

Screening of Solid Waste as Filler Material for Constructed Wetlands

Dina M R Mateus¹ and Henrique J O Pinho²

¹ Technology, Restoration and Arts Enhancement Center (Techn&Art), Instituto Politécnico de Tomar, Portugal

² Smart Cities Research Center (Ci2), Instituto Politécnico de Tomar, Portugal

E-mail: hpinho@ipt.pt

Abstract. The reuse of solid waste can contribute to reducing Earth's resource depletion, directly through use in the original production processes or by valorisation in alternative applications. In the present work, ten solid wastes were evaluated as candidates for filling material in constructed wetlands (CWs). For that purpose, physical characterization, leaching and adsorption tests were conducted. Limestone fragments and brick fragments resulting from construction activities, coal slags resulting from power plants, snail shells resulting from the food and catering industry, and cork granulates resulting from the cork industry have potential for use as CW fillers. These five materials have adequate physical properties and some capacity to adsorb phosphorous and organic compounds from wastewater. On the other hand, crushed eggshells resulting from egg farms, dealcoholized grape pomaces resulting from alcohol distilleries, olive seeds waste from olive-oil mills, and pine bark fragments and wood pellets resulting from forestry cleaning activities, wood mills and pulp mills did not demonstrate sufficient potential to be used as CW fillers, either because they have very low adsorption capacities or leach compounds in contact with water, or because they have less adequate physical properties. None of the tested solid wastes showed the ability to adsorb nitrogen compounds. Although the five selected materials do not present a special capability for adsorption of nitrogen, phosphorous and organic compounds, they can all be valued as CW fillers, representing a way to reduce the amount of solid waste sent to landfills.

1. Introduction

The objectives and strategies underlying the Sustainable Development paradigm are receiving increasing attention from the global community as a way to overcome the continuous increase in world population and the consequent pressure on available resources [1]. The concept of circular economy represents a vast set of possible actions that can contribute to sustainable development [2] [3]. One of the ways to implement the concept of circular economy is the reuse of waste in the same industrial or urban processes where they were originated, or in other processes in which they can be valued as raw materials or for energy conversion [4] [5]. In particular cases, waste can be used to treat waste, as for example in drinking water or wastewater treatment applications [6] [7].

Constructed wetlands (CWs) are an example of eco-efficient wastewater treatment technology and can be an application of the waste to treat waste concept [8]. Water purification processes by CWs are based on the assimilation of pollutants by macrophyte plants and the microbiological community, which contribute mainly to the assimilation of organic compounds [9]. In sub-surface flow CWs, the water under treatment flows through a porous filler material, for example sand. In this type of CW, the filler material serves as a support for plant growth and microbial community development. The filler materials, themselves, can contribute to the removal of water pollutants by physical and chemical



processes such as filtration, adsorption and precipitation [10]. The use of solid waste as filler materials can improve CW sustainability and represent a way to reduce landfill disposal of such materials.

The use of waste materials as CW fillers has already been studied by several researchers, namely for sorption of phosphorous [11]. This work focuses on solid waste generated locally to wastewater treatment facilities, to avoid transport costs, and to be used without any previous treatments, which may improve the sorption potential but require extra energy and material resources. Moreover, the present study is the first step to evaluate the future use of mixtures of these materials as CW fillers, combining their different sorption capacities for different pollutants and minimizing the possible drawbacks of some of them as fillers.

2. Materials and Methods

2.1. Materials

Ten solid waste materials were tested: clay brick fragments are a mineral waste originated from crashed or nonconforming construction clay bricks; coal boiler slags are a mineralized alumina-silicate waste resulting from coal power plants; cork granulates are a lignocellulosic waste resulting from cork processing industries; crushed eggshells are a mineral waste resulting from egg farms; dealcoholized grape pomaces are a lignocellulosic waste material resulting from wine alcohol distilleries; Moleano's rock limestone fragments are a mineral waste originated during the cutting and laying of stone tiles, slabs and similar construction elements used in buildings; olive seeds are a lignocellulosic waste from olive-oil production; pine bark fragments are a lignocellulosic waste resulting from forestry cleaning activities, wood mills and pulp mills; snail shells are a mineral waste from catering and food processing industries; wood pellets are a mechanical aggregate of waste pine wood resulting from forestry cleaning activities and wood mills.

2.2. Methods

The particle size distribution of the studied waste solids was examined using standard sieve analysis techniques and the values of d_{10} and d_{60} were determined [12]. The pycnometer method was used to evaluate the true density of the solids, according to European Standards [13]. The loose bulk density and voids were determined, also following European Standards [14].

To evaluate the possibility of nutrient leaching from the waste materials, a set of tests was carried out. All tested materials were first washed with tap water and dried at 60 °C until constant weight. About 10 g of each material was contacted with 150 ml of tap water in an Erlenmeyer flask for 40 h on an orbital shaker (agitation speed of 200 rpm). After that period, the liquid phase was separated from the solids by filtration and analysed to determine the total phosphorus (TP), total nitrogen (TN) and chemical oxygen demand (COD). pH and conductivity were also assessed.

To evaluate the adsorption potential, samples of the tested waste materials were contacted with an aqueous solution of KH_2PO_4 (ISO, pro analysis) and KNO_3 (ISO, pro analysis), to represent sources of inorganic phosphorous and nitrogen, respectively. To simulate the adsorption of organic compounds, toluene (ISO, pro analysis) was added to the solution. Toluene was chosen as a representative of organic water pollution as it is included on the BTEX group of pollutants. The solution was composed of 19.49 ± 0.81 mg/L of P, 18.68 ± 0.73 mg/L of N and 290 ± 3 mg/L of toluene. About 10 g of each solid material was contacted with 150 mL of the P-N-toluene solution in Erlenmeyer flasks for 24 h on an orbital shaker (agitation speed of 200 rpm). After that period, the liquid phase was separated from the solids by filtration and analysed to determine the total phosphorus, total nitrogen and COD content, pH and conductivity.

The materials that showed the best properties for use as constructed wetland filling were used to evaluate adsorption isotherms. To accomplish that goal, samples of the materials were contacted separately with aqueous solutions of potassium dihydrogen phosphate and aqueous solutions of toluene. About 5 g of solid samples were contacted with 75 mL of the solutions, one set of phosphate solutions of total phosphorus concentration in the range of 2 to 100 mg_P/L, and other set of toluene solutions with COD in the range of 50 to 800 mg_{O₂}/L (13.0 – 261 mg/L toluene). The Erlenmeyer flasks containing the solid samples and the aqueous solutions were incubated during 24 h in a

temperature controlled orbital shaker (agitation speed of 200 rpm and temperature of 22 °C). After that period, the liquid phase was separated from the solids by filtration and analysed to determine the TP and COD content. The adsorbed mass of solute was evaluated from a mass balance to the aqueous phase. Langmuir adsorption isotherm model (eq. 1) was fitted to the experimental data to estimate the maximum adsorption capacity of the materials (W_{\max}) for phosphorus as TP and for organic compounds as COD. The fittings were performed by non-linear regression using the IBM's SPSS software, version 25.

$$W_e = W_{\max} \frac{KC_e}{1+KC_e} \quad (1)$$

W_e in equation 1 represents the solute adsorbed on the solid (mg/g) and C_e represents the equilibrium concentration of the solute in the aqueous solution (mg/L). W_{\max} (mg/g) and K (L/mg) are the Langmuir model parameters associated to the maximum adsorption capacity and the solute affinity for the adsorbent, respectively.

TP, TN and COD analysis were performed with reagent kits from Hanna Instruments. A COD heat block (HI-839800, Hanna Instruments) was used to perform the required digestions and a photometer (HI-83399, Hanna Instruments) was used to perform the analysis. At least two replicates were performed for all assays and measurements.

3. Results

3.1. Physical Properties of the Tested Materials

Table 1 presents the physical properties obtained experimentally for the tested solid waste materials. It was not possible to use the sieve technique for the crushed eggshells and dealcoholized grape pomaces materials. Grape pomace is a very heterogeneous material composed of particles of irregular shapes. The eggshell contains remains of the egg's liquid part, which makes the material sticky. For these reasons, both materials do not freely cross the sieves.

Table 1. Physical properties of the tested solid waste.

Solid waste	Density (Mg/m ³)	Bulk density (Mg/m ³)	d ₁₀ (mm)	d ₆₀ (mm)	d ₆₀ /d ₁₀
Clay brick fragments	2.67 ± 0.03	1.069 ± 0.003	1.9	6.5	3.4
Coal slags	2.10 ± 0.05	0.880 ± 0.004	0.06	1.2	19
Cork granulates	0.15 ± 0.01	0.072 ± 0.001	2.2	3.6	1.6
Crushed eggshells	2.53 ± 0.02	NA	NA	NA	NA
Grape pomaces	1.21 ± 0.01	0.280 ± 0.003	NA	NA	NA
Limestone fragments	2.69 ± 0.01	1.309 ± 0.001	7.2	11.2	1.6
Olive seeds	0.88 ± 0.01	0.586 ± 0.001	1.2	2.8	2.3
Pine bark	0.38 ± 0.01	0.137 ± 0.003	4.8	24.2	5.1
Snail shells	2.56 ± 0.06	0.130 ± 0.001	11.2	14.8	1.3
Wood pellets	1.06 ± 0.01	0.194 ± 0.001	0.28	0.90	3.2

NA = Not available

The d_{10} and d_{60} parameters are the diameters corresponding to 10% and 60% finer in the particle size distribution, by weight, respectively. The ratio d_{60}/d_{10} is the uniformity coefficient, which should be less than 4 to prevent the risk of water flow clogging [15]. Materials with a coefficient of uniformity of more than 4 are not recommended for use in CW unless they are mixed with other materials. This is the case for the coal slags and pine bark.

3.2. Nutrient Release Experiments

Table 2 presents the results of the evaluation of nutrient release by the solid waste. It was found that, in general, the studied materials do not release significant quantities of phosphorus. Among them, inorganic materials showed the least ability to release phosphorus compounds. Snail shells and eggshell residues presented slightly higher values than other inorganic materials, a result which may be explained by the fact that they may contain remains of organic materials. The cork granulates, pine bark, wood pellets, olive seeds and grape pomaces liberate more significant quantities of phosphorus compounds, which may be explained by their organic nature.

All the materials studied release only small quantities of nitrogen compounds. Limestone and brick fragments release very small amounts. The eggshell, wood pellets and grape pomaces liberate higher amounts, but not more than 0.25 mg/g.

Concerning the potential for releasing compounds that contribute to COD, the brick fragments, limestone fragments, snail shell and cork granulate have the lowest values, less than 1 mg/g. Coal slags have a slightly higher value of 1.3 mg/g. The remaining materials present values higher than 5 mg/g. The wood pellets, olive seeds and grape pomaces showed high potential to release compounds that contribute to COD and therefore are not suitable as filling material to be used in CW for wastewater treatment.

Table 2. Potential of nutrients release from the materials upon contact with tap water.

Solid waste	TP (mg _P /g)	TN (mg _N /g)	COD (mg _{O2} /g)	pH	Conductivity (μS/cm)
Tap water	0	0	0	7.96 ± 0.30	152 ± 25
Clay brick fragments	ND	0.004 ± 0.004	0.75 ± 0.42	7.37 ± 0.42	153 ± 21
Coal slags	ND	0.021 ± 0.029	1.61 ± 0.42	7.22 ± 0.43	151 ± 50
Cork granulates	0.016 ± 0.002	0.026 ± 0.003	1.62 ± 0.74	6.95 ± 0.12	203 ± 52
Crushed eggshells	0.031 ± 0.002	0.128 ± 0.052	3.65 ± 0.44	7.55 ± 0.25	461 ± 110
Grape pomaces	0.028 ± 0.039	0.250 ± 0.054	46.1 ± 1.6	3.9 ± 0.1	3420 ± 42
Limestone fragments	ND	0.006 ± 0.001	1.00 ± 0.50	7.55 ± 0.43	113 ± 64
Olive seeds	0.027 ± 0.04	0.026 ± 0.012	11.3 ± 2.7	6.31 ± 0.15	301 ± 35
Pine bark	0.008 ± 0.003	0.076 ± 0.033	6.6 ± 2.3	4.46 ± 0.53	199 ± 12
Snail shells	0.004 ± 0.006	0.042 ± 0.034	1.27 ± 0.87	7.35 ± 0.58	187 ± 18
Wood pellets	0.008 ± 0.011	0.066 ± 0.071	25.8 ± 2.2	4.79 ± 0.04	297 ± 59

ND = Not detected

Table 2 also presents the pH and conductivity of the water, before and after contact with the tested materials. These two parameters should also be considered for the selection of materials to be used as CW fillers. It has been found that all materials tend to decrease the water pH. This reduction is not significant for most materials, particularly for inorganic materials and for the cork granulate. For the other materials, especially for grape pomaces, pine bark and wood pellets, a more significant reduction of pH was observed. The pH reduction is not usually advantageous for the proper functioning of the CW, but may be useful in the case where the CW are used to treat alkaline wastewater.

The increase in the water electrical conductivity by the contact with the materials allows to infer about the possibility of ion release to the aqueous phase [16]. The release of calcium, aluminium, iron and magnesium ions may favour the removal of phosphorus through the formation of insoluble precipitates, but the release of other ions, especially those from heavy metals, are disadvantageous for water treatment. The tested mineral materials and granulated cork did not present a tendency to release ions. Eggshell and the tested organic materials lead to an increase in the water conductivity, particularly the grape pomaces.

Based on the results obtained, it was concluded that eggshell residues are not suitable for use as CW filler because of the high organic load released. However, the disadvantage pointed out can be overcome if the organic residues present in the eggshells are previously removed by calcination, for

example. However, the eggshells pre-treatment can be costly, which reduces the attractiveness of this solution. Grape pomace released phosphorus, nitrogen and COD compounds and led to a significantly acidic pH, so it is also not a good choice. Wood pellets have proved to be a source of nitrogen and COD and cause a significant reduction of pH. This material tends to release wood fibres into the water, which can lead to clogging problems. In view of these observations, the three mentioned materials were not used in the adsorption studies.

3.3. Preliminary Adsorption Experiments

The results of the preliminary adsorption tests are presented in Table 3. It can be seen from the results that none of the materials showed capacity for nitrogen adsorption. Moreover, no adsorption of TP, TN or COD was detected for the olive seeds and pine bark.

Table 3. Preliminary essays to evaluate the potential of adsorption from aqueous solutions.

Solid waste	TP (mg _P /g)	TN (mg _N /g)	COD (mg _{O2} /g)
Clay brick fragments	0.035 ± 0.049	ND	1.79 ± 0.47
Coal slags	0.027 ± 0.002	ND	1.58 ± 0.13
Cork granulates	ND	ND	1.30 ± 0.27
Limestone fragments	0.034 ± 0.016	ND	1.83 ± 0.11
Olive seeds	ND	ND	ND
Pine bark	ND	ND	ND
Snail shells	0.018 ± 0.004	ND	0.58 ± 0.15

ND = Not detected

Limestone fragments, clay brick fragments and coal slags revealed some phosphorus adsorption capacity. The snail shells showed a lower adsorption than the other mineral materials. The remaining materials did not show adsorption capacity for phosphorus compounds. It was observed that most of the materials showed a tendency to adsorb toluene, through the reduction observed in COD content. The potential of the materials to remove COD content from water followed the order limestone>brick>slags>cork>snail shells.

From this set of tests, it was concluded that the limestone fragments, clay brick fragments, coal slags, cork granulates and snail shells may have potential application as CW filler material. On the other hand, olive seeds and pine bark showed a lower potential, so they were not used for the more complete adsorption studies.

3.4. Adsorption Isotherm Experiments

Following the nutrients release and preliminary adsorption tests results, five materials were selected for more extended adsorption essays. The adsorption capacity for phosphorus compounds and for oxidable compounds was studied using different concentrations of phosphate and toluene solutions. The adsorption isotherm of nitrogen compounds was not evaluated, since none of the materials has showed potential to remove TN in the preliminary adsorption experiments.

Figures 1 and 2 show the isotherms obtained by non-linear adjustment for phosphate and toluene adsorption, analysed as TP and COD, respectively. The figures show a high data scattering, which may be due to the irregular particle shape and dimensions, and to the heterogeneous composition of the waste, despite the efforts to use representative and similar samples.

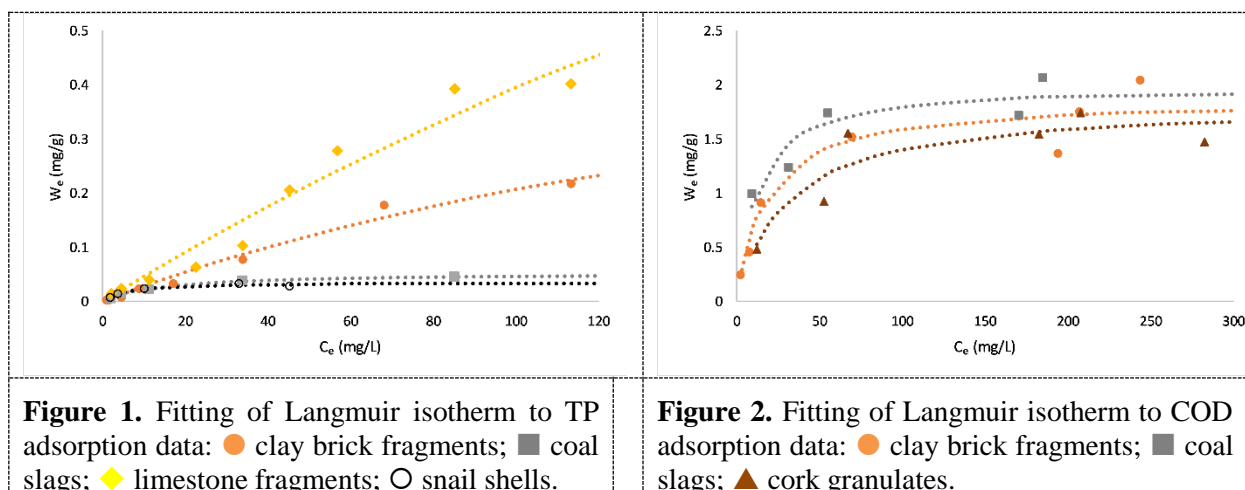


Table 4 contains the parameters obtained for the adjustment of the Langmuir isotherm to the experimental data. The potentiality for TP and COD removal can be related to the parameter W_{\max} .

Table 4. Langmuir isotherm parameters for phosphate and toluene adsorption, analysed as TP and COD, respectively.

Solid waste	Phosphate adsorption (as TP)			Toluene adsorption (as COD)		
	W_{\max} (mg/g)	K (L/mg)	r^2	W_{\max} (mg/g)	K (L/mg)	r^2
Clay brick fragments	0.70 ± 0.47	0.004 ± 0.005	0.984	1.89 ± 0.41	0.054 ± 0.033	0.918
Coal slags	0.052 ± 0.009	0.069 ± 0.026	0.988	2.02 ± 0.75	0.081 ± 0.083	0.838
Cork granulates	ND	ND	ND	1.83 ± 0.36	0.032 ± 0.047	0.831
Limestone fragments	2.31 ± 0.65	0.002 ± 0.003	0.955	ND	ND	ND
Snail shells	0.035 ± 0.007	0.198 ± 0.094	0.961	ND	ND	ND

ND = Not determined; r^2 = coefficient of determination of the non-linear regression.

For the limestone fragments and snail shells the COD data showed a significant uncertainty, resulting in adsorption values close to zero. These results did not correspond to the expected, given the results obtained in the preliminary studies. However, these materials are predominantly composed of calcium carbonate, so it would not be expected that they adsorb organic materials well. Brick fragments, coal slags and cork granulates demonstrated organic matter adsorption capacities, evaluated in COD terms, very similar to each other and of the order of 2 mg_{O2} per g of solid material.

Regarding the adsorption of phosphorus compounds, the results obtained for the cork granulates confirmed the reduced potential of this material. On the other hand, the limestone fragments showed the greatest capacity for the adsorption of TP. The brick fragments had a capacity four times lower compared to limestone fragments, but still much higher than the organic waste materials. The results agree with the mechanisms usually indicated to justify the removal of phosphorus compounds in the CWs, which mainly consist of physical and chemical adsorption of phosphates.

4. Conclusions

Some waste materials can be used as waste-to-treat-waste and can be used as CW fillers, contributing to the treatment of wastewater through adsorption and associated sorption processes.

Among the various residual materials studied in this work, which are mainly deposited in landfills, limestone fragments and brick fragments resulting from construction activities, coal slags resulting from power plants, snail shells resulting from the food and catering industry, and cork granulates resulting from the cork industry have potential to be used as CWs fillers. These materials have

adequate physical properties and some capacity to adsorb phosphorous and organic compounds from wastewaters. The limestone fragments presented a relevant phosphorus adsorption capacity. The brick fragments had some potential to adsorb compounds of phosphorus and organic compounds. Coal slags showed the potential to adsorb organic compounds and, to a lesser extent, phosphorus compounds. The cork granulates showed the ability to adsorb organic compounds. The snail shells are, among these materials, the one with the least potential, as they showed a very low capacity to adsorb phosphorus compounds.

The remaining materials studied did not demonstrate potential to be used as CW fillers, because they have very low adsorption capacities, leach nutrients or other pollutants in contact with water, or because they have less adequate hydraulic properties.

None of the materials tested showed the ability to adsorb nitrogen compounds, but this nutrient is not usually removed by adsorption processes, so this does not limit the use of the materials as CW fillers.

Future work should involve the mixture of materials, taking advantage of their combined properties. Studies on the capacity of the materials for the establishment of microbial communities and for the development of macrophyte species, to promote biological removal processes, should also be carried out.

Although the studied materials did not present exceptional capacities of adsorption of nitrogen, phosphorous and organic compounds, all can be valued as CW fillers, which represents a way to reduce the amount of solid waste sent to landfills. The use of waste materials as CW fillers is an application of the concept of circular economy, replacing engineered filling materials that may present better removal efficiencies but have high production cost, waste generation and high energy consumption processes. The results obtained justify further tests in pilot-scale CWs.

5. References

- [1] United Nations General Assembly on 25 September 2015 *Transforming our world: the 2030 Agenda for Sustainable Development*. Retrieved from http://www.un.org/ga/search/view_doc.asp?symbol=A/RES/70/1&Lang=E Accessed on: 17 jul 2017
- [2] Ghisellini, P, Cialani C and Ulgiati S 2016 A review on circular economy: The expected transition to a balanced interplay of environmental and economic systems *J. Clean. Prod.* 114 11-32
- [3] Winans K, Kendall A and Deng H 2017 The history and current applications of the circular economy concept *Renew Sustain Energy Rev* 68 825-33
- [4] Maina S, Kachrimanidou V and Koutinas A 2017 A roadmap towards a circular and sustainable bioeconomy through waste valorization *Curr. Opin. Green Chem* 8 18-23
- [5] Malinauskaite J, Jouhara H, Czajczynska, D *et al.* 2017 Municipal solid waste management and waste-to-energy in the context of a circular economy and energy recycling in Europe *Energy* 141 2013-44
- [6] Grace M A, Clifford E and Healy M G 2016 The potential for the use of waste products from a variety of sectors in water treatment processes *J. Clean. Prod.* 137 788-802
- [7] Saxena A, Bhardwaj M, Allen T, Kumar S and Sahney R 2017 Adsorption of heavy metals from wastewater using agricultural–industrial wastes as biosorbents *Water Sci.* 31 189-97
- [8] Mateus D M R, Vaz M M and Pinho H J O 2012 Fragmented limestone wastes as a constructed wetland substrate for phosphorus removal *Ecol. Eng.* 41 65-9
- [9] Wang M, Zhang D Q, Dong J W and Tan S K 2017 Constructed wetlands for wastewater treatment in cold climate — A review *J. Env. Sci.* 57 293-311
- [10] Wu J, Xu D, He F, He J and Wu Z 2015 Comprehensive evaluation of substrates in vertical-flow constructed wetlands for domestic wastewater treatment *Water Practice Tech.* 10 625-632
- [11] Wu H, Zhang J, Ngo H H, Guo W, Hu Z, Liang S, Fan J and Liu H 2015 A review on the sustainability of constructed wetlands for wastewater treatment: Design and operation *Bioresource Technol.* 175 594-601
- [12] European Committee for Standardization EN 933-1:2012 *Tests for geometrical properties of aggregates - Part 1: Determination of particle size distribution - Sieving method*

- [13] European Committee for Standardization EN 1097-6:2013 *Tests for mechanical and physical properties of aggregates - Part 6: Determination of particle density and water absorption*
- [14] European Committee for Standardization EN 1097-3:1998 *Tests for mechanical and physical properties of aggregates - Part 3: Determination of loose bulk density and voids*
- [15] Arias C A, Del Bubba M and Brix H 2001 Phosphorus removal by sands for use as media in subsurface flow constructed reed beds *Water Res.* 35 1159-68
- [16] Wang Z, Dong J, Liu L, Zhu G and Liu C 2013 Screening of phosphate-removing substrates for use in constructed wetlands treating swine wastewater *Ecol. Eng.* 54 57 – 65.

Acknowledgments

This work was supported by Program FEDER, ref. POCI-01-0145-FEDER-023314, project VALORBIO. The authors acknowledge the collaboration of the Lab.IPT staff and the assistance of students of chemical and environmental technology courses held at Instituto Politécnico de Tomar. Special thanks to Alcino Serras, Ana Alves, Isabel Silva, Joel Nunes and Nuno Graça.