



Sorption–desorption behaviour of bentazone, boscalid and pyrimethanil in biochar and digestate based soil mixtures for biopurification systems



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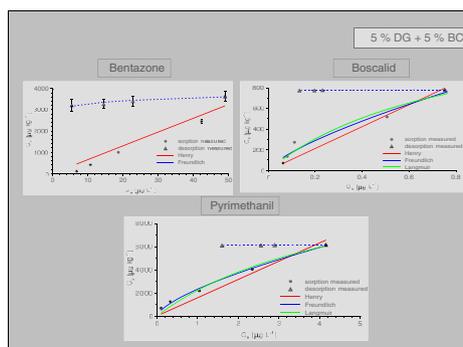
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HIGHLIGHTS

- Biochar and digestate were tested as novel sorbents for biopurification systems.
- Digestate and biochar mixture enhanced the sorption coefficient by a factor of >50.
- Boscalid and pyrimethanil exhibited >25 fold higher K_d/K_{oc} values than bentazone.
- Desorption was hysteretic ($H \geq 0.001$) for biochar and digestate based soil biomixtures.
- Mixture of 5% biochar and (5 and 30%) digestate-soil are the most suitable sorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

Pesticide pollution caused by point or diffuse sources may lead to the contamination of ground and surface water. Biobed or biofilter systems, which are filled with a variety of organic materials (soil, peat and straw), are commonly used on farm to treat pesticide remnants. The objective of this study was to assess the sorption–desorption potential of three pesticides with contrasting physico-chemical properties (bentazone, boscalid, and pyrimethanil) on novel biofilter materials based on bioenergy residues (mixtures of soil with digestate and/or biochar) in laboratory batch equilibrium experiments.

The results show that the biomixtures of digestate and biochar with soil increased pesticides sorption potential and the $1/n_{des}$ values were lower than the $1/n_{ads}$ values indicating that the desorption was hysteretic for all pesticides on these materials. The adsorption and desorption of all the chemicals conformed to linear and Freundlich isotherms. Higher values of distribution [$K_d (>78 \text{ L kg}^{-1})$] and Freundlich sorption coefficient [$K_f (>900 \mu\text{g}^{1-1/n} \text{ L}^{1/n} \text{ kg}^{-1})$] were observed for all pesticides for the digestate and biochar based mixtures compared with the blank soil, which was attributed to the lower organic carbon content of the latter. However, unlike for sorption there was no statistically significant difference between the biochar and the digestate mixtures for pesticides desorption ($p > 0.05$; t -test). Specific UV-absorbances at 254 nm (SUVA_{254}) indicated the aromatic character of digestate (5 and 30%) and biochar (5%) biomixture, which showed the highest organic-carbon-partition coefficients (K_{oc}) and/or K_d values amongst all biomixtures for all pesticides. Therefore, these biomixtures were found to be the

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most promising substrates amongst the tested ones for a novel biobed setup and can be used as effective and alternative adsorbents for removing pesticides from percolating water in biofilters.

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1. Introduction

Worldwide, water contamination from agricultural use of pesticides has received increasing attention within the last decades. In general, sources of pesticide water pollution are categorized into diffuse (stemming from treated fields) and point sources (stemming from farmyards and spillages). Point sources typically contribute 40 to 90% of contamination of natural water resources (Castillo et al., 2008; Karanasios et al., 2010). They mainly arise from on-farm activities, such as filling, mixing, and washing of sprayer equipment (De Wilde et al., 2009). Mitigation or prevention of point sources can be achieved by implementing best management practices, or by using advanced depurification systems based on sophisticated physical, chemical, and/or biological methods to treat any remnants of pesticides on farm (De Wilde et al., 2008). To overcome these limitations, the “biobed” concept was developed in Sweden in the early 1990s to establish an environmentally sustainable low cost technology, which can be easily installed and maintained by the farmers (Torstensson and Castillo, 1997). The principal of the biofilter is that pesticide remnants (aqueous solutions of pesticides stemming from sprayer dead volume, washing operations, spillages, etc.) are percolated over a bioactive matrix, where pesticides are sorbed and degraded. Biofilters may function without any outflow of water, if enough evaporation occurs from the system to eliminate the excess water in the system.

In general, two processes occur simultaneously within the biobed system: i) sorption of the pesticide to the biomixture material, which reduces the pesticide concentration within the liquid phase and therefore reduces leaching and toxic effects for microbes, and ii) degradation which reduces the load directly (Castillo et al., 2008; Karanasios et al., 2010).

Adsorption is considered to be one of the most effective physical processes for pesticide removal (De Wilde et al., 2009; El Bakouri et al., 2007). Hence, there is a growing demand to find relatively efficient, low cost and easily available adsorbents for the adsorption of pesticides for such setups. Although the conventional biomixture used in this system is soil, peat and straw, several recent publications reported the use of low-cost and locally available adsorbents e.g. garden waste compost, cow manure, coconut chips, raw and bio transformed olive cake, mushroom substrate, wood sawdust, grape marc, or sewage sludge (De Wilde et al., 2008; Marín-Benito et al., 2012b and 2014; Rodríguez-Cruz et al., 2007), which improved the sorption and degradation behaviour of the studied pesticides even when the pesticides were added in repeated applications and high dosages. Even if some studies already analyzed sorption and mobility of pesticides in different substrates used for biopurification concepts (e.g., Albarrán et al., 2004; El Bakouri et al., 2007) more investigations are needed for new substrate combinations and different target pesticides.

In the present study, the biomixture was prepared from two bioenergy residues, namely biochar and digestate. Biochar as an anthropogenic pyrogenic solid carbon source has been proven to be a good replacement of peat in horticultural media (Tian et al., 2012) and might therefore be also suitable for biopurification systems. The main process induced by the addition of biochar into the matrix for biopurification systems is strong sorption of the pesticides which lead to the development of non-extractable residues and reduced bioavailability over time (Spokas et al., 2009; Tatarková et al., 2013). Several studies reported that biochar enhanced sorption of pesticides by 400–2500 times compared to soils without biochar addition (Yang and Sheng, 2003; Yu et al., 2010). Loganathan et al. (2009) and Kookana (2010) observed that biochar amendment was even effective in low dosages (<1% w/w)

for the sorption of polar and non-polar pesticides if compared to the sorption in the reference soil. The high sorption capacity of biochar for different pesticides is mainly attributed to its aromaticity, pyrolysis temperature and high specific surface area (Accardi-Dey and Gschwend, 2003). For example, high temperature biochar is characterized by highly condensed aromatic structures, which will lead to surface adsorption of the pesticides whereas hydrophobic partitioning into the amorphous carbon and different site specific interactions with functional groups can be the principle sorption mechanisms for low-temperature biochar (Chun et al., 2004). Additionally, most studies focused on the adsorption processes but did not analyze the desorption mechanism, which is a key process affecting pesticide behaviour in soils and controls the predisposition of a pesticide to be degraded and/or leached at different times (Boivin et al., 2005). This process is equally essential in the assessment of biochar addition in biopurification systems. Especially, the entrapment of organic compounds into biochar micropores can cause pore deformation and changes, which may induce desorption hysteresis.

Digestate as a source of easily available carbon has been investigated with respect to its influence on the microbial activity and microbial growth by e.g. respiration studies (e.g., Mukherjee et al., 2016a). Yet, to our knowledge no study reported on pesticide sorption–desorption properties for digestate amended soils so far.

Therefore, the aim of this study is to analyze the pesticide sorption–desorption behaviour in six different soil/amendment (biochar and digestate) biomixtures including reference soil (without amendment) in laboratory experiments. Additionally, the effects of different biochar and digestate dosages were tested in combination with pesticides of varying chemical properties (bentazone, boscalid, and pyrimethanil). Based on the experimental findings, guidance for appropriate soil/substrate (biochar and/or digestate) biomixtures will be provided, which will help to set up efficient biopurification (biobed) systems for a wide range of pesticides.

2. Materials and methods

2.1. Substrates

A loamy sand topsoil (0 to 10 cm depth) from Kaldenkirchen, Germany (51°19'13 N and 6°11'47E) (Gleyic Cambisol) was used as basis for the soil biomixtures. The soil contained 73.3% sand, 23.1% silt, 4.9% clay, and 0.8% organic matter. A full description of the test site can be found in Karlsson et al. (2016). The soil was mixed with two different organic amendments namely, low temperature biochar (BC) and digestate, each in different mixing ratios. The BC originates from slow pyrolysis processes (400 °C) using Pine woodchips as feedstock and the digestate added was obtained from biogas production using maize silage (60%), chicken manure (4%), as well as beef (20%) and pig urine (16%) as feedstock (% based on dry matter). The main physico-chemical properties of the raw substances and soil biomixtures used for the experiment are listed in Tables 1 and 2. It has to be noted that for the experiments already 6 months aged soil-biomixtures were used for being more representative for the long-term use of the biopurification matrix.

2.2. Pesticides

Three different pesticides were used in the experiments, two fungicides (pyrimethanil and boscalid) and one herbicide (bentazone). These pesticides were selected based on their different environmental properties, namely persistence in soil and extent of sorption to soil. All

Table 1

Main physico-chemical properties of the native soil, biochar and digestate used for incubation. (BC = low temperature biochar).

Material	Soil	Black Carbon (BC)	Digestate
Source (location, texture)/raw materials	Kaldenkirchen (loamy sand)	Woodchips (pine)	Maize-silage, chicken manure and beef waste
pH (in 1:2 soil/CaCl ₂ solution)	6.1	7.8	8.7
Lignin content (in % w/w dry matter)	NA	NA	18 ± 2
C _{org} (in % w/w dry matter)	0.82	76	40
Total N content (%)	0.08 ± 0.01	0.54 ± 0.05	6.51 ± 0.02
Surface area N ₂ (m ² g ⁻¹)	2.0	231	3.1
Surface area CO ₂ (m ² g ⁻¹)	–	634	38
DOC (mg L ⁻¹)	3.4 ± 1.1	4.0 ± 0.4	1302
SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	6.5	1.3	6.0

NA = Not applicable; – = Not determined.

pesticide standards including internal standard (Pyrimethanil-d5) (>99% purity) were purchased from Dr. Ehrenstorfer GmbH (Germany). Stock solutions were prepared in methanol (Merck Lichrosolv, ≥99.9% purity). Working solutions were prepared by dilutions of stock solutions with an aqueous 10 mM CaCl₂ solution. The percentage of solvent in the final pesticide solution was <0.1%. The standard stock and working solutions were stored at 4 °C prior to the experiment. The physico-chemical characteristics of the three compounds are provided in the supplementary information (Table S1).

2.3. Characterization of used soil-biomixtures

Extractable dissolved organic carbon (DOC) from biomixtures was characterized according to Cox et al. (2004). To this aim, 10 g dry mass equivalents of soil-/biomixture and 20 mL 10 mM CaCl₂ were mixed in a jar and placed on a horizontal shaker at 225 rpm (SM25, Edmund Bühler) for 10 min at 20 ± 2 °C. Subsequently, the soil–water slurry was centrifuged (Allegra 6 KR, Beckman Coulter Inc. CA, USA, GH-3.8 Swinging-bucket Rotor) for 15 min at 2910 × g and the supernatant was filtered through a 0.45-µm sterile cellulose acetate membrane filter. DOC was measured with a TOC analyser 5050 A equipped with an autosampler ASI-5000 A from Shimadzu (Kyoto, Japan) after acidification and purging the samples for 1 min.

UV absorbance at 254 nm (UVA₂₅₄) was measured with a Uvikon 860 UV/Vis spectrophotometer (Tegimenta AG, Rotkreuz, Switzerland), and divided by the respective DOC concentrations to give the DOC specific UV-absorbances at 254 nm (SUVA₂₅₄) (Mukherjee et al., 2016a, 2016b). The pH of the soil-/biomixtures was determined by equilibrating soil-/biomixture with 10 mM CaCl₂ at a 1:2 soil/solution ratio (w/v) and was measured with a portable pH-meter (Orion 3-star, Thermo Electron Co., USA) using a glass electrode.

Effective cation exchange capacity (ECEC) of soil (-biomixtures) was determined according to Luer and Böhmer (2000): In a first step 2.5 g soil was equilibrated with 10 mL 1 M NH₄Cl for 24 h. Subsequently, a folded paper filter (640d, Macherey-Nagel, Düren, Germany) was wetted with 1 M NH₄Cl and placed in a filter funnel. The wet soil was completely transferred to the filter and percolated with 1 M NH₄Cl until a volume of 100 mL percolate was collected. Exchangeable cations (Al³⁺, Ca²⁺, K⁺, Mg²⁺, Na⁺) were determined in the filtrate using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Ciros CCD, SPECTRO Analytical Instruments GmbH, Kleve, Germany).

Table 2

Main physico-chemical properties of the soil-biomixtures for the Kaldenkirchen (KK) soil (loamy sand), BC = low temperature biochar and DG = digestate. The percentage indicates the mass ratios (w/w dry mass) in the mixtures.

Soil substrate composition	pH	ECEC (cmol _c kg ⁻¹ soil)	C _{org} (%)	Surface area N ₂ (m ² g ⁻¹)	Extractable DOC (mg L ⁻¹)	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)
Reference soil (KK)	6.1	4.3	0.82	2.0	3.4 ± 1	6.5
5.0% BC	6	8.2	4.8	8.6	3.5 ± 0.5	13
5.0% DG	6.1	8.2	2.8	3.5	9.7 ± 0.2	17
30% DG	6.2	17	12	3.3	42 ± 3	25
5% DG & 5% BC	6.0	10	6.7	6.9	2.6 ± 0.2	11
30% DG & 5% BC	6.5	18	16	4.2	4.9 ± 0.3	9

The specific surface area (SSA) of the soil and biomixtures was determined by the Brunauer, Emmett and Teller (BET) gas adsorption method for dry surface area measurement on a previously degassed 0.2 g sample at 80 °C for 24 h. The principle of measurement is based on nitrogen adsorption–desorption isotherms at 77 K within the 0.03–0.3 relative pressure range (AUTOSORB-1, Quanta chrome apparatus).

Organic carbon of soil and biomixtures was measured with a Leco RC 612 multiphase carbon determinator (LECO instrumentation GmbH, Germany) at the central chemical laboratory (ZEA-3) of the Forschungszentrum Jülich GmbH.

2.4. Equilibrium adsorption experiments

All equilibrium sorption–desorption experiments were performed in accordance with the OECD guideline 106 (OECD, 2000). The experiments consisted of five different biomixtures and one reference soil (see Table 2), whereby all combinations were analyzed in triplicates. Blank soil (without any pesticide) was included in the experiments to check for artifacts and matrix effects caused by them in the analytical method. Additionally, control samples with pesticides but without sorbents such as soil, digestate, or biochar were analyzed on all equipments (shaken for 168 h) to test the stability and their possible adsorption to the batch container surfaces. Neither significant sorption or metabolization could be detected in this process.

Pesticide loads were calculated according to their recommended field application rates (960 g ha⁻¹ for bentazone, 100 g ha⁻¹ for boscalid, and 800 g ha⁻¹ for pyrimethanil) assuming a mixing depth of 5 cm into the soil and a soil bulk density of 1.5 g cm⁻³. To cover a broader spectrum of concentrations for the sorption/desorption study these concentrations were multiplied by a factor of 0.5, 1, 2, 4, and 6. The resulting initial pesticide concentrations (C_i) for the experiment were therefore 7.10, 14.2, 28.4, 57.0, and 85.2 µg L⁻¹ for bentazone, 7.0, 13.0, 23.0, 43.0 and 66.0 µg L⁻¹ for pyrimethanil and 0.71, 1.43, 2.85, 5.70, and 8.54 µg L⁻¹ for boscalid, respectively assuming a 1:100 soil (and biomixtures)/solution ratio. This ratio was selected due to preliminary experiments, which indicated that strong sorption of the pesticides in biochar based biomixtures occurred and that at least 50% of the added pesticide should not be adsorbed, and therefore, be available for analysis as recommended by the OECD guideline.

Equilibrium adsorption experiments were conducted at room temperature (20 ± 2 °C). In total 270 centrifuge tubes (Falcon Corning

centrifugation tubes, Corning, NY, USA) were filled with 1 g biomixture (dry-mass) and the final volume was filled with 100 mL 10 mM CaCl₂. Analytical quality assurance data have shown that recovery of pesticides (based on active ingredient) after mixing the spiked matrix (at concentrations of 0.7, 7.0, and 70.0 µg L⁻¹) to the soils, ranged from 82.3 to 102.4% for soil and 80.0 to 86.2% for biomixtures. The sorption equilibrium time for pesticides was investigated in a preliminary study. According to the results of the kinetic study and in order to achieve a compromise between sorption efficiency and the duration of the full analysis, 168 h were selected as “equilibrium time” for obtaining the adsorption isotherms of all pesticide using 1:100 soil/-biomixture solution ratio. After reaching pseudoequilibrium, <5% variation of pesticide concentration in the solution was observed. A number of sorption studies have been documented, which show considerable variation in the time needed to establish adsorption equilibria for pesticides (Cabrera et al., 2014; De Wilde et al., 2008; Vryzas et al., 2007). When equilibrium conditions are reached, the adsorbate molecules in the solutions are in a state of dynamic equilibrium with the molecules adsorbed by the sorbent. According to Aubee and Lieu (2010); Boivin et al. (2005) and Vanni et al. (2006), no measurable degradation occurred for these studied pesticides during the equilibration time of 168 h. Based on the dissipation study with the same sorbents (Mukherjee et al., 2016b) <5% degradation is to be expected for all pesticides during this time period. Samples were shaken continuously for 168 h on a horizontal shaker at 225 rpm (SM25, Edmund Bühler). After that, the samples were centrifuged for 15 min at 2910 × g and the supernatant was decanted. Equilibrium concentrations (C_e) of pesticides in the supernatant were measured with ACQUITY UPLC (Ultra Performance Liquid Chromatography) system coupled to a Xevo TQ-S triple quadrupole mass spectrometer (both Waters, Eschborn, Germany). Finally, a 10 mL aliquot from supernatant was stored as backup for pH measurement. Percentage of pesticides adsorbed on the different soil/-biomixtures was calculated by:

$$Ads[\%] = \left[\frac{(C_i - C_e)}{C_i} \right] \times 100 \quad (1)$$

where C_i is the initial and C_e (µg L⁻¹) is the equilibrium pesticide concentration in the water phase, respectively. C_s is the amount of sorbed pesticides (µg kg⁻¹) as calculated by:

$$C_s = (C_i - C_e) \times \frac{V}{M} \quad (2)$$

where V is the volume of pesticides solution (L) and M (kg) is the mass of soil/-biomixture.

2.5. Equilibrium desorption experiments

Equilibrium desorption experiments were conducted immediately after the sorption experiments according to the OECD guideline 106 (OECD, 2000) by the decant and refill method. For all three steps of the desorption study 60 mL 10 mM CaCl₂ solution was added to centrifugation bottles, shaken for 24 h, centrifuged and solution was sampled as described before. The shorter time period for desorption was chosen due to practical reasons. Centrifugation tubes were weighed at the start and end of each sorption–desorption step to account for residual solution in the centrifugation tubes. For the desorption study, only the maximum initial pesticide concentrations (85.2 µg L⁻¹ for bentazone, 66.0 µg L⁻¹ for pyrimethanil and 8.54 µg L⁻¹ for boscalid) were chosen because for the lower initial concentrations the expected actual concentrations were lower than the limit of detection of the analytical method.

2.6. Analytical procedures

The analysis of pesticides in the supernatant from both experiments were carried out by Ultra Performance Liquid Chromatography (UPLC) – electrospray (ESI) – mass spectrometry (MS) using an ACQUITY UPLC system coupled to a Xevo TQ-S triple quadrupole mass spectrometer.

UPLC analyses were run at 40 °C column temperature, using a reversed-phase Kinetex Core Shell PFP (pentafluorophenyl) column with TMS endcapping (100 mm × 2.1 mm × 2.6 µm, Phenomenex, Aschaffenburg, Germany). Solvent A was Millipore water (Millipore GmbH, Schwalbach, Germany) buffered with 0.1% formic acid (pH 3.0) for all pesticides. As solvent B methanol (Merck Lichrosolv, ≥99.9% purity) was used for pyrimethanil, and acetonitrile (Merck Lichrosolv, ≥99.9% purity) for bentazone and boscalid. The separation was performed with the following gradient program: 0 to 1.7 min: 34% solvent B, 1.7 to 2.9 min: linear from 34 to 100% solvent B, 2.9 to 3.3 min hold 100% solvent B, 3.3 to 4.5 min switch back to starting conditions and hold for 2 min. The flow rate was 0.60 mL min⁻¹ and the injection volume was 10 µL.

Electrospray ionization parameters were: desolvation temperature 600 °C, capillary voltage 3.6 kV, cone voltage 45 V, source temperature 150 °C. Nitrogen was used as desolvation and cone gas at a flow of 1000 and 150 L h⁻¹, argon was used as collision gas at flow of 0.15 mL min⁻¹. Positive ESI mode was applied for boscalid and pyrimethanil, negative ESI mode for bentazone. Three transitions were considered for each compound (for quantification in bold): Bentazon 239 Da → 132 Da (26 V), 175 Da (18 V) and 197 Da (24 V); Boscalid 343 Da → 112 Da (18 V), 140 Da (20 V) and 307 Da (18 V) and Pyrimethanil 200 Da → 82 Da (26 V), 107 Da (22 V) and 183 Da (22 V), in brackets corresponding collision energies, respectively. As internal standard D5-pyrimethanil was used: 206 Da → 173 Da (26 V), 108 Da (24 V) and 187 Da (26 V). Calibration curves (R² > 0.99) were established from 6 concentrations respectively. The limits of quantification (LOQs) and limits of detection (LODs) for the pesticide concentrations were 1.0 and 0.25 pg mL⁻¹ for bentazone, and 5.0 and 2.0 pg mL⁻¹ for boscalid and pyrimethanil, respectively.

2.7. Equilibrium adsorption–desorption isotherms

Equilibrium sorption–desorption isotherms were used to describe the sorption/desorption characteristics of the different soil/-biomixtures. Three different sorption models (Henry, Freundlich, and Langmuir) were used to fit the experimental data. The simplest sorption model (Henry-model) assumes a linear sorption behaviour over the entire concentration range and can be expressed by:

$$C_s = K_d \cdot C_e \quad (3)$$

where K_d (L kg⁻¹) is the distribution coefficient.

The Freundlich model can be written as:

$$C_s = K_f \cdot C_e^{1/n} \quad (4)$$

where K_f (µg^{-1/n} L^{1/n} kg⁻¹) is the adsorption coefficient and 1/n (–) is the Freundlich exponent. Hereby, K_f refers to the multilayer adsorption capacity and the Freundlich exponent refers to the adsorption intensity. The range of sorption distribution coefficients K_d were determined by calculating C_s/C_e, for each concentration studied in the batch sorption experiment.

The Langmuir model (Langmuir, 1918) can be expressed by:

$$C_s = \frac{C_{smax} K_L C_e}{1 + K_L C_e} \quad (5)$$

where C_{smax} (µg kg⁻¹) is the maximum sorption capacity of the adsorbent, K_L is the Langmuir sorption coefficient (L kg⁻¹) (constant related to the affinity between the adsorbent and the adsorbate).

All models were fitted on the experimental data using the Excel solver routine minimizing the sum of squared residuals (SSR) between observed and simulated concentrations.

The sorption partition coefficient K_d is generally related to the fraction of organic carbon associated with the sorbent to yield an organic-carbon-partition coefficient, K_{oc} (Majumdar and Singh, 2007) and was calculated by:

$$K_{oc} = \frac{K_d \cdot 100}{\%OC} \quad (6)$$

where, % OC is the percentage of organic carbon. The C-normalized partitioning coefficient (K_{oc}) is generally assumed to be constant for a particular chemical when sorption is only occurring on the soil organic matter (De Wilde et al., 2009).

As the isotherms of the Freundlich and Langmuir model are not linear, the K_d values were calculated for all tested sorption concentrations separately. Mean K_{oc} were determined from their corresponding mean K_d values.

Desorption isotherms were calculated using the same models as for the adsorption and the hysteresis coefficient between adsorption and desorption was determined according to Cabrera et al. (2014) by:

$$H = \frac{1/n_{des}}{1/n_{ads}} \quad (7)$$

In general, lower H values indicate increased difficulty of the sorbed pesticide to be desorbed from the matrix (Barriuso et al., 1994).

2.8. Statistical analysis

To judge the reliability of the fitted individual parameters, a single-sided t -test was used Eqs. ((8) and (9)):

$$t = \frac{\text{parameter} - \text{value}}{SD(\text{parameter} - \text{value})} \quad (8)$$

$$\text{type-I error rate} = t - \text{distribution}(t, \text{dof}, 1) \quad (9)$$

where, t is the empirical t -value, SD is the standard deviation of parameter value and dof is the degree of freedom. A statistical significance was considered at $p < 0.05$.

3. Results and discussion

3.1. Characterization of soil, biochar and digestate biomixture

All of the biomixtures as well as the native soil showed slightly acidic pH-values ranging from 6.0 to 6.5 (see Table 2), which is expected due to the sandy character of the Kaldenkirchen soil. Additionally, digestate based biomixtures had highest pH-values, which are caused by the alkaline character of the digestate. The biochar soil biomixture had the highest surface area of $8.60 \text{ m}^2 \text{ g}^{-1}$ of all used soil biomixtures, reflecting the high specific surface area of pure biochar ($231 \text{ m}^2 \text{ g}^{-1}$).

Compared to pH-values, extractable DOC differs greatly between the soil-/biomixtures (Table 2), whereby digestate based biomixtures showed highest extractable DOC. For these biomixtures extractable DOC increased also with increasing digestate content, whereas biochar based biomixtures had much lower extractable DOC. Interestingly, extractable DOC dropped in the biochar/digestate soil biomixtures compared to the digestate alone soil biomixtures by a factor of >1.8 . Based on these data, biochar seems to act as a sink of DOC, as already suggested by Mukherjee et al. (2016a).

3.2. Determination of suitable soil: Solution ratio

Four different soil-/biomixture/solution ratios (1:10, 1:25, 1:50, 1:100) and nine equilibration time lengths (4, 8, 15, 24, 48, 72, 96, 120 and 168 h) were tested in a preliminary study for selecting the suitable ratio and time for the batch equilibrium adsorption experiment. Sorption capacity (%) of the reference soil and 30% DG and 5% BC biomixture was plotted as a function of the equilibrium time (h) for the lowest initial pesticide concentrations (Fig. 1). As can be seen, classically recommended equilibrium times of <48 h did not yield equilibrium sorption for boscalid in the reference soil, whereas bentazone and pyrimethanil are already in equilibrium at this stage. For the 30% DG and 5% BC biomixture equilibrium incubation time needs to be also longer for bentazone and pyrimethanil and equilibrium is reached at about 168 h. It can be hypothesized that the adsorption of these pesticides on the studied organic amendment is a multi-step process, involving fast adsorption on the external surface accompanied by a slow intra-particle diffusion and chemical interaction in the fine matrices (adsorption of the pesticide at the active sites via hydrophobic and/or hydrophilic interaction), which is in line with the observations of El Bakouri et al. (2007 and 2009). After 168 h of shaking the amount of bentazone sorbed on the reference soil was 69% of the initial concentration (matrix to solution ratio = 1:10), and decreased to 5% when the ratio was set to 1:100. Sorption of bentazone in the 30% DG and 5% BC biomixture decreased from 72% to 45% when biomixtures/solution ratio decreased from 1:10 to 1:100.

Additionally, it can be seen that boscalid and pyrimethanil showed strong sorption affinity towards the biomixture. For the reference soil, adsorption of boscalid was 49% of the initial concentration ($8.54 \mu\text{g L}^{-1}$) when the soil/solution ratio was set to 1:10 and dropped to 18% when ratio was changed to 1:100. Yet, for the tested biomixture (30% DG and 5% BC) adsorption of boscalid decreased only slightly from 98% (1:10) to 96% using the 1:100 ratio. Sorption of pyrimethanil dropped dramatically from 72% (1:10) to 3% (1:100) on the reference soil. In contrast, for the 30% DG and 5% BC soil biomixture, again only a slight decrease of sorption was seen for decreasing soil-solution ratios (99% to 95%).

3.3. Equilibrium adsorption isotherms

The sorption (and desorption) behaviour as well as the fitted isotherms of all pesticides on each soil-/biomixtures are depicted in Figs. 2–4 and the fitted sorption parameters are listed in Table 3. As an indicator of the goodness of the fits the R^2 as well as the sum of squared residuals (SSR) are also listed. Irrespectively, of the carefully performed preliminary experiments, recording of sorption data of all pesticides to the 5% BC biomixture was not possible due to analytical limitations, and therefore, no sorption-desorption coefficients could be determined for those combinations. The values of the coefficient of determination (R^2) for almost all other combinations were moderate to high, and quite similar between the Freundlich and Langmuir model.

For boscalid and pyrimethanil, sorption was described using the linear Henry model with R^2 exceeding 0.88 (see Table 3), as well as the Freundlich and Langmuir model. Even if the R^2 is already high for the linear model fit, fitting error decreased for the more complex models, as indicated by a decrease of the sum of squared residuals (SSR). Additionally, the fits are much closer to the measured/observed values (Figs. 3–4) and represent the adsorption over the concentration range much better. The reason for the better fitting results of the non-linear models may be explained by the specific interactions between polar groups of the pesticide and the organic matter of the substrate, as explained by De Wilde et al. (2009). Spectroscopic observations emphasized the prominent role of hydrogen bonding and electron donor-acceptor reactions (via charge-transfer processes through free radical intermediates), for instance in phenylurea-soil organic matter interactions (Senesi and Testini, 1983; Spurlock and Biggar, 1994).

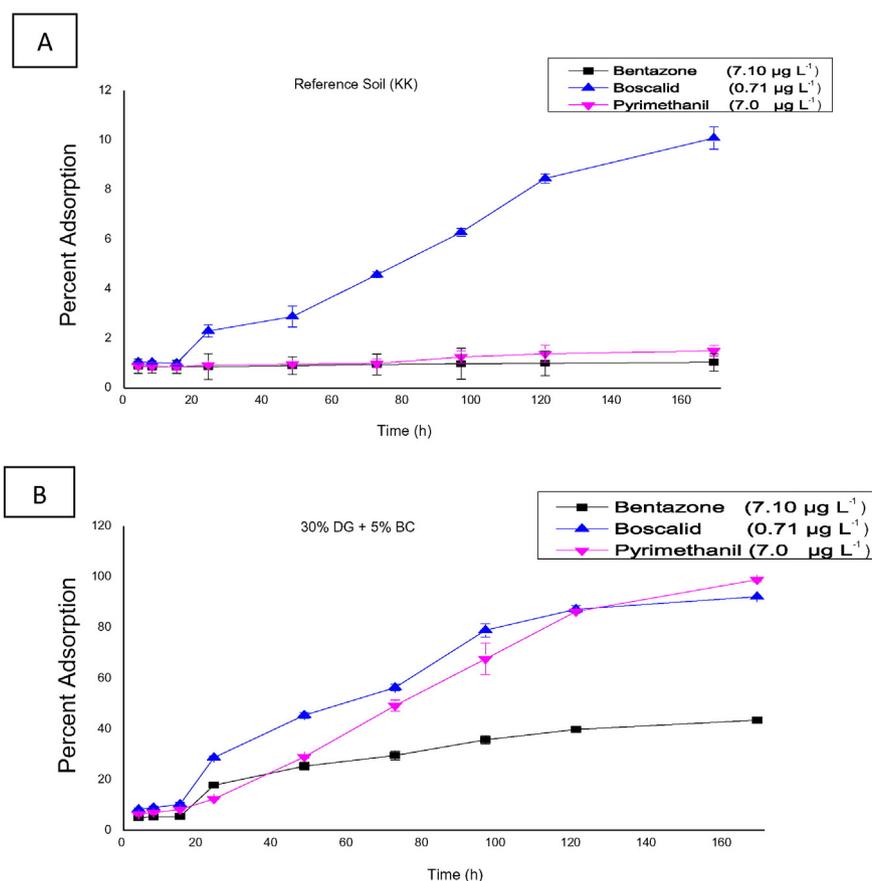


Fig. 1. Sorption kinetics of bentazone, boscalid and pyrimethanil (after an equilibrium time of 168 h and a 1:100 soil/solution mixture) on reference soil (A) and soil amended with 30% DG and 5% BC (B). Data points represent means ($n = 3$) and error bars indicate standard error. Reference soil (KK) = loamy sand, BC = low temperature biochar, and DG = digestate (the percentage indicates the mass ratios in the mixtures).

Hydrophobic interactions were found to be the most vital interaction mechanism for non-polar pesticides (Torrents et al., 1997). Consequently, also the adsorption coefficients of boscalid and pyrimethanil (K_{fads} value) in our experiment were higher than for bentazone (see Table 3). Several other studies have already reported that differences in pesticide sorption capacity are influenced by different qualities of organic residues and soil depending on the hydrophobic characteristics of the compounds (Marín-Benito et al., 2012a, 2012b). The results obtained in these studies differed from results reported by Rouchaud et al. (1996) and Tejada et al. (2011) who showed the higher effectiveness of the organic soil amendments (cow manure, pig slurry, compost, green manure and municipal solid wastes) for the removal of the pesticides.

For boscalid, sorption for all soil-biomixture combinations was fairly well described by the linear model with $R^2 > 0.92$ and only the biomixtures based on digestate and biochar yielded better results (based on SSR values) using the Freundlich and Langmuir model. Looking at the plotted data for boscalid and the fitted model results it becomes clear that the linear model describes the system less well for the pyrimethanil data, for which better fits were obtained using the Freundlich and/or Langmuir models for all tested soil-biomixtures. This good fit is also indicated by the fairly low SSR. Compared with pyrimethanil and boscalid, bentazone indicated a different sorption pattern, which could not be described by the linear model except for the combined digestate-biochar biomixtures. All other combinations could only be described better using the Freundlich and Langmuir concept, whereby the R^2 is much lower and ranges between 0.61 and 0.75. Looking at the plotted data (Fig. 2) it becomes obvious that for these biomixtures, a common phenomenon is observed, as sorption increased steeply linear up to the third highest concentration used ($28.4 \mu\text{g L}^{-1}$)

and then stayed nearly constant for the two higher concentrations tested. This might indicate a kind of sorption saturation plateau for bentazone in these biomixtures, which should be better described by the Langmuir model, which assumes a saturation of the sorption sites for higher concentrations.

Analyzing the fitted sorption parameters it becomes evident, that the different biomixtures show different sorption properties for pesticides. For pyrimethanil the K_d value calculated from the linear model did not increase for the 5% digestate addition compared to the native soil and only doubled in case of 30% DG addition. Addition of biochar on the other hand significantly increased K_d values to 1584 L kg^{-1} for the 5% DG + 5% BC and even to 2153 L kg^{-1} for the adding of 30% DG + 5% BC ($p < 0.05$; t -test). On the contrary, K_{OC} values dropped by more than three times for the low DG addition and even up to >7 times for the higher DG loads, which might indicate that digestate-derived DOC competed with pyrimethanil for sorption sites in the digestate-soil biomixtures. (Loganathan et al., 2009; Mukherjee et al., 2016b). A comparable correlation for pyrimethanil and other fungicides sorption on different types of mushroom substrates was found by Marín-Benito et al. (2012a, 2012b), whereby their relationship was more linear with lower DOC and higher with humified organic carbon content of the substrates. On the other hand, mixing of biochar to the digestate increased K_{OC} values 43 times for the 5% DG + 5% BC and 24 times for the 30% DG + 5% BC. This may be explained by the high affinity of biochar for pyrimethanil and a beginning saturation of biochar sorption sites with digestate-derived DOC in the high digestate-biochar-soil biomixture.

The boscalid data show the same general trend for the K_d and K_{OC} values, whereby K_d values are generally higher than for pyrimethanil. For example K_d for the reference soil is 4.54 L kg^{-1} for pyrimethanil

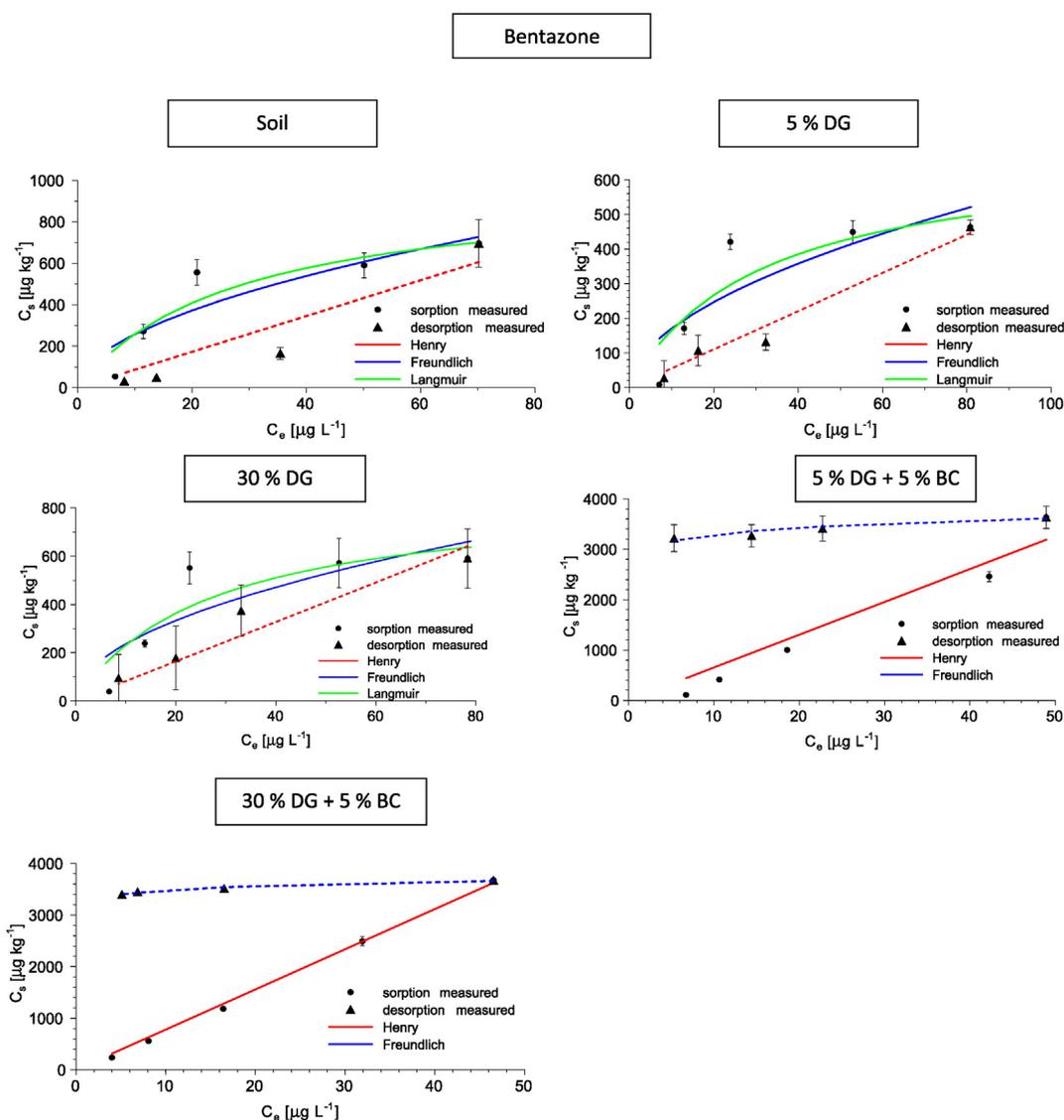


Fig. 2. Adsorption (solid lines fitted with Henry, Freundlich and Langmuir model) and sequential desorption (dashed lines fitted with Henry and Freundlich model) isotherms of bentazone for the different soil/amendment mixtures. Data points represent means ($n = 3$) and error bars indicate standard error. C_s denotes sorbed concentrations and C_e indicates equilibrium water phase concentration. Soil (KK) = loamy sand, BC = low temperature biochar, and DG = digestate (the percentage indicates the mass ratios in the mixtures).

and 19.3 L kg^{-1} for boscalid. The stronger sorption of boscalid has been already reported in several studies (Chen and Zhang, 2010; Karlsson et al., 2016), and can be explained by the lower water solubility and higher hydrophobicity of this substance (see also Table S1). The changes in normalized K_{OC} values are significantly lower ($p < 0.05$; t -test) in relative terms for boscalid compared to pyrimethanil. For the addition of 5% DG the boscalid K_{OC} value drops only by 36% and decreases with higher digestate loads (30%) to 77%, as compared with the one of the reference soil. Adding biochar and digestate at the same time leads to a 6.7 and 5.5-fold increase of the K_{OC} for the 5% DG + 5% BC and 30% DG + 5% BC biomixtures, respectively. This means that the normalized sorption capacity is by more than a factor 1.4 smaller for boscalid in these biomixtures compared with the one of pyrimethanil, which is in contradiction to previously reported sorption coefficients for these two pesticides on natural soils (Table S1).

Bentazone sorption could not be described by one model for all biomixtures, making an interpretation more difficult. Yet, in general bentazone sorption was less strong, as indicated by lower K_d and K_{OC} values as compared with boscalid or pyrimethanil, which is in line with existing results for natural soils (Table S1). For the strongest sorbing biochar + digestate biomixtures, also slightly increased K_d

(65 and 78 L kg^{-1}) but more or less similar K_{OC} values (966 and $470 \text{ L kg}^{-1} \text{ OC}$) were calculated for the lower and higher digestate loads, respectively, in comparison with BC-free soil biomixtures.

For bentazone, the Langmuir model was not applicable to describe sorption on blended biomixture of digestate and biochar, as negative values for Langmuir constants C_{smax} and K_L were obtained, showing the unsuitability of this model for these data (De Wilde et al., 2009). Additionally, soil and digestate based combinations for boscalid could not be described either using this model. This may indicate that monolayer adsorption, assumed in this model, was not valid for these experiments (De Wilde et al., 2009; El Bakouri et al., 2009). On the other hand, the Freundlich model was applicable to describe three biomixture combinations for bentazone and two combinations for boscalid. However, for polar pesticides and metabolites it was shown that the influence of biochar addition to soil with regard to sorption was rather limited (Dechene et al., 2014).

Based on the Freundlich exponent, or more precisely on the inverse of the exponent ($1/n$), isotherms can be classified as an L (non-linear or Langmuir), S (side-by-side association), or C (constant partitioning) type according to Giles et al. (1960). These commonly used isotherms have frequently been found to describe the sorption of other pesticides

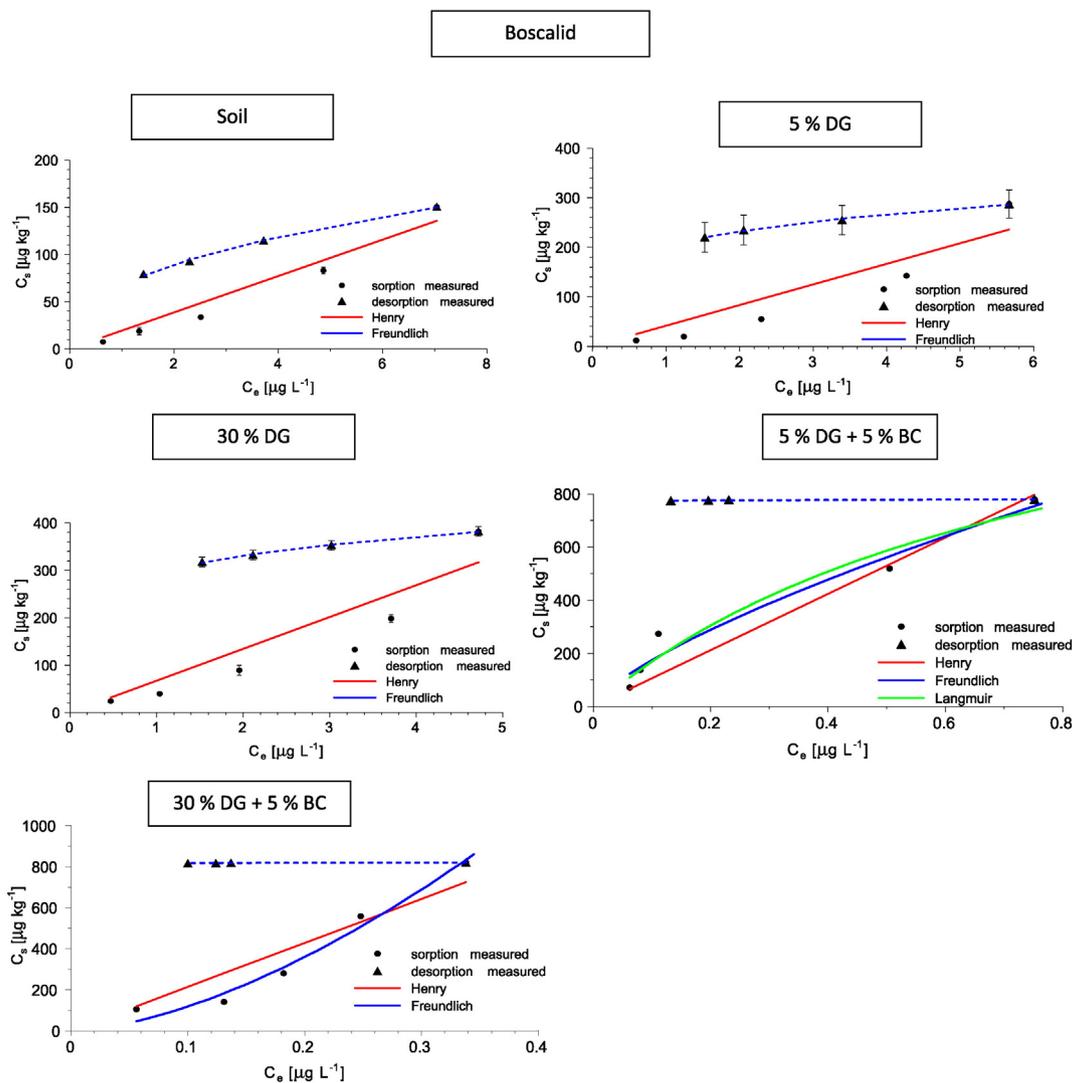


Fig. 3. Adsorption (solid lines fitted with Henry, Freundlich and Langmuir model) and sequential desorption (dashed lines fitted with Freundlich model) isotherms of boscalid for the different soil/amendment mixtures. Data points represent means ($n = 3$) and error bars indicate standard error. C_s denotes sorbed concentrations and C_e indicates equilibrium water phase concentration. Soil (KK) = loamy sand, BC = low temperature biochar, and DG = digestate (the percentage indicates the mass ratios in the mixtures).

on soils, such as triazines, organophosphates, or phenylureas (Wauchope et al., 2002). For the studied pesticides/biomixtures combinations, it was observed that isotherms were of the L-type ($1/n < 1$), which indicates that the pesticides molecules are adsorbed in a horizontal orientation on sorbents/biomixtures with strong intermolecular attraction, without being affected by a strong competition with the solvent molecules, which explains the high affinity of sorbent for solute at low concentrations (Giles et al., 1960).

3.4. Equilibrium desorption isotherms

The equilibrium desorption isotherms for the different biomixtures and pesticides are plotted in Figs. 2–4. The desorption isotherms were fitted using the Henry (linear) and Freundlich equation [Eqs. (3) and (4)]. The Henry desorption ($K_{d \text{ des}}$ and $K_{oc \text{ des}}$) and Freundlich coefficients ($K_{f \text{ des}}$ and $1/n_{\text{des}}$), the coefficient of determination (R^2), the sum of squared residuals (SSR) as well as the hysteresis coefficients (H) are listed in Table 4.

For pyrimethanil, desorption could be described using the linear model for reference soil and 5% DG-soil biomixture only, whereas for the 30% DG and DG/BC based biomixtures the Freundlich model was used. For the Freundlich based desorption, the isotherm is always higher than for the adsorption, which indicates that pyrimethanil cannot be

desorbed well from the 30% DG and DG/BC-soil biomixtures. On the other hand, linear desorption isotherms as observed for the soil and 5% DG biomixture falls close or even below the adsorption isotherm indicating somewhat better desorption from these matrix. Looking at the desorption parameters (Table 4) this pattern is underpinned e.g., the desorption K_d for the soil (3.78) and 5% DG (4.21), which are close to the adsorption K_d (4.54 and 4.93). The hysteresis effect between adsorption–desorption as calculated by Eq. (7) showed lowest H values for the 5% DG + 5% BC and highest for the 30% DG + 5% BC biomixture. As with increasing H values higher desorption is associated, it can be concluded that retention on digestate seems to be less strong as retention on the added biochar.

For boscalid, all desorption experiments could only be described by the Freundlich model. Hereby, strong retention is indicated by always higher desorption isotherms compared adsorption isotherms and extremely low H values were obtained for combinations of 5% DG + 5% BC and 30% DG + 5% BC. This strong sequestration and low desorption characteristics were expected from the physicochemical characteristics of boscalid with its higher molecular weight and low water solubility.

On the other hand, bentazone desorption seems to be influenced strongly by the sorbent properties. For the reference soil and digestate biomixtures (without biochar) desorption is easier than adsorption, as indicated again by the desorption isotherms lying below the adsorption

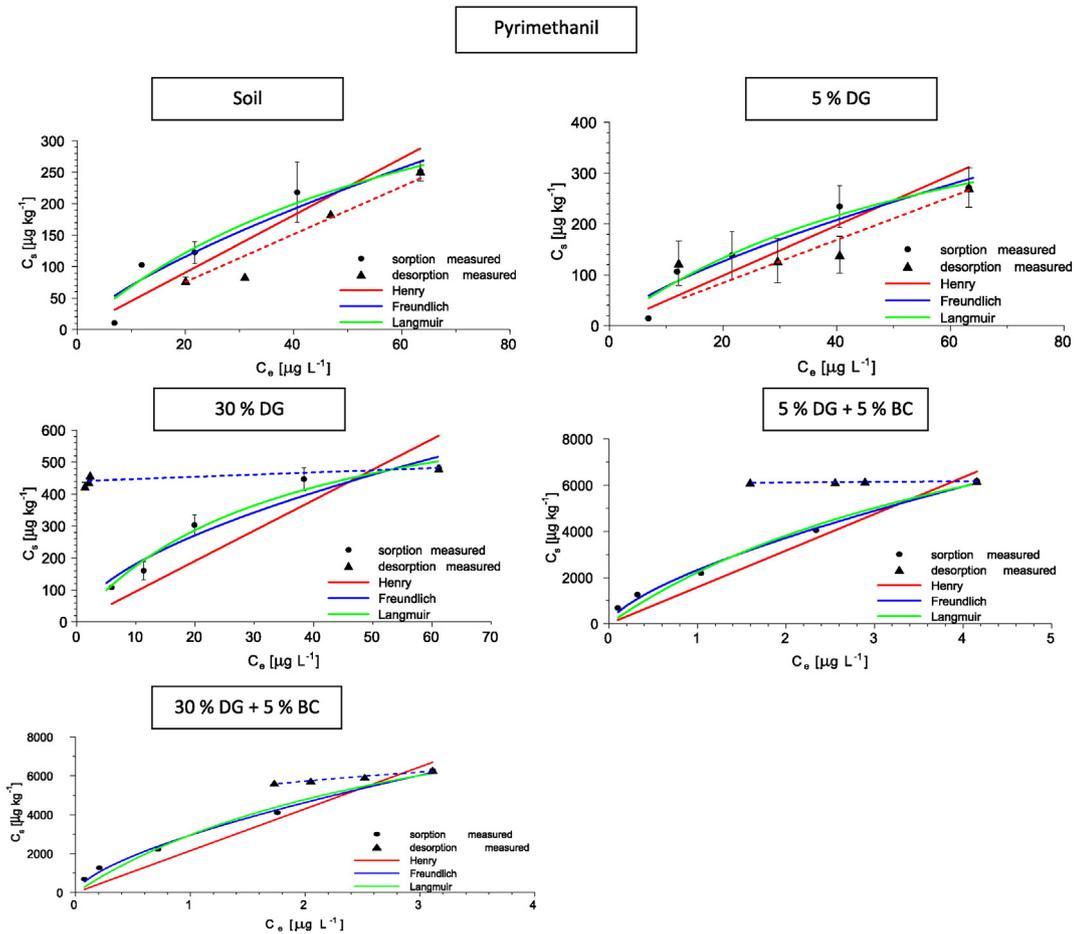


Fig. 4. Adsorption (solid lines fitted with Henry, Freundlich and Langmuir model) and sequential desorption (dashed lines fitted with Henry and Freundlich model) isotherms of pyrimethanil for the different soil/amendment mixtures. Data points represent means ($n = 3$) and error bars indicate standard error. C_s denotes sorbed concentrations and C_e indicates equilibrium water phase concentration. Soil (KK) = loamy sand, BC = low temperature biochar, and DG = digestate (the percentage indicates the mass ratios in the mixtures).

ones, which is in line with the observations of Loganathan et al. (2009). From the physicochemical characteristics (e.g., high water solubility), bentazone would be expected to sorb only weakly and also to be

desorbed better as compared with the other two pesticides studied. Additionally, our findings corroborated with the observations of Gebremariam (2011) and Zhang and He (2013), who hypothesized a

Table 3
Estimated model parameters for the fitted adsorption isotherms of pesticides to different sorbent systems and calculated K_d/K_{OC} values.

Pesticide	Substrate	Henry				Freundlich				Langmuir					
		$K_{d\ ads}$ (L kg ⁻¹)	R ²	SSR	K_{OC} (L kg ⁻¹)	$K_{f\ ads}$ ($\mu\text{g}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$)	$1/n_{\ ads}$	R ²	SSR	K_d (L kg ⁻¹)	K_{OC} (L kg ⁻¹)	$C_{s\max}$ ($\mu\text{g} \text{kg}^{-1}$)	K_L (L kg ⁻¹)	R ²	SSR
Bentazone	KK	NA	NA	NA	NA	49.8	0.53	0.67	45,011	1.1–17.5	133–2132	699	0.03	7	31,218
	5% DG	NA	NA	NA	NA	74.6	0.50	0.65	69,176	6–24.2	207–870	856	0.04	0.65	47,543
	30% DG	NA	NA	NA	NA	75.2	0.54	0.61	54,877	8.1–27	65–212	980	0.03	0.75	38,059
	5% DG + 5% BC	65.1	0.98	515,966	966	NA	NA	NA	NA	16.1–74.2	240–1101	NA	NA	NA	NA
Pyrimethanil	KK	4.54	0.90	5847	550	13.2	0.72	0.83	3241	1.5–9	182–1045	544	0.01	0.88	2436
	5% DG	4.93	0.92	6534	177	14.3	0.72	0.85	3263	2.1–9	76–322	574	0.01	0.90	2275
	30% DG	9.53	0.94	35,383	76	47.8	0.58	0.88	7025	7.8–18.2	63–146	791	0.03	0.95	3026
	5% DG + 5% BC	1584	1.00	1,422,997	23,500	2329	0.67	0.99	126,670	1487–6880	22,069–102,077	13,405	0.20	0.98	459,309
Boscalid	KK	19.3	0.98	635	2337	NA	NA	NA	NA	11.4–21.4	1385–2591	NA	NA	NA	NA
	5% DG	41.6	0.93	6728	1497	NA	NA	NA	NA	16–51	569–1824	NA	NA	NA	NA
	30% DG	67.1	0.92	9577	535	NA	NA	NA	NA	38–81	303–645	NA	NA	NA	NA
	5% DG + 5% BC	1061	0.96	27,473	15,732	928	0.72	0.96	12,835	1028–2457	15,255–36,447	1530	1.24	0.94	15,790
Boscalid	30% DG + 5% BC	2142	0.94	41,777	12,934	4718	1.60	0.97	9002	1073–2424	6481–14,836	NA	NA	NA	NA

NA = not applicable; $K_{d\ ads}$: linear sorption constant. K_{OC} : normalized organic carbon coefficient, calculated for each sorption concentration as $(K_d / \%OC) * 100$. $1/n_{\ ads}$: Freundlich exponent. $K_{f\ ads}$ ($\mu\text{g}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$): Freundlich constant. $C_{s\max}$ ($\mu\text{g} \text{kg}^{-1}$): Langmuir constant representing the maximum sorption capacity relative to the total surface coverage. K_L : Langmuir constant representing the enthalpy of sorption. R²: coefficient of determination. SSR: sum of squared residuals. KK = loamy sand soil, BC = low temperature biochar, DG = digestate (the percentage indicates the mass ratios in the mixtures).

Table 4
Estimated model parameters for fitted desorption isotherms of pesticides and calculated K_d , K_{OC} and H values.

Pesticide	Substrate	Henry			Freundlich			K_d (L kg ⁻¹)	K_{OC} (L kg ⁻¹)	H		
		$K_{d\ des}$ (L kg ⁻¹)	R ²	SSR	$K_{OC\ des}$ (L kg ⁻¹)	$K_{f\ des}$ (μg ^{1-1/n} L ^{1/n} kg ⁻¹)	1/n _{des}					
Bentazone	KK	5.52	0.98	3115	669	NA	NA	NA	NA	3.3–6.5	404–795	NA
	5% DG	8.18	0.94	14,107	295	NA	NA	NA	NA	7.5–11.3	271–408	NA
	30% DG	8.62	0.94	34,665	69	NA	NA	NA	NA	4–10	28–79	NA
	5% DG + 5% BC	NA	NA	NA	NA	2878	0.06	0.78	11,487	74.2–602	2226–8927	NA
	30% DG + 5% BC	NA	NA	NA	NA	3215	0.04	0.96	819	79–664	1285–4006	NA
Pyrimethanil	KK	3.78	0.96	1272	459	NA	NA	NA	NA	3–4	328–474	NA
	5% DG	4.21	0.78	6109	152	NA	NA	NA	NA	3.4–10	124–362	NA
	30% DG	NA	NA	NA	NA	432	0.03	0.54	411	200–302	1594–2409	0.05
	5% DG + 5% BC	NA	NA	NA	NA	6070	0.01	0.83	231	2127–3831	31,561–56,838	0.01
	30% DG + 5% BC	NA	NA	NA	NA	5017	0.20	0.93	882	2021–3246	14,217–19,601	0.31
Boscalid	KK	NA	NA	NA	NA	67	0.41	1.0	6.7	31–56	3748–6776	NA
	5% DG	NA	NA	NA	NA	202	0.20	0.98	14.8	51–144	2698–5179	NA
	30% DG	NA	NA	NA	NA	295	0.16	1.00	5.5	81–208	930–1655	NA
	5% DG + 5% BC	NA	NA	NA	NA	780	0.004	0.85	1.93	3367–5865	49,954–87,014	0.005
	30% DG + 5% BC	NA	NA	NA	NA	823	0.003	0.70	1.02	5962–8166	36,000–49,309	0.005

NA = not applicable; $K_{d\ des}$: linear desorption constant K_{OC} : normalized organic carbon coefficient, calculated for each and every concentration as ($K_d/\%OC$)*100, 1/n_{des}: Freundlich exponent $K_{f\ des}$ (μg^{1-1/n} L^{1/n} kg⁻¹): Freundlich constant. H: hysteresis coefficient. R²: coefficient of determination. SSR: sum of squared residuals. KK = loamy sand soil, BC = low temperature biochar, and DG = digestate (the percentage indicates the mass ratios in the mixtures).

higher desorption (no hysteresis) for polar compounds due to the presence/interference of dissolved organic matter. This is particularly important for the sorption of acidic (anionic) pesticides like bentazone, where this effect can be also attributed to repulsion between negatively charged bentazone molecules and COO⁻ groups of the DOC derived from biomixtures. Basically, the effects of DOC on the sorption-desorption of pesticides and hydrophobic compounds on soils were discussed contradictory by previous researchers (Barriuso et al., 1994; Müller et al., 2007).

4. Conclusions

The selection of appropriate substrates in biobed systems, used for elimination of pesticides from aqueous remnants, is crucial for their effectiveness. Biochar and digestate, from bioenergy production seem to be a promising novel organic amendment for effective biofilter systems because they are widely available and might replace traditional compounds such as peat.

In our batch sorption experiments the best sorption capacities were obtained for pyrimethanil and boscalid when sorbed to digestate and biochar based mixtures. Blank soil without any organic amendment was the less effective adsorbate. Bentazone showed the highest adsorption by blended biomixture of digestate and biochar followed by only digestate based biomixture. 5 and 30% digestate combinations with biochar showed almost similar sorption capacity for bentazone and pyrimethanil respectively. From this we conclude that a biomixture of biochar and digestate significantly increases the adsorption and decreases the desorption potential of pesticides compared to bare soil ($p < 0.05$; t -test).

However, more work is required to analyze the quality of organic carbon as well as other physico-chemical characteristics (hydraulic responses) and their interactions which are fundamental for the setup of an optimal biobed system. It is also imperative to study desorption potential of the metabolites in aged biomixtures for longer time periods (> 1 year). This information will be crucial to assess the availability of aged pesticide residues in biofilter matrix for plant uptake and leaching, after their potential return to topsoil in agricultural fields.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.03.145>.

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