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The role of water in the performance of biofilters: Parameterization of pressure drop and sorption capacities for common packing materials

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ABSTRACT

The presence of water in a biofilter is critical in keeping microorganisms active and abating pollutants. In addition, the amount of water retained in a biofilter may drastically affect the physical properties of packing materials and packed beds. In this study, the influence of water on the pressure drop and sorption capacities of 10 different packing materials were experimentally studied and compared. Pressure drop was characterized as a function of dynamic hold-up, porosity and gas flow rate. Experimental data were fitted to a mathematical expression based on a modified Ergun correlation. Sorption capacities for toluene were determined for both wet and dry materials to obtain information about the nature of interactions between the contaminant, the packing materials and the aqueous phase. The experimental sorption capacities of materials were fitted to different isotherm models for gas adsorption in porous materials. The corresponding confidence interval was determined by the Fisher information matrix. The results quantified the dynamic hold-up effect resulting from the significant increase in the pressure drop throughout the bed, i.e. the financial cost of driving air, and the negative effect of this air on the total amount of hydrophobic pollutant that can be adsorbed by the supports. Furthermore, the results provided equations for ascertaining water presence and sorption capacities that could be widely used in the mathematical modeling of biofilters.

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1. Introduction

Biological treatments have become an effective and economical alternative to traditional systems of gas treatment based on physical–chemical techniques. Several packing materials have been used in biofiltration to treat a wide range of pollutants such as volatile organic compounds (VOCs), sulfurous compounds and ammonia, among others [1]. Although the nature of a packing material has proven to be a fundamental factor for the successful application of biofilters [2], the amount of water supplied to a bioreactor is one of the most important parameters that must be taken into account to prevent poor system operation. Around 75% of all reported problems in biofiltration are caused by poor humidity control [3]. Furthermore, water consumption must be optimized, especially in places where water is a scarce and declining resource. Indeed, its management can have an impact on the flow and biological quality of rivers and streams. In dry Mediterranean areas, the use of water for agricultural, industrial or urban purposes places a great deal of stress on a river's biological community [4], compared with rivers in northern European regions.

Several authors have reported that packing materials must store considerable amounts of water to keep microorganisms immobilized on the active support media (high water holding capacities) and make water readily available during periods of drying (high water retentivity). Auria et al. [5] treated ethanol vapors in a peat biofilter with various initial water contents. Their study showed that there was a sharp drop in the elimination capacity from 27 to 4 g toluene m^{-3} h^{-1} when packing materials dried from 70 to 60% in water content. Likewise, the number and types of microbial communities present in the support and the performance of a biofilter depend on the moisture content of the packing material [3]. In general, a water content of 40 to 80% is desirable [2].

In addition, in the biofiltration of some common pollutants such as ammonia, optimal water irrigation control is necessary to prevent the excessive accumulation of nitrogen species in the reactor bed, which may have inhibitory effects on nitrifying bacteria and thus diminish the bioreactor's efficiency [6,7]. The accumulation of inhibitors may be reduced by changing the amount of water added to the reactor, which is the sole manipulated variable for controlling the wash-out of inhibitory byproducts. Although less EC and RE are obtained as a consequence of a deficient water supply [8], excessive watering may increase the fraction of ammonia recovered as ammonium [9].

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There is scarce mention in the literature of the impact of water on biofilter characteristics such as pressure drop and sorption capacities. Morgan-Sagstume et al. [10] showed that the pressure drop of a filter medium depends to a large extent on the structure and composition of the medium, the gas flow rate and the moisture content of the packing material. Excessive moisture can increase both the pressure drop across the filter bed and the mass transfer resistance, as a result of which anaerobic zones are created [11]. An increase in pressure drop is important for economic reasons, since the main operating cost in such systems is the energy consumption for foul air extraction [12]. In addition to the effect of water on pressure drop, the sorption capacities of packing materials are one of the parameters most affected by the presence of water in a bed. A high adsorption capacity of the medium is critical for dampening concentration fluctuations and may reduce stress on the microbial population. Rapid desorption may keep microorganisms healthy and degradation rates high when inlet concentrations are decreased, and it may reduce toxic shock when inlet concentrations rise [13,14]. It has been reported that peak inlet concentrations of 1000 mg toluene m^{-3} can be decreased to an average inlet concentration of 300 mg m^{-3}, which is subsequently completely degraded in a biofilter [15]. The negative influence of water on the sorption capacity is greater for the treatment of hydrophobic compounds and in the use of packing materials with a high water holding capacity and high water retentivity.

The aim of this study was to evaluate the effect of water on the pressure drop and sorption capacity of common biofiltration packing materials, to characterize these phenomena under usual conditions of operation in biofiltration and to obtain equations that may be useful in modeling the biofiltration process. Pressure drop was evaluated in relation to the gas flow rate, the bed porosity and the dynamic water hold-up of the packing material, in order to find a mathematical expression that reflected the effects of the factors studied. Toluene adsorption was determined for both wet and dry materials to obtain information about the nature of the interactions between the contaminant, the packing materials and the aqueous phase. The sorption capacities of the packing materials were characterized using isotherm models for gas adsorption in porous materials.

2. Materials and methods

2.1. Analytical parameters

The characterization of the packing materials was carried out according to standard methods [16–18]. Dynamic hold-up (DHU) and water holding capacity (WHC) were determined according to test methods for the examination of composting and compost. Dynamic hold-up is defined as the liquid held by the bed with a constant introduction of fresh water and is expressed as a percentage of the water in the empty bed (v/v). The water retentivity of the packing material was determined by passing dry air through a column filled with wet materials and measuring the decrease in weight at constant time intervals of 10 min [19]. The experimental setup to determine the water retentivity is shown as item 11 in Fig. 1.

2.2. Packing materials

The effects of water on pressure drop and sorption capacities were evaluated in a total of 10 common packing materials used in biofiltration. The organic packing materials analyzed were coconut fiber, pine leaves, a mixture of peat and heather, and compost made from the sludge of a wastewater treatment plant. The inorganic or synthetic packing materials studied were polyurethane foam (PUF), lignite from mines in Mequinenza (Spain), lava rock and a hybrid material composed of a thin layer of compost on a clay pellet. Moreover, the pressure drop and sorption capacities of the packing materials were compared with two adsorbent carbons, a commercial activated carbon (CAC) supplied by Chemviron Carbon (UK) and a sludge-based carbon (SBC) provided by the Department of Civil and Environmental Engineering, Imperial College, London. The physical–chemical characteristics of the packing materials used in this study can be found elsewhere [20].

2.3. Experimental setup for pressure drop assessment and adsorption capacity test

Pressure drop assessment experiments were carried out in a lab-scale plant consisting of a PVC column with an inner diameter of 4.6 cm and a height of 70 cm (Fig. 1). The compressed air was conveyed through a first line in which the air stream was fed completely dry to a fixed bed, and through a second line in which the air stream was passed through a water column in order to increase the relative humidity. The former served to determine the water retentivity of a packing material and the latter for pressure drop and sorption capacity tests. The inlet air pressure and the gas flow rate were controlled and measured by means of a pressure regulator (Norgren Excelon) and a flowmeter (Tecfluid 2100), respectively. Tap water was sprinkled continuously on the top of the fixed bed by means of a peristaltic pump (Magdos LT-10) in down-flow mode, while the dynamic hold-up was measured by an optical level sensor located in the water storage tank. Pressure drop was determined by means of two digital differential pressure meters used according to the limits of detection and precision (0.01 and 1 mmH_2O, respectively) (Testo 512-20 hPa and Testo 506-200 hPa). Superficial velocities for testing pressure drop on packing materials were selected to cover the wide range of typical velocities in the treatment of waste gases by bioreactors (up to 350 m h^{-1}).

For the sorption assessment experiments, the inlet pollutant concentration was achieved by dispensing toluene (Panreac 99.5%) by means of a peristaltic pump (Masterflex) into the inlet air stream. The air flow was controlled and measured by a mass flow controller (Bronhorst F-201CV). Toluene concentration was measured by an online photo ionization detector (Photovac 2020) placed at the inlet and outlet of the bed and connected to a computer for continuous data collection. Support materials were previously sterilized using sodium azide (Sharlau) in a 10% (w/w) ratio to prevent the interference of biological activity in the adsorption measurements [21]. The bed porosities and dynamic hold-up tested were set as a function of the physical characteristics of each material according to their shape, size and maximum degree of compaction in the bed. The materials were watered continuously for 1 h to obtain the wet conditions.

2.4. Sorption capacities of packing materials

The sorption capacities of the packing materials were evaluated by frontal analysis of the toluene measurements at the inlet and outlet of a fixed bed, following the staircase method [22]. Isotherms were determined from the breakthrough curves of step changes in the feed concentration. Detailed information about the staircase method and calculations of the adsorption capacity are provided in Appendix A.

Experimental data were also fitted to adsorption isotherms models available in the literature. Since many isotherms can be used to describe sorption behavior in a wide range of adsorbents and with an extensive list of adsorbates, the most well known of these were used in this study, including two-parameter isotherms (Langmuir, Freundlich and Dubinin–Radushkevich), three-parameter isotherms (Radke–Prausnitz, Brunauer–Emmett–Teller

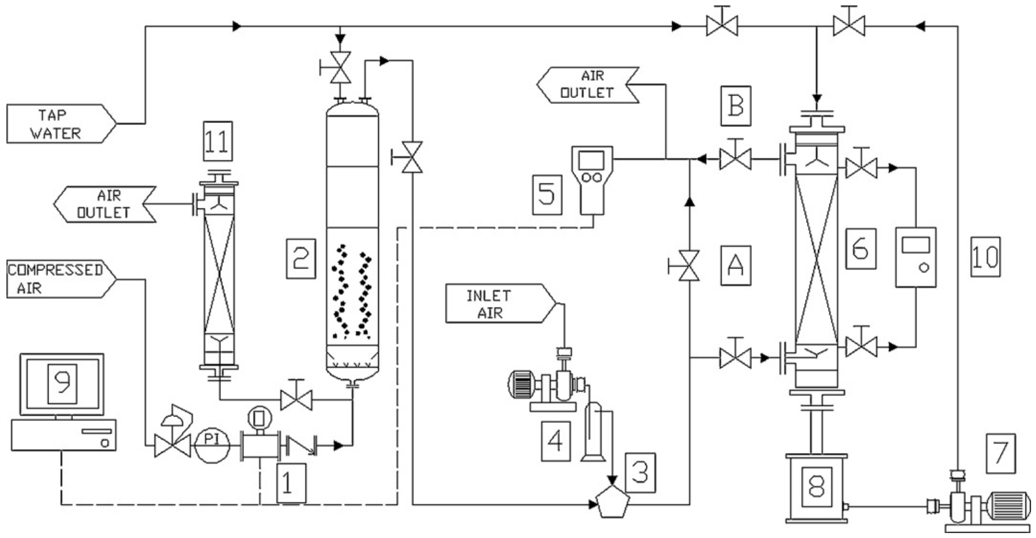

Fig. 1. Experimental setup of the lab-scale plant. 1: mass flow controller, 2: humidification column, 3: mixing chamber, 4: toluene injection by peristaltic pump, 5: VOC detector, 6: fixed bed, 7: membrane pump, 8: storage tank and optical level sensor, 9: data acquisition and control computer, 10: differential pressure meter, 11: bed for water retentivity experiments. A: sample port for gas inlet and B: sample port for gas outlet.

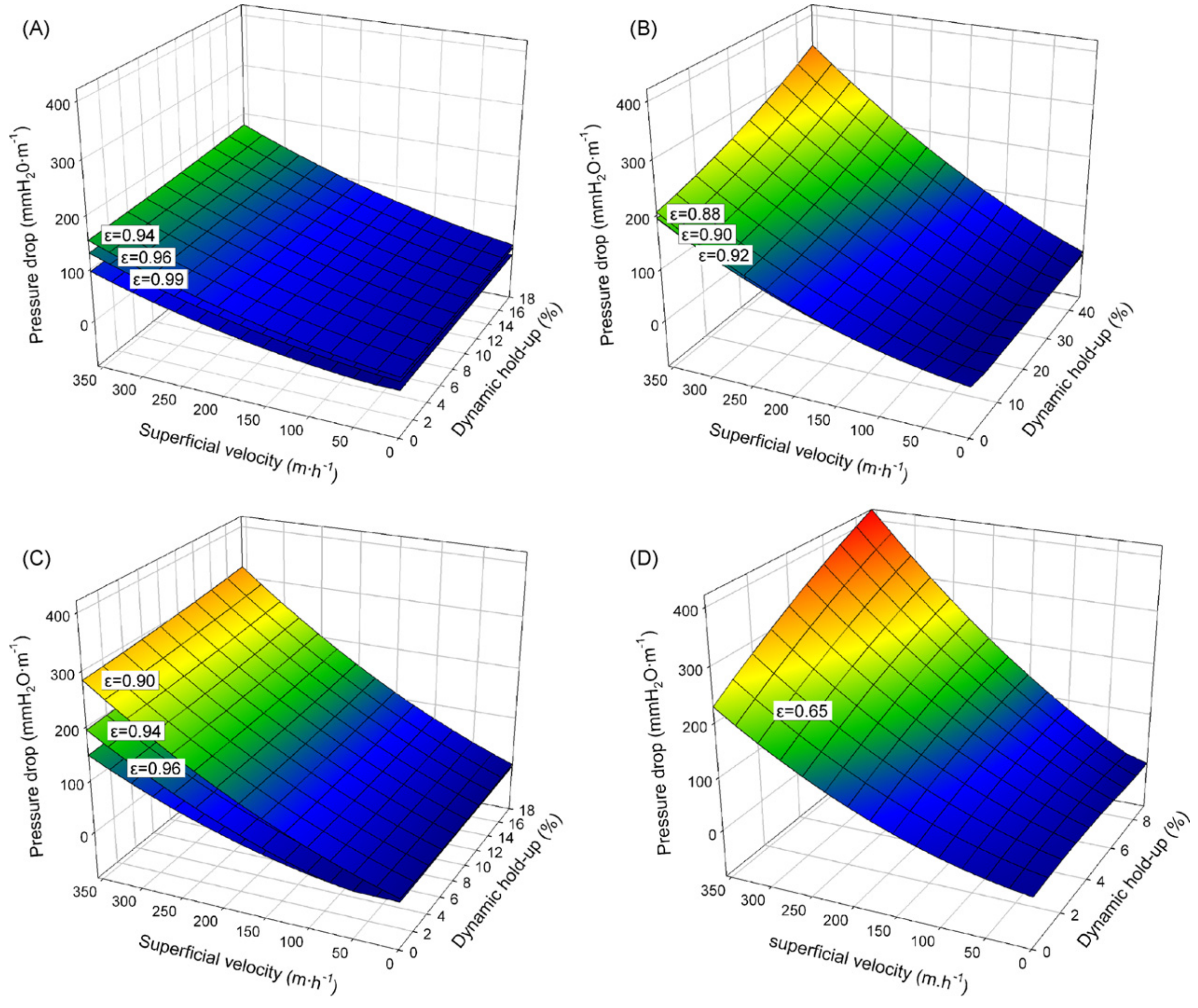

Fig. 2. Influence of operational parameters on pressure drop for coconut fiber (A), peat with heather (B), PUF (C) and the hybrid material (D).

Table 1
Water holding capacities (WHC) and water retentivity (WR) of carrier materials and modified parameters of the Ergun equation as a function of water content in biofilters.

	WHC ($g\,g^{-1}$)	WR (% day^{-1})	ε	n	m	n'	m'
Compost	0.68	−57.89	0.70	12.634	−0.069	0.250	0.003
			0.76	132.370	0.720	0.595	0.009
			0.79	432.090	4.077	1.199	0.004
Coconut fiber	3.90	−192.24	0.94	0.626	0.004	0.062	0.001
			0.96	2.145	0.019	0.090	0.000
			0.99	9.130	0.750	0.333	−0.011
Lava rock	0.18	−23.33	0.73	75.398	0.340	0.512	0.005
			0.76	115.150	0.384	0.531	0.001
			0.77	234.900	2.276	0.766	0.002
Lignite	0.28	−41.62	0.58	14.618	0.212	0.176	0.001
			0.63	35.182	0.387	0.248	0.002
			0.64	100.830	0.270	0.466	0.007
Pine leaves	1.51	−422.78	0.91	1.885	0.014	1.146	0.058
			0.92	2.524	0.016	2.517	0.144
			0.96	9.378	0.059	11.196	0.000
Peat with heather	1.80	−66.38	0.88	442.870	6.002	0.946	0.032
			0.90	1112.800	29.587	1.197	0.034
			0.92	6135.000	8.161	8.043	0.014
PUF	1.56	−416.56	0.90	38.342	0.523	0.397	0.002
			0.94	41.279	2.944	0.383	0.002
			0.96	0.528	156.450	0.950	−0.003
Advanced material	0.58	−41.90	0.65	12.342	1.458	0.160	0.009
CAC	0.39	−17.42	0.76	43.745	0.233	0.128	0.005
SBC	0.34	−17.57	0.93	1002.900	2.819	3.492	0.008

and Redlich–Peterson) and a combination of the two. Detailed information about the abovementioned isotherms is provided in Appendix A.

The parameter estimation was performed using a MATLAB algorithm based on a multidimensional unconstrained non-linear minimization (Nelder–Mead). This is a direct search method that does not use numerical or analytical gradients. The confidence intervals of the estimated parameters were assessed using a numerical method based on the Fisher information matrix (FIM) [23,24], which has been satisfactorily employed in the calibration of mathematical models in the field of biofiltration [25].

3. Results and discussion

3.1. Influence of water on the pressure drop of packing materials

The results of the pressure drop tests were expressed as surface plots to simultaneously observe the influence of gas velocity, dynamic hold-up and bed porosity on pressure drop. Fig. 2 shows the results for coconut fiber (Fig. 2A) and peat with heather (Fig. 2B) as examples of the behavior of organic packing materials, and for PUF (Fig. 2C) and the hybrid material (Fig. 2D) as examples of the behavior of non-organic materials. Surface plots for the rest of the materials are provided in Appendix A. The results show a greater impact of air velocity compared with dynamic hold-up and bed porosity on pressure drop. In general, the pressure drop measured in a biofilter in operation is substantially higher than the initial pressure drop of the material. This is due to a higher resistance to air circulation as a result of the presence of water. Moreover, the effect on the pressure drop of water circulating through the bed is greater at high bed porosities for most materials due to the higher volume to be occupied by the aqueous phase.

In organic materials, the results revealed small differences for all packing materials at the various possible porosities and, in general, the pressure drop was well below 250 mm wc m^{-1} in all conditions. As an exception, peat and heather showed a higher head loss value (up to 350 mm wc m^{-1}) due to a larger dynamic hold-up, which was related to the high WHC and WR of these materials. The lowest pressure drop among the organic packing materials was found in coconut fiber, which is consistent with the high bed porosity generally found using this material. Some authors have also suggested that an increase in pressure drop due to moisture is more significant in a medium with granular particles than in fibrous materials [10]. In general, organic materials show a high WHC (Table 1), which increases their swelling capacity, thus increasing the packing volume. This means there is a lower cross-sectional area and a higher pressure drop. For the same reason, the range of possible dynamic hold-up that prevents the flooding of the bed in organic materials is narrower than in the rest of materials.

Regarding non-organic materials, pressure drops are greater in the range of study than those determined in organic materials. Materials showed significant differences for the various bed porosities tested. The dependence on dynamic hold-up is more pronounced at high flow rates, when resistance to the flow towards the bed increases. The lowest pressure drop among the non-organic and organic packing materials was found in the CAC (below 100 wc m^{-1}), which is consistent with the regular shape of the particles, despite their relatively larger size. Regarding the latter, some authors have pointed out that pressure gradients or friction factors are smaller for spherical glass beads than for irregularly shaped materials [26]. In contrast, the hybrid material and SBC showed the highest pressure drop detected among the organic and non-organic support media. The pressure drop detected in the two materials, in the only possible porosities allowed by their shape and structure, showed a strong dependence on water that proved to be greater at high flow rates. Because of the small size of the particles, the low bed porosity of the hybrid material hinders the water trickling through the bed, a fact that has direct repercussions on the pressure drop. Moreover, PUF exhibits high bed porosity due to its open pore structure, despite the fact that high bed pressure drops have previously been related to its structure [27]. Regarding the effect of porosity in non-organic materials, the results show significant differences in the interval tested at three different degrees of compaction, unlike the rest of the support media studied. PUF and lava

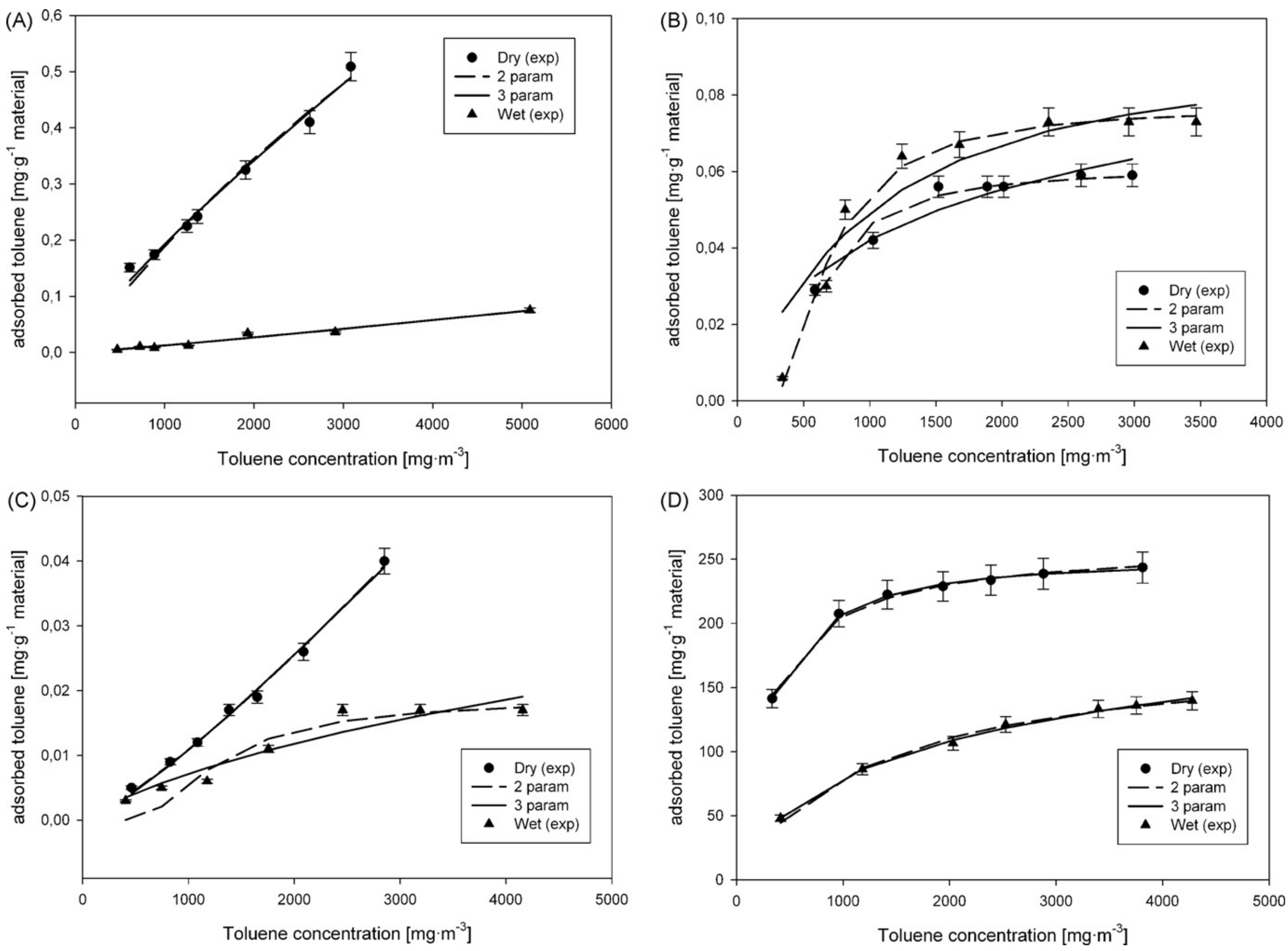

Fig. 3. Experimental data and model predictions for toluene adsorption on the compost (A), coconut fiber (B), hybrid material (C) and commercial activated carbon (D) for dry and wet conditions.

rock beds are examples of the significant effect of bed porosity on head loss.

In order to parameterize the experimental data, the pressure drop in a fixed bed was described through several semi-empirical mathematical expressions. In most works, the pressure drop is described by the well-known Ergun equation [28]. The degree to which the pressure drop increases and the range of air velocities at which the linear behavior becomes non-linear depend on the packing material used [10]. The Ergun equation may be written as (Eq. (1)):

$$\frac{\Delta P}{H} = a\frac{\mu v_0}{d_p^2}\frac{(1-\varepsilon)^2}{\varepsilon^3} + b\frac{\rho {v_0}^2}{d_p}\frac{(1-\varepsilon)}{\varepsilon^3} \qquad (1)$$

where ΔP is the pressure drop, in kPa; H is the height of the fixed bed, in m; μ is the viscosity of the air, in Pa s; v_0 is the superficial velocity, in m s^{-1}; ε is the porosity of the bed; d_p is the equivalent spherical diameter of the particle in m; and a and b are the constant parameters of the Ergun equation.

Parameters a and b of Ergun's correlation are related to the friction factor. The expression term related to parameter a is significant for flow under very viscous conditions, while parameter b is only significant when viscous effects are not as great as inertia. Some authors have satisfactorily fitted experimental data to a modified Ergun equation by adapting the coefficients of the expression using a correction factor [30]. Macdonald et al. [31] described a modified Ergun equation, which takes into account the dependence on porosity of the viscous and kinetic energy losses (first and second term, respectively). Other authors have used a specific relation due to the heterogeneity of the material and the difficulty in modeling pressure drop using the classic Ergun equation [32]. It was reported that a moisture content of between 10 and 45% of the packing material does not have a stronger effect on the Comiti and Renaud parameters [33].

In this study, parameters a and b were fitted as a function of the dynamic hold-up in the bed in order to find a relationship that describes the effect of water on the pressure drop estimation according to Eq. (2):

$$\frac{\Delta P}{H} = (n + m\cdot DHU)\frac{\mu v_0}{{d_p}^2}\frac{(1-\varepsilon)^2}{\varepsilon^3} + (n' + m'\cdot DHU)\frac{\rho {v_0}^2}{d_p}\frac{(1-\varepsilon)}{\varepsilon^3} \qquad (2)$$

where DHU is the dynamic hold-up (% by volume), n is the y-intercept of the linear function of parameter a with the DHU, m is the gradient for parameter a, n' is the y-intercept for parameter b and m' is the gradient for b.

Table 1 shows the effect of water on each material according to the parameter obtained from Eq. (2). Parameters n and n' in the modified Ergun equation are not dependent on the amount of water present in the bed and only show the effect of the bed's porosity and the physical characteristics of the materials in the total head loss. Instead, m and m' provide direct information about the effect of water on the packing material. The larger values of parameter m, i.e. the gradient of the DHU, for the PUF, compost and hybrid material biofilter showed that the effect of water was strongest on

Table 2
Estimation of parameters and confidence intervals for the most common isotherms for packing materials in dry conditions.

Material		Advanced material	Lava rock	Pine leaves	Peat	Lignite	AC	SBAC	Compost	Coconut fiber
Langmuir	k_1	8e+13 ± 4e+19	0.021 ± 0.001	6.474 ± 2.834	2e+14 ± 2e+14	1e+15 ± 7e+20	262.2 ± 5.1	187.0 ± 3.7	2.1 ± 0.4	0.08 ± 0.003
	k_2	6e+18 ± 3e+24	6609.3 ± 501.0	6e4 ± 25922	1e+19 ± 1e+19	5e+18 ± 3e+24	274.9 ± 24.9	359.9 ± 29.2	9999 ± 1953.0	887.2 ± 77.4
	OF	0.005	0.002	0.052	0.003	0.175	5.672	7.100	0.045	0.007
Freundlich	k_f	2e−06 ± 3e−07	1e−05 ± 9e−07	1e−4 ± 7e−6	7e−06 ± 4e−07	2e−06 ± 2e−07	50.8 ± 5.2	29.0 ± 2.8	0.001 ± 0.0001	0.003 ± 0.0004
	n	1.23 ± 0.016	0.774 ± 0.009	0.997 ± 0.009	1.061 ± 0.008	1.573 ± 0.012	0.20 ± 0.01	0.22 ± 0.01	0.82 ± 0.02	0.38 ± 0.02
	OF	0.002	0.002	0.054	0.002	0.033	27.838	20.500	0.040	0.01
Dubinin	B	1.23 ± 0.032	0.774 ± 0.020	0.997 ± 0.027	1.06 ± 0.029	1.573 ± 0.042	96.9 ± 6.3	137.6 ± 7.7	1397.0 ± 43.3	450.6 ± 21.0
	q_m	0.04 ± 0.001	0.008 ± 2e−4	0.467 ± 0.010	0.062 ± 0.001	0.968 ± 0.023	234.5 ± 3.0	165.5 ± 2.1	0.5 ± 0.0	0.06 ± 0.0009
	OF	0.002	0.002	0.019	0.002	0.074	18.213	16.400	0.200	0.006
Radke	a	29.83 ± 2e+08	−5.9 ± 7e+06	−2.115 ± 8e+06	−10.505 ± 6e+08	9.809 ± 3e+05	0.84 ± 0.14	0.48 ± 0.07	2.10 ± 21000	3e−4 ± 0.0004
	b	2e−06 ± 2e−06	1e−05 ± 2e−05	0.0001 ± 0.020	7e−06 ± 0.0003	2e−06 ± 2e−06	362.7 ± 170.4	228.3 ± 111.4	0.001 ± 0.003	0.007 ± 0.008
	B	1.23 ± 0.368	0.774 ± 0.095	0.997 ± 0.435	1.06 ± 3.10	1.573 ± 0.137	0.04 ± 0.1	0.001 ± 0.002	0.80 ± 0.34	0.28 ± 0.13
	OF	0.002	0.002	0.054	0.002	0.033	3.624	6.900	0.040	0.01
BET	C_s	16309 ± 2e+05	3e+09 ± 1e+11	3e+21 ± 4e+26	82102 ± 3e+06	9638.6 ± 18655	9e5 ± 5e5	3e+05 ± 2e+06	4472 ± 98	2.6e9 ± 1e11
	B	0.156 ± 27.127	5e+05 ± 2e+07	1e+21 ± 1e+26	0.873 ± 37.818	0.196 ± 3.941	3480 ± 1568	10310 ± 54127	9185 ± 682170	3e9 ± 1e11
	Q	1.025 ± 192.22	0.021 ± 0.010	0.217 ± 0.008	1.07 ± 80.03	5.222 ± 115.13	261.2 ± 15.5	185.0 ± 11.4	0.16 ± 0.006	0.08 ± 0.01
	OF	0.001	0.002	0.370	0.003	0.040	5.920	7.200	0.070	0.009
Reddlich	a	1e+09 ± 8e+14	5e−06 ± 1e−06	2e−4 ± 0.385	1e−05 ± 1e−06	22.8 ± 6e+06	7e−5 ± 4e−4	0.48 ± 0.06	0.003 ± 3842	2.6e9 ± 1e9
	b	4e+14 ± 3e+20	0.034 ± 0.0544	0.988 ± 3555.6	18.337 ± 23.387	6e+05 ± 2e+11	67.8 ± 336.3	0.002 ± 0.001	3.6 ± 4469	3e6 ± 4e9
	n	−0.213 ± 0.021	0.458 ± 0.1409	0.006 ± 11.067	−0.646 ± 0.273	−0.217 ± 0.405	0.29 ± 0.20	1.00 ± 0.04	0.20 ± 0.29	0.08 ± 0.01
	OF	0.002	0.002	0.054	0.002	0.105	0.002	6.900	0.040	0.007
Combination	b	3e−06 ± 2e−06	5e−06 ± 2e−4	4e−07 ± 2e−07	5e−06 ± 7e−06	2e−09 ± 5e−10	0.0012 ± 0.0002	0.001 ± 0.001	0.00001 ± 0.0003	4.8e6 ± 1e7
	q_m	0.444 ± 0.417	2.445 ± 88.015	0.597 ± 0.026	1.257 ± 1.953	1.285 ± 0.1183	252.5 ± 106.7	180.3 ± 10.8	52.7 ± 1476.0	0.06 ± 0.006
	n	0.776 ± 0.025	1.289 ± 0.056	0.538 ± 0.014	0.915 ± 0.015	0.400 ± 0.003	0.84 ± 0.03	0.85 ± 0.19	1.2 ± 0.10	0.53 ± 0.11
	OF	0.002	0.002	0.019	0.002	0.074	2.766	6.400	0.040	0.004

The amount of toluene adsorbed on PUF is negligible.

Table 3

Estimation of parameters and confidence intervals for the most common isotherms for packing materials in wet conditions.

Material		Advanced material	Lava rock	Pine leaves	Peat	Lignite	AC	SBAC	Compost	Coconut fiber
Langmuir	k_1	0.039 ± 0.002	0.002 ± 4e−05	7e−02 ± 0.002	4e+13 ± 4e+19	6e+13 ± 3e+19	180 ± 5.195	146.29 ± 12.344	9e+13 ± 9e+13	0.109 ± 0.0027
	k_2	4419 ± 338	371 ± 23.1400	808 ± 48.061	8e+18 ± 7e+24	7e+18 ± 3e+24	1271 ± 86.618	8e4 ± 810.550	6e+18 ± 6e+18	1282 ± 45.3
	OF	0.004	0.0005	0.009	0.002	0.005	6.33	9.53	0.012	0.024
Freundlich	k_f	5e−05 ± 5e−6	3e−4 ± 2e−05	0.003 ± 0.000	3e−06 ± 3e−07	1e−06 ± 1e−07	4.14 ± 0.424	0.05 ± 0.005	6e−06 ± 5e−07	0.002 ± 7e−05
	n	0.705 ± 0.011	0.217 ± 0.0106	0.381 ± 0.012	1.079 ± 0.012	1.254 ± 0.011	0.43 ± 0.013	0.83 ± 0.011	1.110 ± 0.011	0.488 ± 0.0073
	OF	0.005	0.0006	0.014	0.002	0.002	9.92	10.69	0.011	0.031
Dubinin	B	0.699 ± 0.019	0.217 ± 0.0075	0.194 ± 0.006	1.079 ± 0.025	1.254 ± 0.031	0.16 ± 0.005	0.73 ± 0.020	1.110 ± 0.025	0.488 ± 0.0078
	q_m	0.019 ± 3e−4	0.002 ± 2e−05	0.050 ± 0.001	0.019 ± 0.000	0.040 ± 0.001	126 ± 1.586	49.96 ± 0.865	0.077 ± 0.002	0.077 ± 0.0010
	OF	0.005	0v0002	0.010	0.004	0.009	35.12	6.44	0.022	0.008
Radke	a	0.001 ± 0.037	−3e8 ± 7e+21	0.0001 ± 3e−05	1.365 ± 4e+07	14.97 ± 4e+07	0.19 ± 0.035	0.04 ± 0.065	−14.21 ± 2e+08	−8e9 ± 2e+23
	b	6e−05 ± 6e−5	3e−4 ± 0.0002	0.013 ± 0.008	3e−06 ± 0.000	1e−06 ± 7e−07	45.67 ± 33.873	0.18 ± 0.610	6e−06 ± 2e−05	0.002 ± 0.0011
	B	0.699 ± 0.099	0.217 ± 0.0791	0.194 ± 0.076	1.079 ± 6.204	1.254 ± 0.225	0.16 ± 0.086	0.73 ± 0.313	1.110 ± 0.831	0.488 ± 0.0811
	OF	0.005	0.0006	0.011	0.002	0.002	4.46	10.55	0.011	0.031
BET	C_s	3e+09 ± 9e+10	3e+09 ± 8e+10	2e+09 ± 5e+10	2e+09 ± 1e+14	32864 ± 1e+06	2e+22 ± 3e+29	−6e21 ± 8e+28	4e4 ± 3e+05	3e+09 ± 5e+10
	B	6e+05 ± 2e+7	7e+06 ± 2e+08	3e+06 ± 7e+07	6894 ± 4e+08	0.105 ± 77.0	7e+22 ± 8e+29	2e+22 ± 2e+29	0.686 ± 12.9	2e+06 ± 4e+07
	Q	0.039 ± 0.013	0.002 ± 8.9e−05	0.066 ± 0.005	1.51 ± 1509.4	2.26 ± 1747.8	110 ± 4.036	30.61 ± 1.242	0.699 ± 19.3	0.109 ± 0.0099
	OF	0.004	0.0005	0.009	0.002	0.003	81.34	37.74	0.011	0.024
Reddlich	a	1e−05 ± 2e−6	3e−06 ± 2e−07	1e−04 ± 1e−05	6e−06 ± 1e−06	7e−05 ± 0.000	0.21 ± 0.035	0.02 ± 0.011	2e−05 ± 3e−06	8e−05 ± 2e−06
	b	0.008 ± 0.011	4e−4 ± 0.0001	0.003 ± 0.002	27.3 ± 93.7	67.80 ± 336.29	0.01 ± 0.004	0.02 ± 0.092	20.41 ± 30.3	0.0003 ± 0.0002
	n	0.636 ± 0.155	1.194 ± 0.0307	0.912 ± 0.057	−0.70 ± 0.651	−0.28 ± 0.205	0.82 ± 0.065	0.44 ± 0.346	−0.573 ± 0.312	1.119 ± 0.0657
	OF	0.005	0.0004	0.010	0.001	0.002	4.54	10.33	0.011	0.023
Combination	b	3e−05 ± 4e−4	5e−05 ± 6e−05	0.001 ± 0.019	2e−06 ± 2e−05	5e−07 ± 3e−06	−6e+7 ± 8e+20	−11.27 ± 2e+14	2e−06 ± 7e−06	0.002 ± 1.1296
	q_m	1.572 ± 21.026	0.002 ± 6e−05	3.404 ± 91.2	1.446 ± 15.8	2.207 ± 13.841	110 ± 3e+07	30.62 ± 0.329	3.279 ± 14.6	11.435 ± 5854.4
	n	1.405 ± 0v093	0.600 ± 0.0805	2.586 ± 0.685	0.920 ± 0.037	0.790 ± 0.019	6e+07 ± 1e+21	0.18 ± 1e+12	0.890 ± 0.02	9.007 ± 21.0
	OF	0.005	0.0003	0.014	0.002	0.002	81.41	37.72	0.011	0.053

The amount of toluene adsorbed on PUF is negligible.

parameter *a*. In the case of parameter *b*, related to the materials' roughness, the dependence on the DHU was markedly lower for most carrier materials in comparison to parameter *a*.

The results show which materials are most affected by the presence of water and therefore in which ones the accurate control of watering is critical to prevent the high energy consumption that results from circulating air through the bed [10,29]. The high correlation coefficients in this study demonstrate that it is possible to express a modified Ergun equation by incorporating the effect of water on the pressure drop predictions for some packing materials in a wide range of operating conditions. By way of example, the results obtained herein may be useful for incorporating pressure drop phenomena in classic biofilter models that consider the presence of water in beds and for calculating the financial cost of blowing air through a biofilter.

3.2. *Influence of water on the adsorption capacities of materials*

Adsorption phenomena in biofilters are poorly understood but play a major role in the operation of biofilters [2]. The effects of adsorption on biofilter performance are complex and depend on the medium, contaminant and microorganisms [34]. Toluene sorption was determined for both wet and dry materials to obtain information about the nature of the interactions between the contaminant, the packing materials and the aqueous phase. The adsorption capacities of dry materials were evaluated to describe the behavior on the non-colonized patches in a biofilter in operation. They also served to characterize the use of packing materials as a buffer to adsorb intermittent pollutant loads when the material is placed in front of the inlet of a biofilter. The adsorption capacities of a wet material describe its ability to absorb intermittent pollutant loads when the media supports are used under the normal operating conditions of a biofilter.

By way of example, the experimental quantities of toluene adsorbed on wet and dry materials are shown in Fig. 3 for two organic materials (compost and coconut fiber) and two inorganic materials (hybrid material and CAC). The rest of the materials are included in Appendix A. As expected, the adsorption capacities of the CAC and SBC were substantially higher than the quantity of pollutant adsorbed on the rest of the packing materials for the toluene concentration interval studied. In the case of the SBC, the amount of contaminant adsorbed doubled at high pollutant concentrations and increased the capacities up to six times at low concentrations. The amount of pollutant retained in its structure increased up to 500 times for the CAC in comparison to the rest of the materials. The higher adsorption capacity of the CAC and SBC is in part explained by the high surface area detected in the characterization of these materials (950 and 90 $\mathrm{m}^2\,\mathrm{g}^{-1}$, respectively) in comparison to the other support media (between 0.02 and 3 $\mathrm{m}^2\,\mathrm{g}^{-1}$).

The most relevant observation in Fig. 3 is that the adsorption capacities for all the materials drastically decrease when they are in wet conditions, except in the case of coconut fiber. The sorption capacity in wet coconut fiber is slightly higher than in dry conditions, which is explained by the predominant role of the absorption process over the low adsorption capacity of this material under dry conditions. Overall, the decrease in the sorption capacities due to the DHU was around 60% under dry conditions in most materials, with the difference increasing up to 90% in some materials, e.g. compost. The water film on materials creates a high resistance to the mass transfer of a hydrophobic compound such as toluene. Thus, pollutant concentrations on the liquid-solid interface of wet materials are lower than the concentrations on the gas-solid interface in dry conditions. As liquid-phase diffusion is much slower than gas-phase diffusion, the toluene is hardly adsorbed over short contact times. Moreover, previous works have reported that water competes for adsorptive sites when a biofilter is put into operation [35]. Our results show that the advantages of materials with a high adsorption capacity in biofiltration disappear when the materials are completely wet. However, if a separate carbon column is placed before the biofilter, the presence of water is prevented and a stable pollutant concentration is buffered to degrade in the biofilter.

Tables 2 and 3 show estimations by non-linear regression of isotherm parameters under wet and dry conditions for all the packing materials tested. In Fig. 3, the experimental quantities of toluene adsorbed on porous materials at 22 °C in wet and dry conditions are fitted to a two-parameter isotherm, and to a three-parameter isotherm for the compost, coconut fiber, hybrid material and CAC. Graphs for the rest of the materials are provided in Appendix A. The experimental data were fitted to the best fit among the two- and three-parameter isotherms according to the minimum value of the objective function and the interval of the confidence interval.

In general, parameter estimation is based on achieving the minimal value of the OF but without considering the error associated with the estimation. However, this study also incorporates an estimation of the confidence interval of parameters associated with the fitting of the isotherm. Although several isotherms make it possible to accurately predict the experimental data (low OF), the huge confidence intervals determined in most cases show that problems of identifiability of parameters are occurring [23]. Wider confidence intervals are obtained in three-parameter isotherms in particular. This is due to the large number of possible combinations of parameters that are able to fit model predictions to the experimental toluene adsorbed on the materials. Thus, estimated parameters show a low sensitivity to the final result of the isotherm expression. Depending on the value of the parameters and the differences in the degrees of magnitudes between them, practical identifiability may be a phenomenon that is worth considering. Confidence intervals are also a function of the number of experimental data (seven different inlet concentrations) and the experimental error in measurements (5% of the value). For instance, the Radke–Prausnitz isotherm satisfactorily predicts the quantity of toluene adsorbed on most of the materials but gives wide confidence intervals. However, the most important problems related to identifiability in the estimation of constant parameters are shown in the well-known BET isotherm. The difference between the magnitudes of the three parameters in the mathematical expression is more marked than in the rest of the isotherms. The uncertainty value of the parameters is nevertheless able to ensure a single solution. Taking identifiability problems into consideration, the Freundlich, Langmuir, Dubinin–Radushkevich and Redlich–Peterson isotherm is the most suitable for fitting the experimental data and for interpreting the influence of water on the sorption of pollutants in common packing materials.

Regarding the Freundlich parameters, the estimated values of n are lower in the SBC and the CAC than in the rest of the packing materials. The adsorption isotherm's behavior deviates further from the linear isotherm, so it approaches a rectangular isotherm or irreversible isotherm. The value of this parameter is higher in each material depending on the presence of water, i.e. an increase in moisture in the bed weakens the affinity between the contaminant and the material. The lowest values of parameter n were found in the compost, coconut fiber and pine leaves, as well as in the activated carbons. In wet conditions, the maximum affinities between the pollutant and the materials, according to parameter n, follow the same comparative degree as in dry conditions. The lowest result obtained was for the bed packed with lava rock. The results in Tables 2 and 3 for Langmuir data fitting show that the affinities between the pollutant and the materials (value K_2) are also higher in the SBC and CAC if an acceptable confidence interval is considered, i.e. an interval lower than 10% of the value of the parameter. In other materials, e.g. coconut fiber, it does not matter whether the material is wet or dry, which is borne out by the interpretation of the Freundlich parameters and experimental observation. Regarding K_1, which is related to the maximum adsorption capacity of the material, the CAC had the highest capacity, as expected.

The Dubinin–Radushkevich isotherm also gives an accurate estimation of parameters in a wide range of materials (confidence intervals lower than 7%). The determination of parameter E for the experimental conditions (maximum value of 7 kJ g^{-1} at the highest gas concentration) demonstrates that the interaction between the pollutant and the surface of the materials is a physical bond rather than a chemisorption bond. Maximum values of B, which is related to sorption energy, are once again achieved by the compost, SBC and CAC. This parameter decreases significantly in wet conditions in all the carrier materials without exception. It is evident that the presence of water in the bed weakens the interaction bond between the contaminant and the surface of the materials.

Previous results are partially improved by means of the Redlich–Peterson isotherm. According to the interpretation of the parameters, n is close to 0 in dry conditions, i.e. it exhibits behavior similar to that of Henry's law, except in the case of the SBC. In contrast, parameter n increases until it approaches the unit with the presence of water in most materials, i.e. the performance of the Langmuir isotherm. Thus, the sorption capacities of materials in the same range of gas-phase concentrations are quickly saturated due to the presence of water. An interpretation of the isotherm reveals how water becomes a key competitor for the active sites of the material. Furthermore, the total amount of pollutant abated by the adsorbent and the affinity between them at higher moisture contents in the bed are reduced.

4. Conclusions

The influence of water on the pressure drop and sorption capacities of 10 common packing materials used in biofiltration were evaluated. Coconut fiber, pine leaves, peat and heather, compost, polyurethane foam, immature coal, lava rock, a hybrid material, commercial activated carbon and sludge-based carbon were studied in wet and dry conditions. Pressure drop was determined for each packing material as a function of flow rate, dynamic water hold-up and bed porosity so that all of the effects could be represented simultaneously and a mathematical expression could be obtained that would allow the phenomena to be included in classic biofilter models. A further aim was to calculate the financial cost of blowing air through a bed in any possible situation. A dependence on dynamic hold-up was found through a modified Ergun equation for several packing materials. The financial assessment predicted a substantial increase in the cost of energy for driving air through a biofilter due to the presence of the water needed to maintain the conditions that keep the biomass active. Regarding the sorption capacities of materials, the adsorption capacity of those parts of materials covered with water during a biofilter's normal operations is considerably depleted, especially for hydrophobic pollutants such as toluene. Isotherm interpretation shows that the presence of water in a bed weakens the interaction bond between a contaminant and the surface of materials. Although moisture content generally improves the performance of a biofilter, too much water seriously affects bed compaction and the sorption capacities of materials. Moreover, since water is a scare resource, especially in dry areas of Spain, the water supply in a biofilter must be optimized. The results show that a detailed characterization of materials in wet conditions must be performed to avoid overestimating the adsorbed properties of the carrier materials or underestimating the energy consumption requirements of a plant.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.04.093.

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