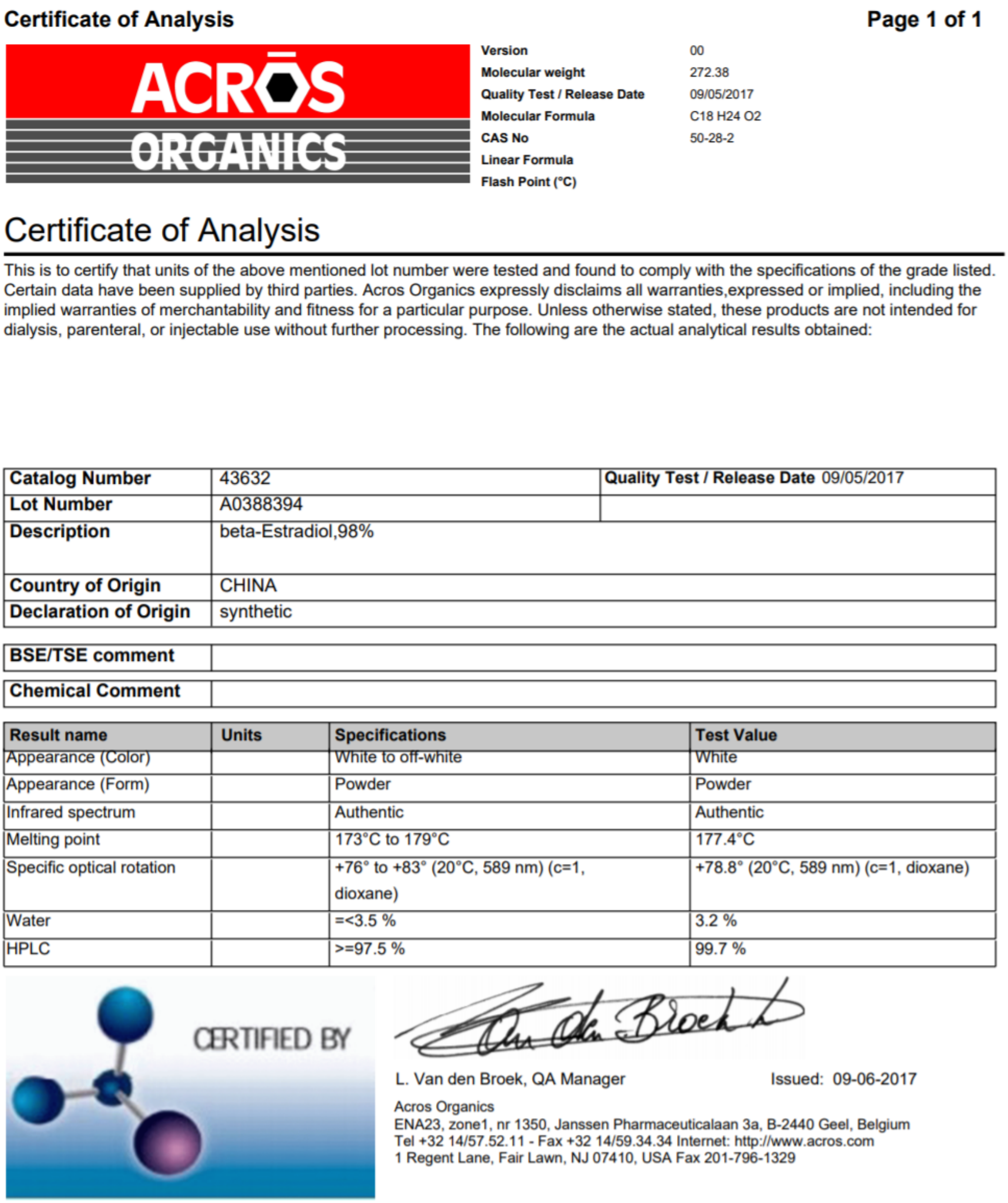
Specification Sheet

SIGMA-ALDRICH

Product Name	Estrone, VETRANAL®, analytical standard
Product Number	46573
Product Brand	SIAL
CAS Number	53-16-7
Molecular Weight	270.37

TEST	**SPECIFICATION**
APPEARANCE (COLOR)	White to Faint Yellow to Faint Beige
APPEARANCE (FORM)	Powder or Solid
PURITY (HPLC AREA %)	≥ 98.0 %
SPECIFIC ROTATION (20/D)	152 ± 5 Degrees
CONCENTRATION	C=0.5 in TRICHLOROMETHANE
MELTING POINT	256 - 262 C
WATER	≤ 1.0 %
PROTON NMR SPECTRUM	CONFORMS TO STRUCTURE
EXPIRY PERIOD	60 MONTHS

Annex II – 17β-estradiol Product Datasheet



Certificate of Analysis **Page 1 of 1**

ACROS ORGANICS

Version	00
Molecular weight	272.38
Quality Test / Release Date	09/05/2017
Molecular Formula	C18 H24 O2
CAS No	50-28-2
Linear Formula	
Flash Point (°C)	

Certificate of Analysis

This is to certify that units of the above mentioned lot number were tested and found to comply with the specifications of the grade listed. Certain data have been supplied by third parties. Acros Organics expressly disclaims all warranties,expressed or implied, including the implied warranties of merchantability and fitness for a particular purpose. Unless otherwise stated, these products are not intended for dialysis, parenteral, or injectable use without further processing. The following are the actual analytical results obtained:

Catalog Number	43632	**Quality Test / Release Date** 09/05/2017
Lot Number	A0388394	
Description	beta-Estradiol,98%	
Country of Origin	CHINA	
Declaration of Origin	synthetic	

BSE/TSE comment	
Chemical Comment	

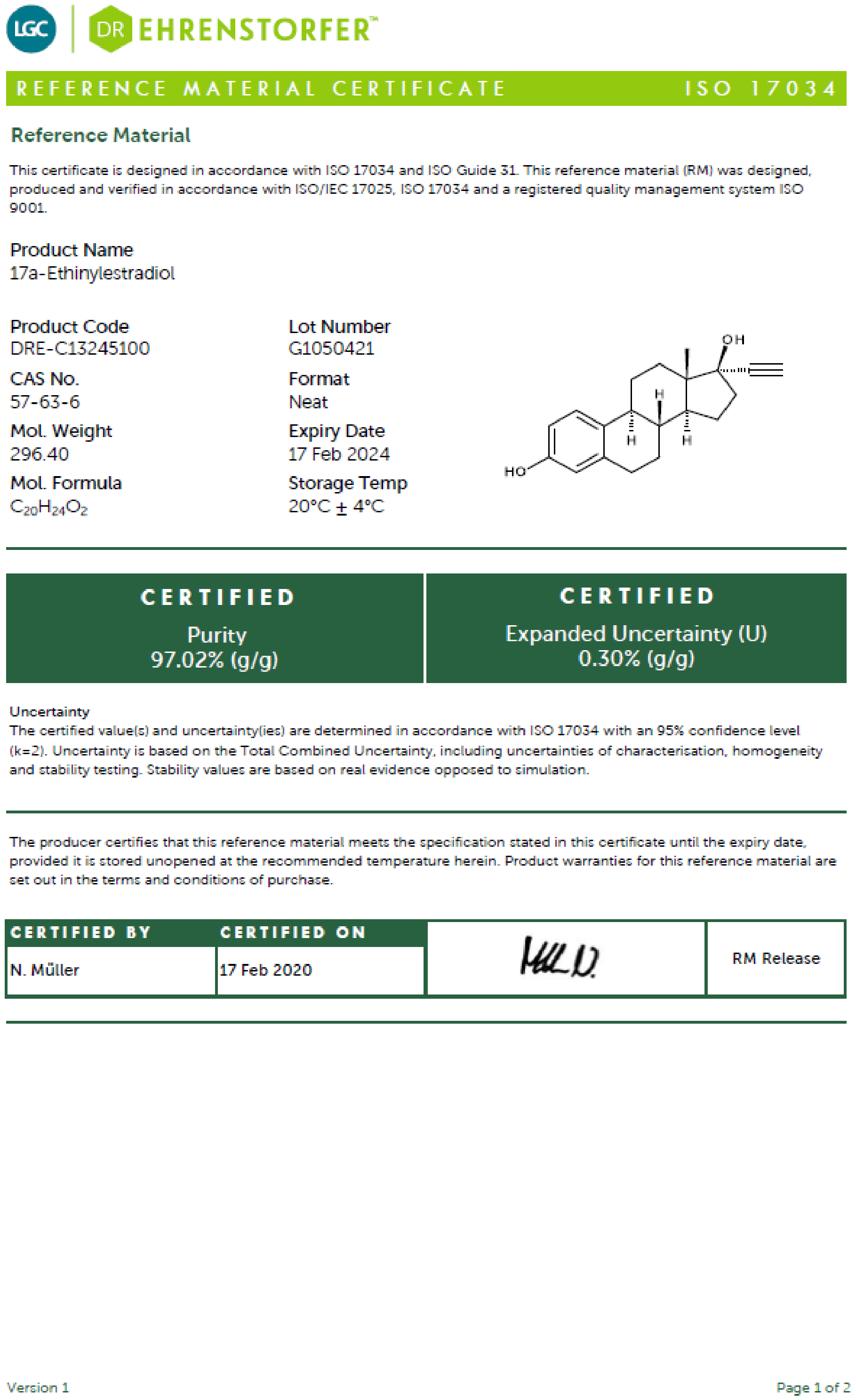
Result name	**Units**	**Specifications**	**Test Value**
Appearance (Color)		White to off-white	White
Appearance (Form)		Powder	Powder
Infrared spectrum		Authentic	Authentic
Melting point		173°C to 179°C	177.4°C
Specific optical rotation		+76° to +83° (20°C, 589 nm) (c=1, dioxane)	+78.8° (20°C, 589 nm) (c=1, dioxane)
Water		=<3.5 %	3.2 %
HPLC		>=97.5 %	99.7 %

CERTIFIED BY

L. Van den Broek, QA Manager Issued: 09-06-2017

Acros Organics
ENA23, zone1, nr 1350, Janssen Pharmaceuticalaan 3a, B-2440 Geel, Belgium
Tel +32 14/57.52.11 - Fax +32 14/59.34.34 Internet: http://www.acros.com
1 Regent Lane, Fair Lawn, NJ 07410, USA Fax 201-796-1329

Annex III – 17α-ethinylestradiol Product Datasheet



DR EHRENSTORFER™

REFERENCE MATERIAL CERTIFICATE ISO 17034

Reference Material

This certificate is designed in accordance with ISO 17034 and ISO Guide 31. This reference material (RM) was designed, produced and verified in accordance with ISO/IEC 17025, ISO 17034 and a registered quality management system ISO 9001.

Product Name
17a-Ethinylestradiol

Product Code
DRE-C13245100

CAS No.
57-63-6

Mol. Weight
296.40

Mol. Formula
$C_{20}H_{24}O_2$

Lot Number
G1050421

Format
Neat

Expiry Date
17 Feb 2024

Storage Temp
20°C ± 4°C

CERTIFIED	CERTIFIED
Purity 97.02% (g/g)	Expanded Uncertainty (U) 0.30% (g/g)

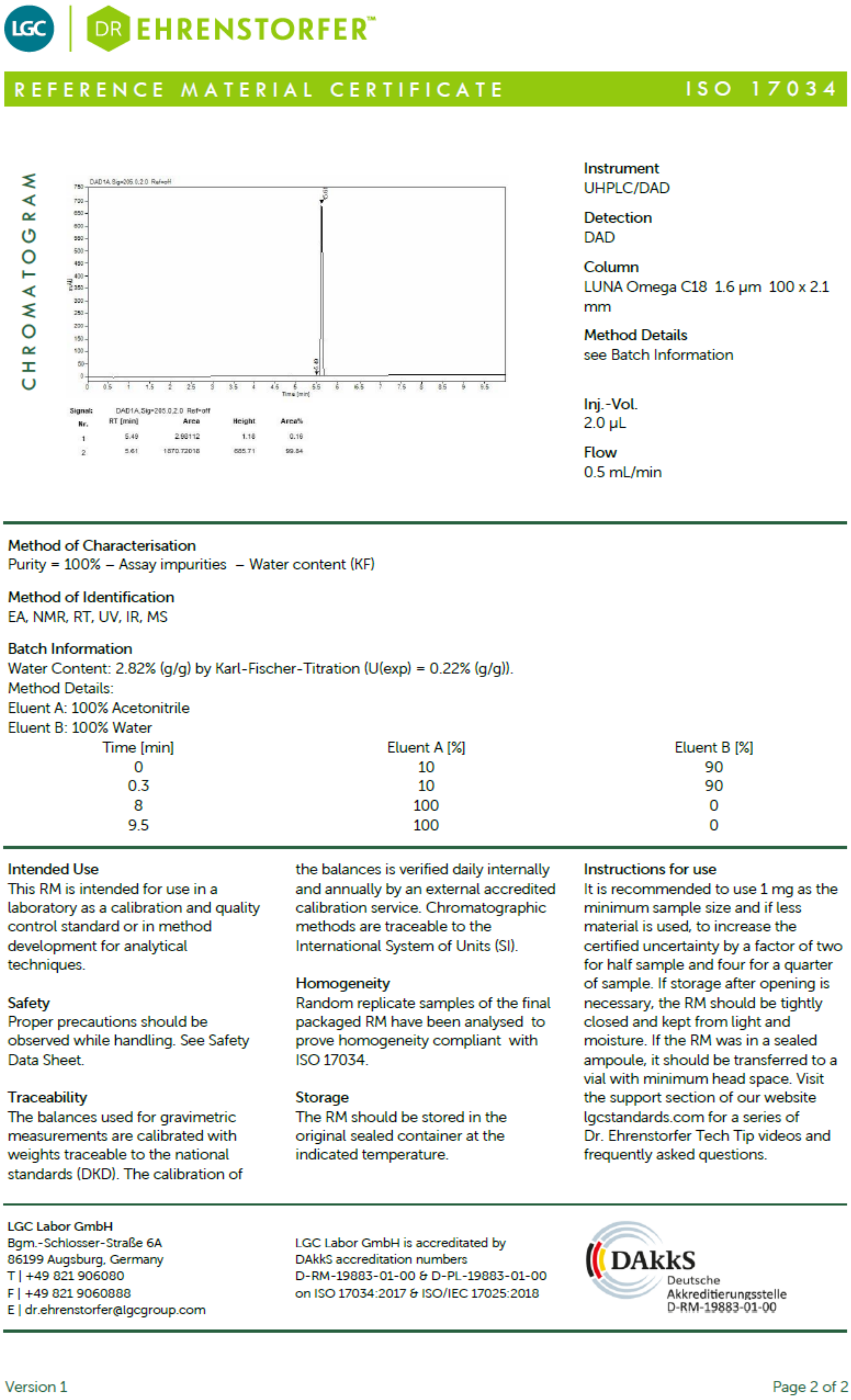
Uncertainty
The certified value(s) and uncertainty(ies) are determined in accordance with ISO 17034 with an 95% confidence level (k=2). Uncertainty is based on the Total Combined Uncertainty, including uncertainties of characterisation, homogeneity and stability testing. Stability values are based on real evidence opposed to simulation.

The producer certifies that this reference material meets the specification stated in this certificate until the expiry date, provided it is stored unopened at the recommended temperature herein. Product warranties for this reference material are set out in the terms and conditions of purchase.

CERTIFIED BY	CERTIFIED ON		
N. Müller	17 Feb 2020		RM Release

Version 1

Page 1 of 2



LGC | DR EHRENSTORFER™

REFERENCE MATERIAL CERTIFICATE ISO 17034

CHROMATOGRAM

Signal: DAD1A,Sig=205.0,2.0 Ref=off

Nr.	RT [min]	Area	Height	Area%
1	5.49	2.98112	1.18	0.16
2	5.61	1870.72018	685.71	99.84

Instrument
UHPLC/DAD

Detection
DAD

Column
LUNA Omega C18 1.6 µm 100 x 2.1 mm

Method Details
see Batch Information

Inj.-Vol.
2.0 µL

Flow
0.5 mL/min

Method of Characterisation
Purity = 100% – Assay impurities – Water content (KF)

Method of Identification
EA, NMR, RT, UV, IR, MS

Batch Information
Water Content: 2.82% (g/g) by Karl-Fischer-Titration (U(exp) = 0.22% (g/g)).
Method Details:
Eluent A: 100% Acetonitrile
Eluent B: 100% Water

Time [min]	Eluent A [%]	Eluent B [%]
0	10	90
0.3	10	90
8	100	0
9.5	100	0

Intended Use
This RM is intended for use in a laboratory as a calibration and quality control standard or in method development for analytical techniques.

Safety
Proper precautions should be observed while handling. See Safety Data Sheet.

Traceability
The balances used for gravimetric measurements are calibrated with weights traceable to the national standards (DKD). The calibration of the balances is verified daily internally and annually by an external accredited calibration service. Chromatographic methods are traceable to the International System of Units (SI).

Homogeneity
Random replicate samples of the final packaged RM have been analysed to prove homogeneity compliant with ISO 17034.

Storage
The RM should be stored in the original sealed container at the indicated temperature.

Instructions for use
It is recommended to use 1 mg as the minimum sample size and if less material is used, to increase the certified uncertainty by a factor of two for half sample and four for a quarter of sample. If storage after opening is necessary, the RM should be tightly closed and kept from light and moisture. If the RM was in a sealed ampoule, it should be transferred to a vial with minimum head space. Visit the support section of our website lgcstandards.com for a series of Dr. Ehrenstorfer Tech Tip videos and frequently asked questions.

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LGC Labor GmbH is accredited by DAkkS accreditation numbers D-RM-19883-01-00 & D-PL-19883-01-00 on ISO 17034:2017 & ISO/IEC 17025:2018

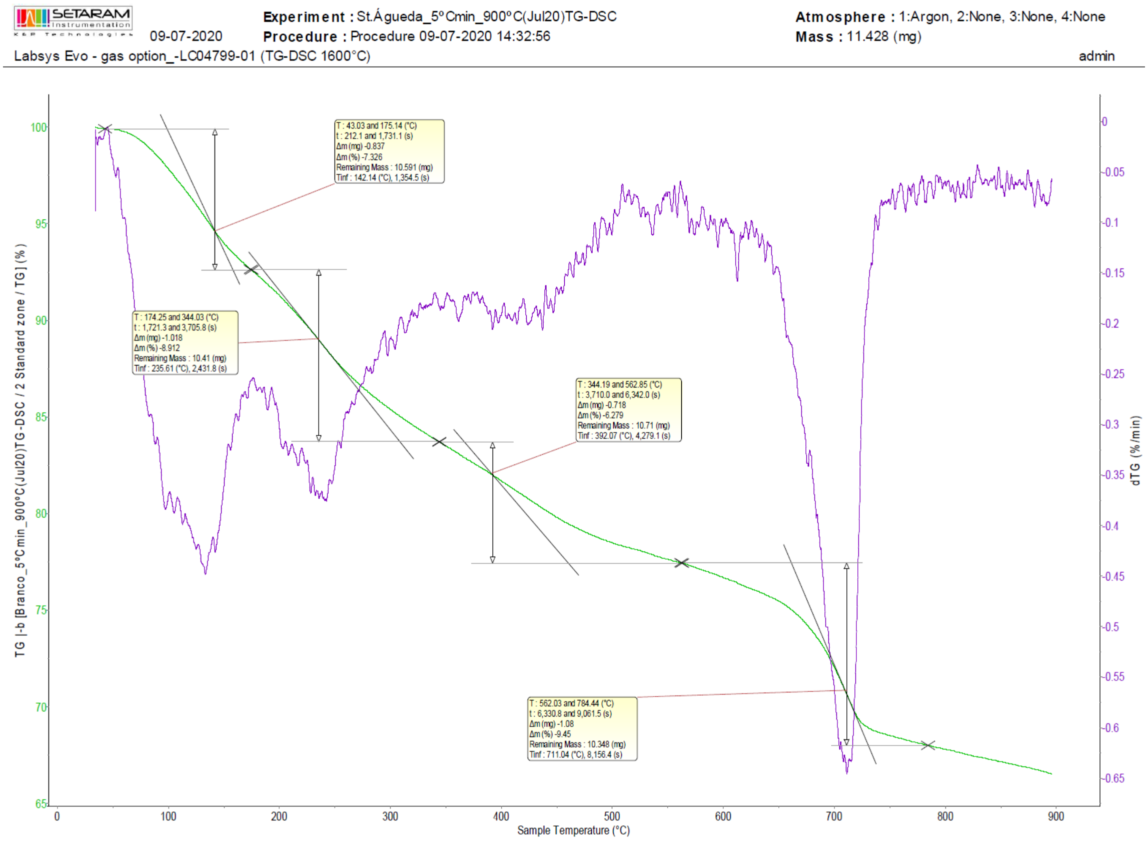
DAkkS
Deutsche
Akkreditierungsstelle
D-RM-19883-01-00

Annex IV – Ash Content

Table IV.1 – Ash content

WTS	Crucible (g)	WTS+ Crucible (g)	Ash + Crucible (g)	Ash (g)	Ash (wt.%)
Caldeirão	25.697	26.699	26.014	0.317	31.6
	24.144	25.148	24.445	0.301	30.0
Sta. Águeda	30.508	31.537	30.947	0.439	42.7
	31.276	32.293	31.714	0.438	43.1

Annex V – St. Águeda WTS TGA Results



SETARAM Instrumentation 09-07-2020

Experiment : St.Águeda_5ºCmin_900ºC(Jul20)TG-DSC

Procedure : Procedure 09-07-2020 14:32:56

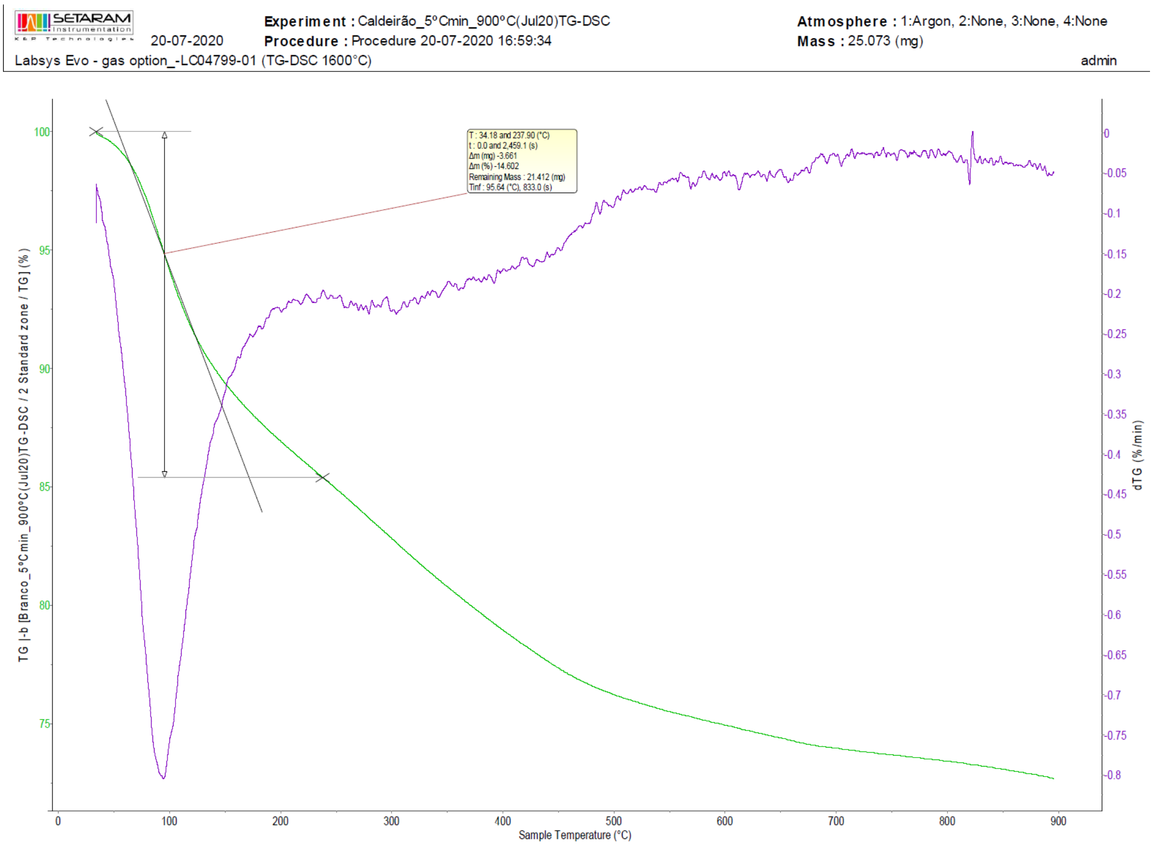
Atmosphere : 1:Argon, 2:None, 3:None, 4:None

Mass : 11.428 (mg)

Labsys Evo - gas option_-LC04799-01 (TG-DSC 1600°C)

admin

Annex VI – Caldeirão WTS TGA Results



SETARAM Instrumentation KEP Technologies 20-07-2020

Experiment : Caldeirão_5°Cmin_900°C(Jul20)TG-DSC

Procedure : Procedure 20-07-2020 16:59:34

Atmosphere : 1:Argon, 2:None, 3:None, 4:None

Mass : 25.073 (mg)

Labsys Evo - gas option_-LC04799-01 (TG-DSC 1600°C)

admin

T : 34.18 and 237.90 (°C)
t : 0.0 and 2,459.1 (s)
Δm (mg) -3.661
Δm (%) -14.602
Remaining Mass : 21.412 (mg)
Tinf : 95.64 (°C), 833.0 (s)

Annex VII – Mineral Analysis Results

Table VII.2 – Mineral analysis results

Element	St. Águeda WTS		Caldeirão WTS	
	Replica 1 (wt.%)	Replica 2 (wt.%)	Replica 1 (wt.%)	Replica 2 (wt.%)
Al	53800.00	52200.00	49100.00	59800.00
As	36.47	38.32	57.73	73.43
Ca	113700.00	117000.00	5696.13	7162.95
Cd	ND	ND	ND	ND
Cr	ND	ND	ND	ND
Cu	3.73	4.47	9.37	11.64
Fe	6387.57	7393.42	8114.09	10771.01
Hg	ND	ND	ND	ND
K	286.6	265	106.9	133
Mg	5535.83	5311.98	1821.574	2738.973
Mn	449.625	487.648	136.271	164.523
Mo	5.44	5.16	4.58	5.84
Na	15.86	16.38	4.91	5.97
Ni	ND	ND	ND	ND
P	33258.13	34375.07	30705.05	39189.61
Pb	12.98	13.30	11.42	16.70
Sb	36.39	37.62	33.59	41.18
Se	38.21	38.59	37.50	45.09
Zn	20.44	23.16	14.06	16.92
Total	213 587.2	217 210.2	95 853.1	120 176.7

ND - non detect

Annex VIII – Preliminary Study Removal Efficiency Results

Table VIII.3 – Removal efficiency results

Compound	Initial Concentration (ng/L)	Removal Efficiency (%)	
		St. Águeda WTS	Caldeirão WTS
E1	1100	90.00	>94.54
	700	80.00	>91.42
	400	85.00	>85.00
E2	500	88.00	>90.00
	350	77.14	>85.71
	200	>75.00	>75.00
EE2	500	70.00	>90.00
	350	51.43	>85.71
	200	50.00	>75.00