

Organochlorine pesticides removal from wastewater by pine bark adsorption after activated sludge treatment

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Pesticides have been responsible for strong environmental impacts, mainly due to their persistence in the environment. Removal technologies are usually combined, because degradation of organic matter is needed prior to a tertiary treatment to guarantee pesticides elimination to levels below legal limits (normally $0.1 \mu\text{g L}^{-1}$). Pine bark was studied as an alternative to activated carbon, for organochlorine pesticides removal. A combination of technologies based on biodegradation with activated sludge followed by pine bark adsorption treatment was used for lindane (LIN) and heptachlor (HEP) removal from contaminated waters. Pesticides were quantified throughout the process by GC-ECD preceded by solid-phase microextraction (SPME). An experimental set-up was maintained for 4 months, by feeding a standard solution with pesticides concentration of $1 \mu\text{g L}^{-1}$ each and known organic matter (Chemical Oxygen Demand, COD, $\sim 563 \text{ mg O}_2 \text{ L}^{-1}$) on a daily basis. COD suffered a reduction of about 81% in the biological step and no increase was detected in the subsequent adsorption treatment. Overall removal efficiency was 76.6% and above 77.7% for LIN and HEP, respectively.

Keywords: adsorption; biological treatment; heptachlor; lindane; pine bark

Introduction

Although pesticides, as trace pollutants, are found in the environment in very small concentrations, they are responsible for considerable toxicity effects found in living organisms [1]. Their toxicity depends on the biologically available fraction as well as on its critical concentration in organisms and contact or exposure time [2]. Despite pesticides' importance on the control of almost all kinds of pests such as insects, fungi or rodents [3] and bacteria, it has been proved that their use can lead to mutations, cancers and enzymatic inhibitions and also hormonal, nervous and reproductive system alterations [4,5].

Between the 1960s and the 1980s, there was a massive utilization of organochlorine pesticides [6], which doubled in the period from 1977 to 1987 [5]. This led to strict regulation and interdiction in most countries, although they are still used in Africa, South Asia and Central and South America [7,8]. Nevertheless, they can still be found in surface and ground waters at significant levels worldwide [9,10].

Organochlorine pesticides (OCPs) can reach wastewater treatment plants (WWTPs) from urban or agricultural runoff or drainage, atmospheric deposition or industrial discharges [11,12]. Lindane (LIN) is one of

the most common organochlorine pesticides found in WWTPs, with concentrations up to $0.23 \mu\text{g L}^{-1}$ [13–15]. Therefore, studies were developed to improve its reduction down to legal limits ($0.1 \mu\text{g L}^{-1}$, according to European Union regulations for drinking water) [16]. Conventional activated sludge has proven incomplete in the reduction of toxic loads [17,18]. Several studies present low LIN removal efficiencies (between 18% and 41%) when resorting to biological treatment with activated sludge [17,19–21] or even no removal at all [22]. On the other hand, Kipopoulou *et al.* [23] reported 67% to 91% of LIN removal in the whole WWTP process, but only 0.1% to 2.8% were concentrated in the activated sludge. Heptachlor (HEP) is also found in WWTPs, [11,12] in some cases in similar levels to LIN. The behaviour of HEP is somewhat different from LIN, since the percentage of elimination of the former provided by biodegradation with activated sludge ranges from 48% to 90% [11,17,20].

Biological processes are, however, necessary to remove the organic matter associated with contaminated waters (around 80%), in order to lower the competition in the subsequent treatment stages. The most popular tertiary treatments include adsorption and oxidation processes [24–27]. Concerning the former, the activated

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carbon is the most common adsorbent [28] due to its high superficial area and other advantageous characteristics, and is usually employed in powdered (PAC) or granular (GAC) form [29–31]. GAC adsorbs organochlorine pesticides with high efficiency, LIN and HEP included – 97% and 78%, respectively [32]. The major drawback is the frequent need for an expensive regeneration process. The latter use ozone and/or ultraviolet treatment and have the advantage of reaching complete elimination of the refractory organic pollutants under good performance conditions [33]. The potential for removing pesticides with these methodologies by themselves or combined with other treatments have also been tested with good results [34–39]. The main disadvantage of these methods is the high costs associated with the large-scale oxidation of some contaminants [40,41].

Pine bark has been studied as a cheap alternative adsorbent for some pollutants in aqueous matrices, especially metallic compounds [42–44], but also organochlorine pesticides [45–47] or phenol [48]. Being a wood industry by-product, pine bark can be easily obtained and once it is biodegradable, its use assures an environmental-friendly and low cost process. Brás *et al.* [32] obtained an average removal efficiency of 93% for HEP, in contrast with LIN (38%), while the studies performed by Ratola *et al.* [45] showed a much better value for LIN removal (81%) and a similar result for HEP (94%). Pine bark has high affinity to hydrophobic compounds, which derives from its organic composition with only 0.5% of ashes and a highly complex structure of 39.3% of materials soluble in polar solvents and 59.7% of aromatic content [32]. Lower K_{ow} [45] and, consequently, low affinity to pine bark surface probably explains the value obtained for LIN removal in comparison with HEP.

This work studied the performance of a combined technology (activated sludge followed by pine bark adsorption) to remove LIN and HEP from contaminated waters, taking advantage of the excellent properties of pine bark to adsorb organochlorines and of the reduction of the water's organic content granted by a preliminary treatment step.

Materials and methods

Reagents

LIN, purity 99% and HEP, purity 99% were obtained from PolySciences (Eppelheim, Germany).

Pine bark preparation

Samples were by-products from a wood factory at S. João da Madeira, in the north of Portugal. A Retsch KG mill (Haan, Germany) and Endecotts sieves (London, UK) were used for grinding and separating,

followed by drying in a WTB F53 oven from Binder (Tuttlingen, Germany). Preparation was as described by Brás *et al.* [32]

SPME extraction for pesticides analysis

The SPME assembly with a 100 μm PDMS fibre was obtained from Supelco (Bellafonte, PA, USA). Pesticides were extracted, either from standards (vials half-filled with pure water and spiked with a known amount of pesticide) or samples, prior to chromatographic analysis. 15 mL vials were half-filled with solution for extraction. The 100 μm PDMS fibre was then inserted in the vial headspace for 30 minutes (extraction time). Temperature was carefully controlled and maintained at 40°C. Stirring was kept constant.

Chromatographic analysis

The chromatograph was an HP5890 from Hewlett-Packard (Palo Alto, CA, USA) equipped with an Electron Capture Detector (ECD) and the data were recorded by Chromatography Data Station for Windows (CSW 1.7) software (DataApex, Prague, Czech Republic). Chromatographic separation was performed in a J&W Scientific (Folsom, CA, USA) DB-1701 capillary column (30 m \times 0.32 mm i.d. \times 0.25 μm film). Both carrier and make-up gas were argon/methane (95/5) at 2.80 and 50 mL min^{-1} , respectively. Pesticides were desorbed from the fibre in the injector port for 3 min. Injector and detector temperatures were 250 and 300°C, respectively, supplied by Air Liquide (Maia, Portugal). The initial oven temperature was kept at 80°C for 1 min and then sequentially raised to 210°C at 35°C min^{-1} , held for 4 min; raised to 215°C at 5°C min^{-1} , held for 1 min; raised to 270°C at 55°C min^{-1} and finally held for 1 min, to complete a 12.7 min run.

Pesticides quantification and recovery assays

LIN and HEP were quantified by external standard method. Calibration curves were constructed with standards extracted in the same conditions as the samples. Recovery assays were performed as follows: First, a 15-mL vial was half-filled with pure water and SPME extraction levels quantified. Then, the same procedure was used with a pesticide solution of 1 $\mu\text{g L}^{-1}$ instead of pure water. Finally, a third vial was half-filled with same amount of pure water and 1 $\mu\text{g L}^{-1}$ pesticide solution and the extraction results evaluated in terms of recovery.

Other analysis

The COD analysis employed a 45600 reactor from Hach Company (Loveland, CO, USA). Optical density

was measured with an UV/Visible PU 8620 Series spectrophotometer from Philips (Amsterdam, The Netherlands) at 610 nm. COD, Total Suspended Solids (TSS), Optical Density and Colour were measured according to Standard Methods for the Examination of Water and Wastewater [48].

Inoculum preparation

One litre of raw water was added to 100 g of non-sterile earth collected from a local garden. The inoculum was gathered after 30 min of sedimentation from the resulting suspension, and preserved in aerobic conditions between collecting and utilization.

Water treatment system

The apparatus was custom built (Figure 1), based on the OECD legislation on biodegradation of non-volatile soluble organic compounds in water [49]. The assembly included an aerobic tank with a mixture volume of 3 L, a clarification tank (~ 3-litre volume) and an adsorption column (3.99 cm i.d. and 70.0 cm height). Tanks were made in Perspex, the column in glass and tubing was Tygon R3603 from Saint-Gobain (Courbevoie, France).

The system was fed with synthetic water with the following composition, per litre of raw water: 160 mg of peptone, 110 mg of meat extract, 30 mg of urea ($\text{CO}(\text{NH}_2)_2$), 7 mg of NaCl, 4 mg of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 2 mg of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 28 mg of K_2HPO_4 . First, the aerobic tank and the clarification one were filled with ~ 6 L of synthetic water. Then, 3 mL of inoculum were added to the aerobic tank and an air admission system

(compressed air pump), capable of recirculating the sludge from the clarification tank into the aerobic tank, was switched on. This activated sludge system functioned continuously in closed circuit for 7 days to achieve satisfactory cellular growth. The system was then changed to open circuit (start-up phase), with a daily feed of the synthetic water. A few days after the stabilization of the biological treatment, $1 \mu\text{g L}^{-1}$ of each pesticide was added to this synthetic water. At the same time, the adsorption column, filled with 100 g of pine bark with particle sizes between 125 and 300 μm , was included in the system (at the end of the biological step).

Water treatment system control

The COD of the synthetic water entering the biological process was determined for a few days at the beginning of the experimental work and twice a day (for about two months) for the effluents leaving this and the adsorption processes. The TSS and colour levels were evaluated for the effluent treated by the column, three times a day, during the first five days. The optical density of the biomass inside the aerobic tank was evaluated throughout the entire experimental period. LIN and HEP analysis were performed for about two and a half months with frequency ranging from three samples to one sample a day, respectively at the beginning and at the end of the experiment. Samples were either from the feed synthetic solution or from the effluents of the biological and adsorption processes.

Results and discussion

Although belonging to the same pesticides family (the organochlorines) LIN and HEP were chosen because they have different physical-chemical properties (Table 1) that may help to extrapolate some conclusions of this work to similar compounds in the future. For example, HEP is likely to be more hydrophobic than LIN, whose smaller size may explain its higher solubility in water.

The start-up phase of the water treatment system enabled the evaluation of the organic contents removal in the biological stage, after stabilization without pesticides addition. The subsequent experiment (with pesticides in the feed synthetic water) allowed the study of the COD removal efficiency in both stages (biological and adsorption), as well as pesticides interference in COD removal efficiency. The final step of the experimental work consisted in a gradual increase of the pesticides concentration, in order to evaluate the toxicity limits for the activated sludge bed. When dealing with trace analytes it is essential to know the validation parameters of the analytical methodology, in order to distinguish the uncertainty of the results from a

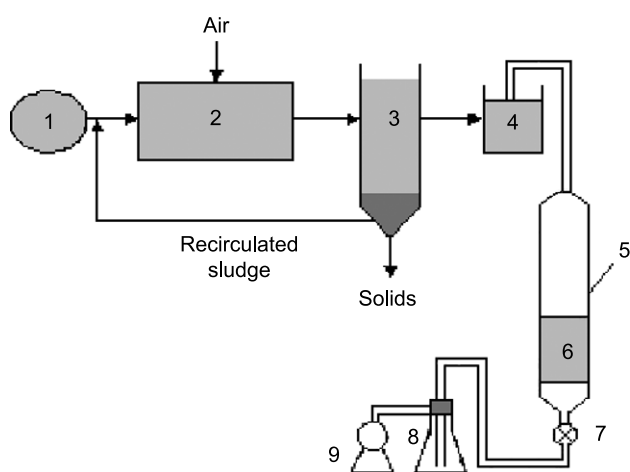
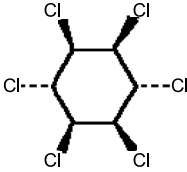
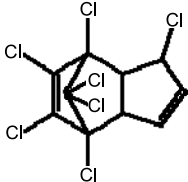


Figure 1. Custom-built apparatus (activated sludge treatment plus pine bark adsorption) used in the experimental work (1 – Peristaltic pump; 2 – Aerobic tank; 3 – Clarification tank; 4 – Flow equalisation tank; 5 – Pine bark column; 6 – Pine bark; 7 – Flow control valve; 8 – Treated effluent; 9 – Vacuum pump).

Table 1. Physical properties and structural formulas of the studied pesticides.

	LIN	HEP
IUPAC Name	1,2,3,4,5,6-hexachlorocyclohexane	1,4,5,6,7,8,8-heptachlor-3a,4,7,7a-tetrahydro-4,7-methanoindene
Molecular Formula	C ₆ H ₆ Cl ₆	C ₁₀ H ₅ Cl ₇
Molecular Weight (g mol⁻¹)	290.8	373.3
Melting Point	112.5–113.5°C	95–96°C (pure)
Water Solubility	7.3 mg L ⁻¹ (25°C) 12.0 mg L ⁻¹ (35°C)	0.056 mg L ⁻¹ (25–29°C)
log K_{ow} (Octanol-Water Partition Coefficient)	3.17	4.85
Structural Formula		

significant decrease/increase in concentration after a treatment procedure.

Validation parameters of the analytical method

Calibration curves were obtained with five standards for LIN (from 0.01 to 1.00 µg L⁻¹) and six standards for HEP (from 0.26 to 3.00 µg L⁻¹). The limits of detection (LODs) were calculated according to Miller and Miller [50]. While LOD for LIN (0.01 µg L⁻¹) was clearly under the limit imposed by legislation for drinking waters, a similar detection limit for HEP could not be achieved with this analytical technique (0.26 µg L⁻¹). Nevertheless, it was considered adequate to this experiment, because it is still lower than the reference limits applied to organochlorines in effluents from water treatment systems (~ 1 µg L⁻¹). Precision of the chromatographic analysis was evaluated by the standard deviation of 5 replicate extractions of a 0.3 µg L⁻¹ standard solution. LIN and HEP presented an average coefficient of variation of 5.74% and 12.78%, respectively. Accuracy was evaluated by recovery assays (6 for LIN and 5 for HEP) with pesticide-spiked solutions of 1 µg L⁻¹ each. Average recoveries were 97.30% and 83.40% for LIN and HEP respectively. The average global uncertainties associated to LIN and HEP concentrations, according to EURACHEM/CITAC Guide [51], are 12.3% and 36.6%, respectively.

Start-up phase

COD removal efficiency of the activated sludge system after stabilization was evaluated from the COD values of the synthetic solution before and after treatment, for 12 days. The average removal efficiency was 70.8%,

after an initial phase of stabilization of about 44 hours (Figure 2), which is comparable to other values found in literature [13,20].

Results obtained after pesticide addition

One µg L⁻¹ of LIN and HEP each were added to the synthetic water fed to the biological treatment. Average COD of the synthetic water was 563.1 mg O₂ L⁻¹. Simultaneously, the pine bark packed adsorption column was connected downstream of the biological treatment.

COD values were evaluated at the end of the biological (Figure 3) and adsorption (Figure 4) processes, as well as for the solution entering the system. Results show an average COD level after biological treatment of 105.4 mg O₂ L⁻¹, resulting in a removal efficiency of 81.3% in the activated sludge system, which supports the fact that the addition of pesticides does not inhibit biological treatment. Given the fact that COD levels at the end of the biological process are close to those found at the end of the adsorption process (COD of 98.7 mg O₂ L⁻¹), it can be concluded that pine bark does not contribute to an increase of the organic content of the effluent, after stabilization, which favours its use.

Colour (in Abs) and TSS values were measured at the end of the adsorption stage (Figure 5). It was concluded that the first 3–4 litres of solution through the column presented high colour levels due to the organic compounds released by pine bark. Tree barks have a complex chemical structure mainly composed by lignin, polyphenols (tannins), extractives, carbohydrates and ashes, with varying compositions according to the species [52]. Fradinho *et al.* [53] reported that the weight percentages for *Pinus pinaster* bark are lignin

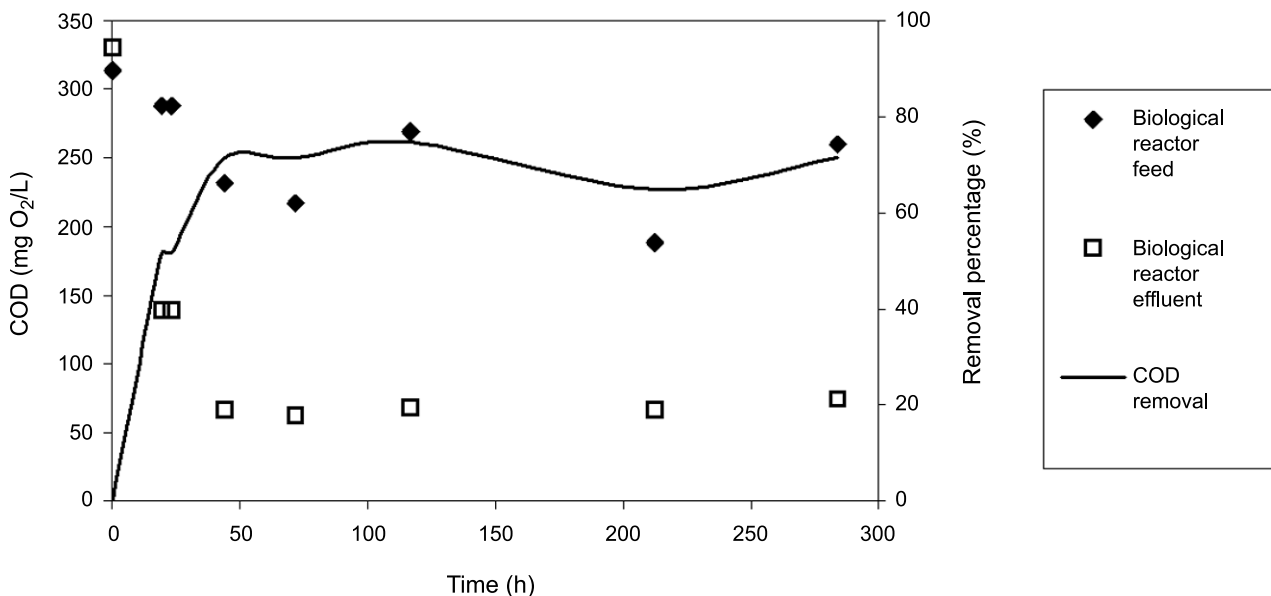


Figure 2. COD evolution, in feed solution and biological reactor effluent, in start-up phase.

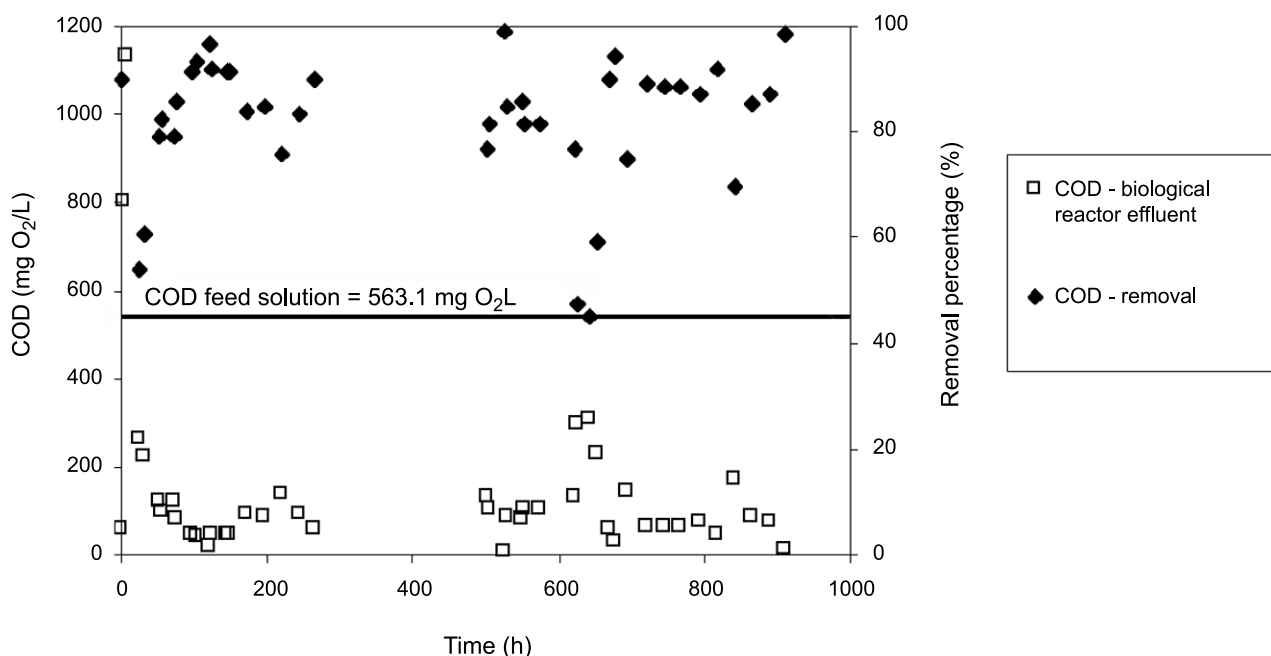


Figure 3. COD evolution in biological system after pesticides addition.

33%, polyphenols 11%, polysaccharides 39%, extractives 17% and less than 1% ashes. When the contaminated solution first reaches the bark, some of the polyphenolic contents probably leach from the matrix and induce an initially high colour incidence in the solution. In a subsequent phase, when the most of this leaching was completed, those levels lowered and stabilized. Pine bark was also not responsible for the occurrence of high TSS contents.

The optical density of the biomass in the aerobic tank of the activated sludge system has been studied to qualitatively control the viability of the microorganisms. Figure 6 refers to two different phases: start-up (~ 450 hours) and pesticides addition. After start-up, where an irregular pattern of optical density is observed, there is an increase, even with the pesticides addition, meaning that the biological system is not completely adjusted to such addition.

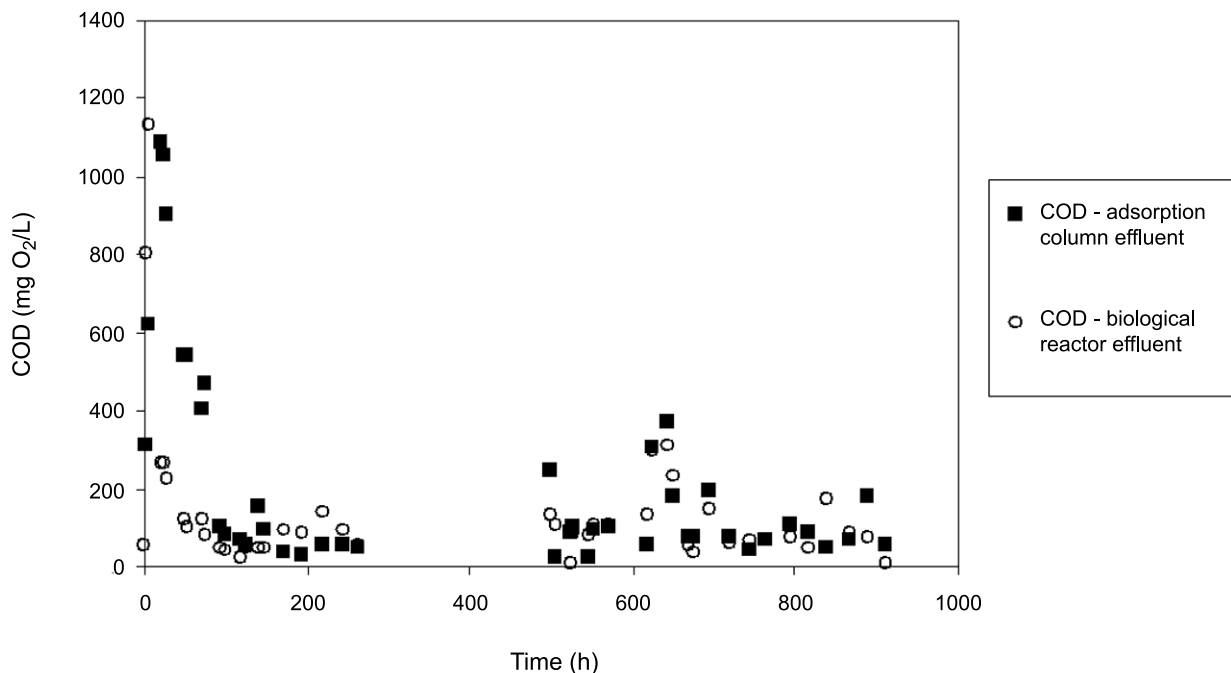


Figure 4. COD evolution in pine bark column after pesticides addition.

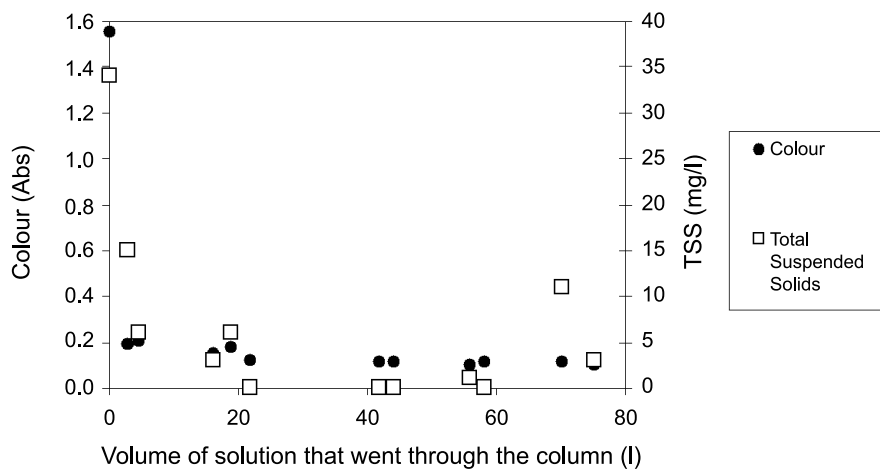


Figure 5. Colour (in Abs) and TSS (in mg L^{-1}) levels in the adsorption process effluent.

LIN and HEP removal efficiencies were evaluated. Figure 7 and Figure 9 depict LIN and HEP concentrations obtained at the end of each treatment. LIN concentration at the end of the biological treatment stabilizes around $0.97 \mu\text{g L}^{-1}$. This represents a removal efficiency of 15.7%, relative to the entering average of $1.15 \mu\text{g L}^{-1}$. In spite of the evident stabilization of the final LIN levels, some oscillation occurs around the value of $0.97 \mu\text{g L}^{-1}$, which is normally acceptable when dealing with living organisms.

LIN concentrations in the effluent from pine bark column are significantly low at the beginning of the

operation, with an average of $0.27 \mu\text{g L}^{-1}$, until ~ 800 L of the solution leaving the biological reactor has passed through (Figure 7). A gradual increase is then noticeable, which might probably mark the beginning of the column saturation. Although saturation could not be proved with these experiments, assuming that final LIN concentrations obtained are close to the saturation capability of pine bark, it is estimated that the maximum adsorption capacity rounds up to $5.6 \mu\text{g}$ of LIN per gram of pine bark. This result is an underestimation, since HEP is competing for the adsorption sites of the adsorbent.

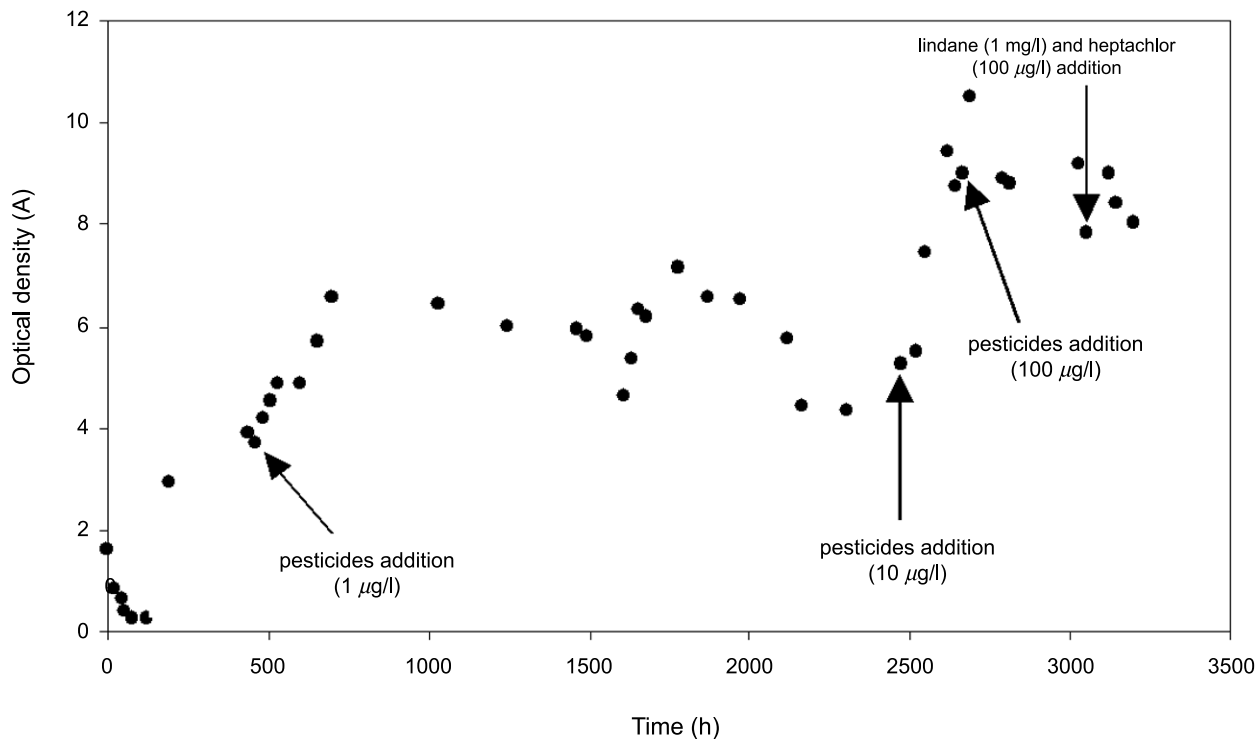


Figure 6. Cellular growth in the biological reactor.

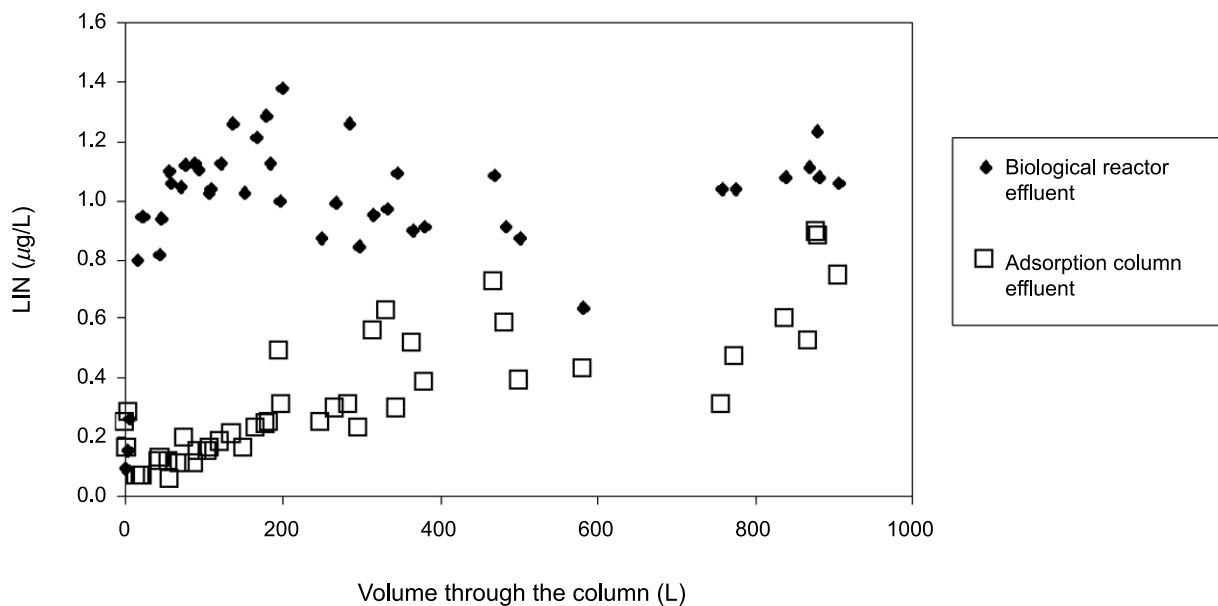


Figure 7. LIN concentration in biological system and pine bark (100 g) column.

LIN removal efficiencies are represented in Figure 8. Up to an effluent volume of 800 L, the average removal efficiency for LIN is 72.2%. This represents a significantly better value than the obtained by Brás *et al.* [32]

(38%), but of the same order than the one described by Ratola *et al.* [45] (81%). The overall efficiency of the system for LIN elimination is 76.6%, which is higher than that described for biological processes alone, 18%

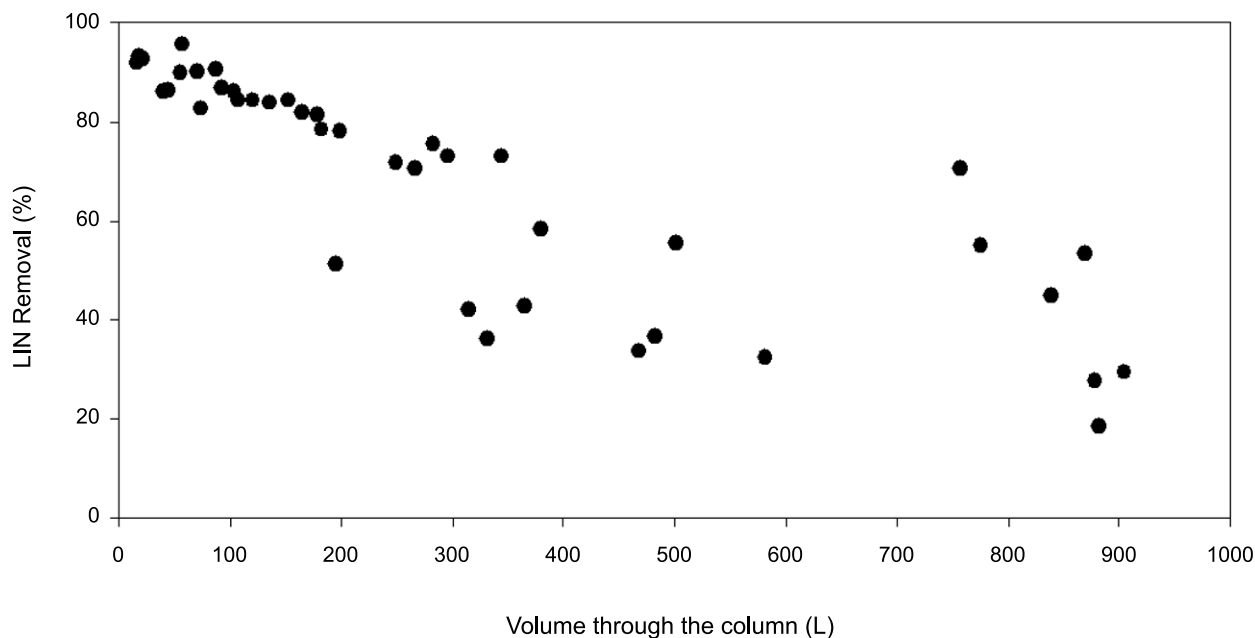


Figure 8. LIN removal efficiency in pine bark (100 g) column.

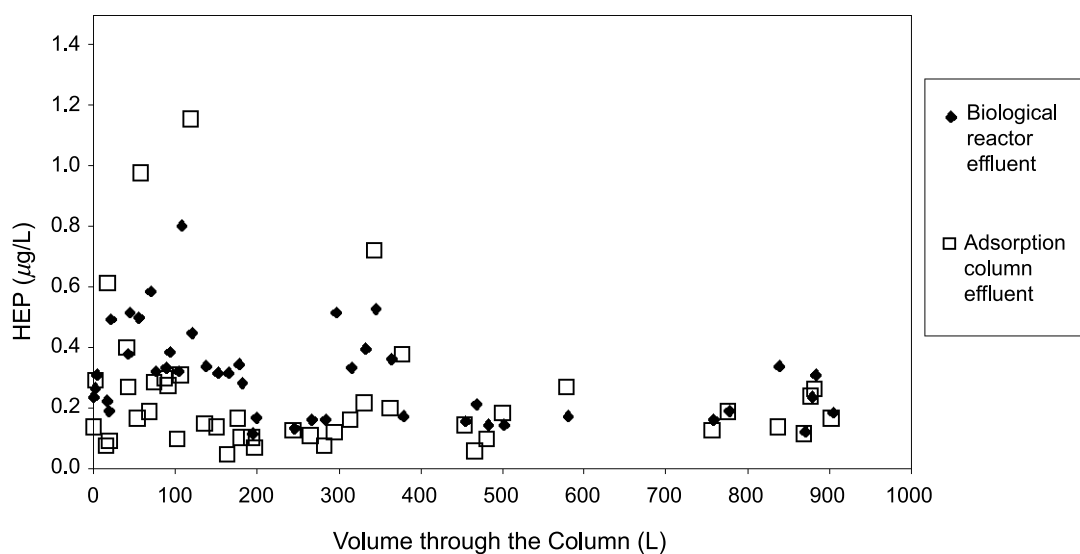


Figure 9. HEP concentration in biological system and pine bark (100 g) column.

to 41% [22] but still lower than the 97% obtained with activated carbon. Nevertheless, pine bark should be considered as an alternative, due to its low cost.

The high variation obtained for HEP concentration values in the collected samples at the end of the biological process may be a result of either the uncertainty of the result associated to the analytical method ($\sim 36.6\%$) or the fact that some results are lower than the detection limit ($0.26 \mu\text{g L}^{-1}$). Despite this, HEP concentrations were measured whenever the chromatographic

signal-to-noise ratio made the calculation possible (Figure 9).

Average HEP removal efficiency in the biological system was 77.7%, using the average value of $0.42 \mu\text{g L}^{-1}$ for the HEP concentration at the outlet of the biological reactor and $1.88 \mu\text{g L}^{-1}$ as the inlet concentration. It is difficult to define the accurate average removal efficiency for HEP in the pine bark column, because some of the inlet concentration values were below the detection limit for the analytical method. Even so, Figure 10

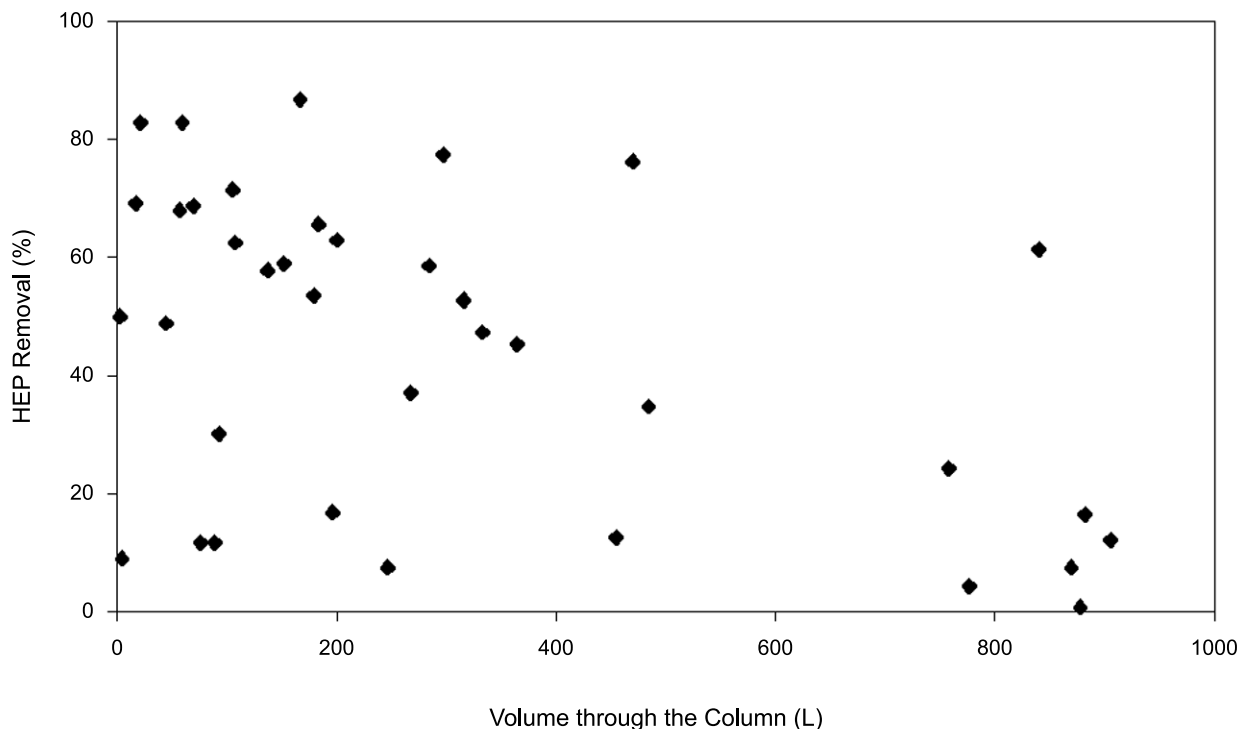


Figure 10. HEP removal evolution in pine bark (100 g) column.

shows that HEP is still removed in the column, which agrees with previous results [32,45]. In contrast to the observation for LIN, no saturation seems to occur.

As to LIN, pine bark column behaviour in the presence of higher concentrations of HEP should be studied in the future, as well as the sorption model, in order to accurately define the saturation limits of the adsorbent.

Pesticides adsorption to biomass

The knowledge of the dominant mechanism of pesticides elimination in the biological treatment (adsorption or degradation) is a very important issue due to the need for correct disposal of the formed sludge if these compounds were adsorbed on the surface of biomass particles. Some preliminary experiments were performed, aiming the detection of pesticides in the biomass. No significant conclusion could be reached (due to the difficulty to accurately quantify the analytes), except for the fact that both pesticides were detected in the biomass. This issue should be carefully investigated in future work.

Tolerance limits of pesticides in the biological bed

The limiting concentration above which pesticides become toxic for the microorganisms was controlled through the addition of increasing levels of those

compounds to the biological reactor. No sign of decreasing COD removal percentage was detected and the optical density slightly increased (Figure 6), until LIN and HEP levels attained 1 mg L^{-1} and 0.1 mg L^{-1} , respectively, in the feed synthetic solution. Nevertheless, it should be stressed that the solubilities of LIN and HEP in water are 7.3 mg L^{-1} and $56 \text{ } \mu\text{g L}^{-1}$, respectively. COD removal ranged from 70.9% to 76.8%, whereas average COD removal with $1 \text{ } \mu\text{g L}^{-1}$ of pesticide addition was 81.3%.

Conclusions

This study reinforces the utility of pine bark in water treatment plants as an alternative to activated carbon columns, for the organochlorine pesticides lindane and heptachlor. Employing an experimental set-up comprised by a biological activated sludge treatment followed by adsorption in a pine bark-filled column, overall removal for LIN was 76.6% and above 77.7% for HEP. Limits of detection for LIN and HEP analysis were above $0.01 \text{ } \mu\text{g L}^{-1}$ and $0.26 \text{ } \mu\text{g L}^{-1}$, respectively. The global uncertainty associated to the analytical method (SPME prior to GC-ECD quantification) was 12.3% for LIN and 36.6% for HEP. Although activated carbon can reach higher removal percentages, pine bark has the advantage of being an abundant natural by-product material with no need for complicated activation and

regeneration processes and, consequently, much lower operating costs. In addition, and in spite of its composition, pine bark does not contribute to the increase of the organic content of the effluent.

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References

- [1] S. Chen, L. Shi, Z. Shan, and Q. Hu, *Determination of organochlorine pesticide residues in rice and human and fish fat by simplified two-dimensional gas chromatography*, *Food Chem.* 104 (2007), pp. 1315–1319.
- [2] T.M. Younos and D.L. Weigmann, *Pesticides: A continuing dilemma*, *J. Wat. Pollut. Control Fed.* 60 (1988), pp. 1199–1205.
- [3] P. Kaushik and G. Kaushik, *An assessment of structure and toxicity correlation in organochlorine pesticides*, *J. Hazard. Mater.* 143 (2007), pp. 102–111.
- [4] M. Roychowdhury, *Reproductive hazards in the work environment*, *Prof. Saf.* 35 (1990), pp. 17–22.
- [5] P. Baird, *Pesticides*, *Restaurant Business*, 90 (1991), p. 115.
- [6] M.S. El-Shahawi, A. Hamza, A.S. Bashammakh, and W.T. Al-Saggaf, *An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants*, *Talanta*, 80 (2010), pp. 1587–1597.
- [7] S. Villa, A. Finizio, R. Diaz Diaz, and N. Vighi, *Distribution of organochlorine pesticides in pine needles of an oceanic island: the case of Tenerife (Canary Islands, Spain)*, *Wat. Air Soil Pollut.* 146 (2003), pp. 335–349.
- [8] K. Kumar, K. Watanabe, H. Takemori, N. Iseki, S. Masunaga, and T. Takasaga, *Analysis of UNEP priority POPs using HRGC-HRMS and their contamination profiles in livers and eggs of great cormorants (Phalacrocorax carbo) from Japan*, *Arch. Environ. Contam. Toxicol.* 48 (2005), pp. 538–551.
- [9] N. Sankaramakrishnan, A.K. Sharma, and R. Sanghi, *Organochlorine and organophosphorous pesticide residues in ground water and surface waters of Kanpur, Uttar Pradesh, India*, *Environ. Int.* 31 (2005), pp. 113–120.
- [10] R.J. Gilliom, *Pesticides in U.S. streams and groundwater*, *Env. Sci. Technol.* 41 (2007), pp. 3408–3414.
- [11] A. Katsoyiannis and C. Samara, *Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: fate and mass balance*, *Environ. Res.* 97 (2005), pp. 245–257.
- [12] D. Fatta, St. Canna-Michaelidou, C. Michael, E. Demetriou Georgiou, M. Christodoulidou, A. Achilleos, and M. Vásquez, *Organochlorine and organophosphoric insecticides, herbicides and heavy metals residue in industrial wastewaters in Cyprus*, *J. Hazard. Mater.* 145 (2007), pp. 169–179.
- [13] W.J. Weber Jr., N.H. Corfis, and B.E. Jones, *Removal of priority pollutants in integrated activated sludge – activated carbon treatment systems*, *J. Wat. Pollut. Control Fed.* 55 (1983), pp. 369–376.
- [14] A.I. Stubin, T.M. Brosnan, K.D. Porter, L. Jiménez, and H. Lochan, *Organic priority pollutants in New York city municipal wastewaters: 1989–1993*, *Water Environ. Res.* 68 (1996), pp. 1037–1044.
- [15] A. Katsoyiannis and C. Samara, *Comparison of active and passive sampling for the determination of persistent organic pollutants (POPs) in sewage treatment plants*, *Chemosphere* 67 (2007), pp. 1375–1382.
- [16] EU Council Directive 80/778/EEC of 15 July 1980 relating to the quality of water intended for human consumption as amended by Council Directives 81/858/EEC and 91/692/EEC (further amended by Council Regulation 1882/2003/EC), *Off. J. European Communities* 1980, L. 229, 11.
- [17] A.C. Petrasek, I.J. Kugelman, B.M. Austern, T.A. Pressley, L.A. Winslow, and R.H. Wise, *Fate of toxic compounds in wastewater treatment plants*, *J. Wat. Pollut. Control Fed.* 55 (1983), pp. 1286–1296.
- [18] K.L. Willett, E.M. Ulrich, and R.A. Hites, *Differential toxicity and environmental fates of hexachlorocyclohexane isomers*, *Environ. Sci. Technol.* 32 (1998), pp. 2197–2207.
- [19] A. Van Luin and W. Starckenburg, *Hazardous substances in wastewater*, *Wat. Sci. Technol.* 17 (1984), pp. 843–853.
- [20] S.A. Hannah, B.M. Austern, A.E. Eralp, and R.H. Wise, *Comparative removal of toxic pollutants by six wastewater treatment processes*, *J. Wat. Pollut. Control Fed.* 58 (1986), pp. 27–34.
- [21] N. Nyholm, B.N. Jacobsen, B.M. Pedersen, O. Poulsen, A. Damborg, and B. Schultz, *Removal of organic micro pollutants at ppb levels in laboratory activated sludge reactors under various operation conditions: biodegradation*, *Wat. Res.* 26 (1992), pp. 339–353.
- [22] W.J. Weber Jr., B.E. Jones, and L.E. Katz, *Fate of toxic organic compounds in activated sludge and integrated PAC systems*, *Wat. Sci. Technol.* 19 (1987), pp. 471–482.
- [23] A.M. Kipopoulou, A. Zouboulis, C. Samara, and Th. Kouimtzi, *The fate of lindane in the conventional activated sludge treatment process*, *Chemosphere* 55 (2004), pp. 81–91.
- [24] P.R. Gogate and A.B. Pandit, *A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions*, *Adv. Environ. Res.* 8 (2004), pp. 501–551.
- [25] U. Goren, A. Aharoni, M. Kummel, R. Messalem, I. Mukmenev, A. Brenner, and V. Gitis, *Role of membrane pore size in tertiary flocculation/adsorption/ultrafiltration treatment of municipal wastewater*, *Sep. Purif. Technol.* 61 (2008), pp. 193–203.
- [26] A.H. Joss, H. Siegrist, and T.A. Ternes, *Are we about to upgrade wastewater treatment for removing organic micropollutants?* *Wat. Sci. Technol.* 57 (2008), pp. 251–255.
- [27] K.Y. Foo and B.H. Hameed, *Detoxification of pesticide waste via activated carbon adsorption process*, *J. Hazard. Mater.* 175 (2010), pp. 1–11.
- [28] J. Qu, *Research progress of novel adsorption processes in water purification: A review*, *J. Environ. Sci.* 20 (2008), pp. 1–13.
- [29] J.L. Sotelo, G. Ovejero, J.A. Delgado, and I. Martínez, *Comparison of adsorption equilibrium and kinetics of four chlorinated organics from water onto GAC*, *Wat. Res.* 36 (2002), pp. 599–608.
- [30] D. Abdessemed and G. Nezzal, *Tertiary treatment of a secondary effluent by the coupling of coagulation-adsorption-ultrafiltration for reuse*, *Desalination* 175 (2005), pp. 135–141.

- [31] C. Faur, H. Métivier-Pignon, and P. Le Cloirec, *Multicomponent adsorption of pesticides onto activated carbon fibres*, *Adsorption* 11 (2005), pp. 479–490.
- [32] I.P. Brás, L. Santos, and A. Alves, *Organochlorine pesticides removal by Pinus bark sorption*, *Environ. Sci. Technol.* 33 (1999), pp. 631–634.
- [33] D.R. Medley and E.L. Stover, *Effects of ozone on the biodegradability of biorefractory pollutants*, *J. Wat. Pollut. Control Fed.* 55 (1983), pp. 489–493.
- [34] M.S. Lai, J.N. Jensen, and A.S. Weber, *Oxidation of simazine: Ozone, ultraviolet, and combined ozone/ultraviolet oxidation*, *Wat. Environ. Res.* 67 (1985a), pp. 340–346.
- [35] M.S. Lai, J.N. Jensen, and A.S. Weber, *Oxidation of simazine: Biological oxidation of simazine and its chemical oxidation by-products*, *Wat. Environ. Res.* 67 (1985b), pp. 347–354.
- [36] M.P. Ormad, N. Miguel, A. Claver, J.M. Matesanz, and J.L. Ovelleiro, *Pesticides removal in the process of drinking water production*, *Chemosphere* 71 (2008), pp. 97–106.
- [37] N. García-Flor, R. Alzaga, L. Ortiz, J.M. Bayona, and J. Albaigés, *Determination of organochlorine compounds in neuston from the Mediterranean*, *Environ. Technol.* 29 (2008), pp. 1275–1283.
- [38] D. Kassinos, N. Varnava, C. Michael, and P. Piera, *Homogeneous oxidation of aqueous solutions of atrazine and fenitrothion through dark and photo-Fenton reactions*, *Chemosphere* 74 (2009), pp. 866–872.
- [39] A. Zapata, I. Oller, C. Sirtori, A. Rodríguez, J.A. Sánchez-Pérez, A. López, M. Mezcuca, and S. Malato, *Decontamination of industrial wastewater containing pesticides by combining large-scale homogeneous solar photocatalysis and biological treatment*, *Chem. Eng. J.* 160, (2010), pp. 447–456.
- [40] A.S. Stasinakis, *Use of selected advanced oxidation processes (AOPs) for wastewater treatment – a mini review*, *Global NEST J.* 10 (2008), pp. 376–385.
- [41] W. Li, Q. Zhou, and T. Hua, *Removal of organic matter from landfill leachate by advanced oxidation processes: A review*, *Int. J. Chem. Eng.* 2010 (2010), pp. 1–10.
- [42] S. Al-Asheh and Z. Duvnjak, *Sorption of cadmium and other heavy metals by pine bark*, *J. Hazard. Mater.* 56 (1997), pp. 35–51.
- [43] J. Hanzlík, J. Jehlička, O. Šebek, Z. Weishauptová, and V. Machovič, *Multi-component adsorption of Ag(I), Cd(II) and Cu(II) by natural carbonaceous materials*, *Wat. Res.* 38 (2004), pp. 2178–2184.
- [44] A. Gundogdu, D. Ozdes, C. Duran, V.N. Bulut, M. Soylak, and H.B. Senturk, *Biosorption of Pb(II) ions from aqueous solution by pine bark (Pinus brutia Ten.)*, *Chem. Eng. J.* 153 (2009), pp. 62–69.
- [45] N. Ratola, C. Botelho, and A. Alves, *The use of pine bark as a natural adsorbent for persistent organic pollutants – study of lindane and heptachlor adsorption*, *J. Chem. Technol. Biotechnol.* 78 (2003), pp. 347–351.
- [46] I. Brás, L. Lemos, A. Alves, and M.F.R. Pereira, *Sorption of pentachlorophenol on pine bark*, *Chemosphere* 60 (2005), pp. 1095–1102.
- [47] G. Vázquez, R. Alonso, S. Freire, J. González-Álvarez, and G. Antorrena, *Uptake of phenol from aqueous solutions by adsorption in a Pinus pinaster bark packed bed*, *J. Hazard. Mater.* B133 (2006), pp. 61–67.
- [48] *Standard Methods for the Examination of Water and Wastewater*. M.A.H. Franson (ed.), 18th ed., American Public Health Association Publishers, Washington DC, 1992.
- [49] Norme OCDE 303A. *Simulation Assay – Aerobic Treatment of Used Waters: Assay of Coupled Units (Essai de Simulation – Traitement Aérobic des Eaux Usées: Essai d’Unités Couplées)*, 1981.
- [50] J.C. Miller and J.N. Miller, *Statistics for Analytical Chemistry*. R.A. Chalmers and M. Masson (eds.), 2nd ed., Ellis Harwood Publishers, Chichester, UK, 1988, pp. 101–125.
- [51] EURACHEM/CITAC Guide. *Quantifying Uncertainty in Analytical Measurement*. S.L.R. Ellison, M. Rosslein, and A. Williams (eds.), 2nd ed., Teddington, UK, 2000.
- [52] I. Brás, L.T. Lemos, A. Alves, and M.F.R. Pereira, *Application of pine bark as a sorbent for organic pollutants in effluents*, *Manage. Environ. Qual.* 15 (2004), pp. 491–501.
- [53] D.M. Fradinho, C.P. Neto, D. Evtuguin, F.C. Jorge, M.A. Irle, M.H. Gil, and J.P. Jesus, *Chemical characterisation of bark and alkaline bark extracts from maritime pine grown in Portugal*, *Ind. Crop. Prod.* 16 (2002), pp. 23–32.