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

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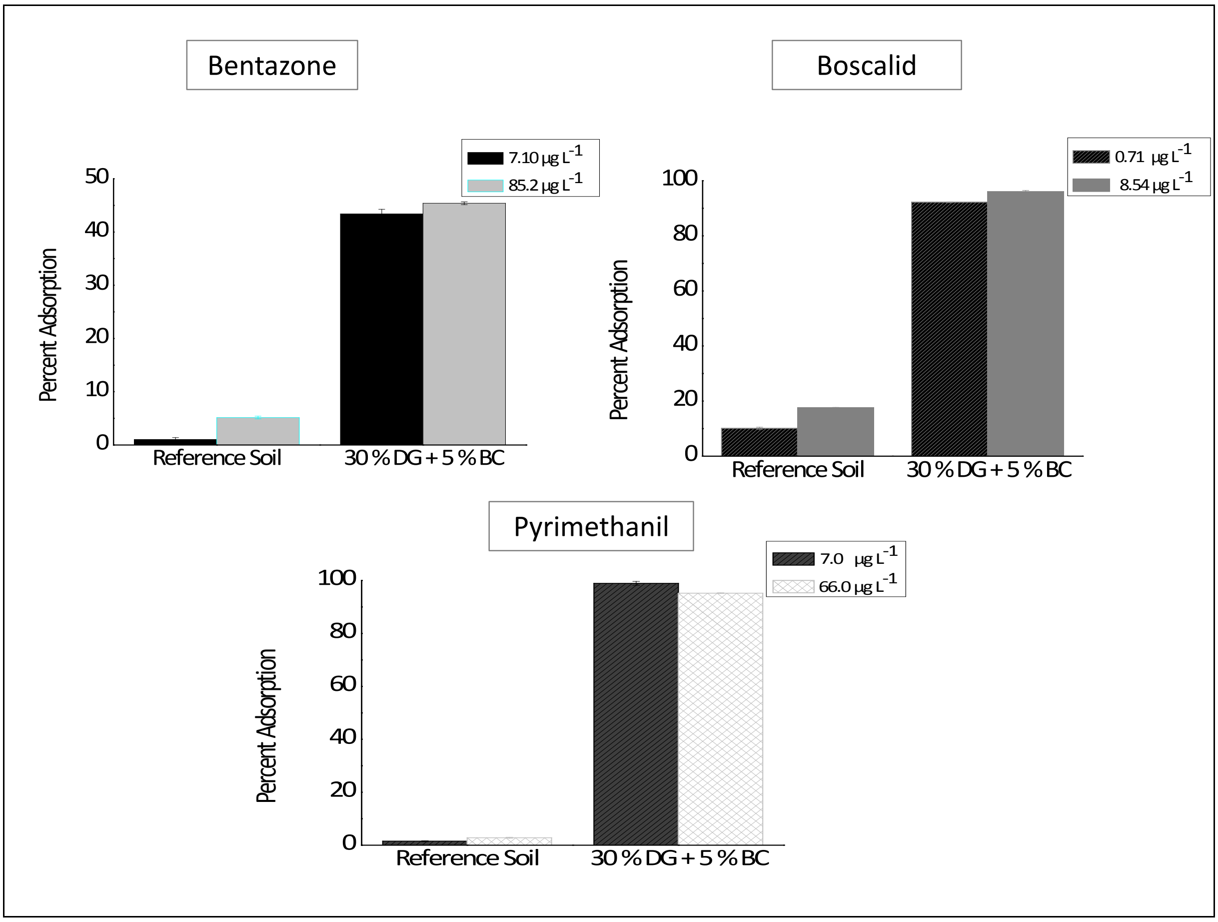
Highlights:

- Biochar and digestate were tested as novel sorbents for biopurification systems.
- Digestate and biochar mixture enhanced the sorption coefficient by a factor of >50.
- Hydrophobic pesticides exhibited >25 fold higher K_d/K_{oc} values than hydrophilic ones.
- 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:



Abstract

Pesticide pollution caused by point or diffuse sources may lead to the contamination of ground and surface water. Biobed or biofilter systems are commonly used on farm to treat pesticide remnants and filled with organic materials (soil, peat and straw).The objective of this study was to assess the sorption-desorption potential of three contrasting pesticides (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 showed that the biomixture 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. However, unlike sorption there was no statistically significant difference between the biochar and the digestate mixtures for pesticides desorption ($p>0.05$; *t*-test). The adsorption and desorption of all the chemicals conformed to linear and Freundlich isotherms. A higher values of distribution coefficient [K_d (>78 L kg^{-1})] and sorption coefficient [K_f (>900 µg$^{1-1/n}$ L$^{1/n}$ kg^{-1})] were observed for all pesticides for the digestate and biochar based mixtures compared to the blank soil, which was attributed to the lower organic carbon content of the blank soil. Specific UV-absorbances at 254 nm ($SUVA_{254}$) indicated the aromatic character of digestate (5%) and biochar (5%) biomixture, which showed highest organic-carbon-partition coefficient (K_{oc}) values among all biomixtures for all pesticides. Therefore, these biomixtures were found to be the most promising substrates amongst the tested ones for a biobed setup and can be used as an effective and alternative adsorbents for removing pesticides.

Keywords: Pesticide, Biobed, Biochar, Digestate, Sorption, Desorption

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). The contamination potential is larger when farmers are located close to any open water body or if washing activities are performed on gravelly or sandy soils with low retention capacity for any spilled pesticides (Karanasios et al., 2010). Mitigation or prevention of point sources can on one hand be achieved by implementing best management practices, on the other hand 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). Unfortunately, many methods for remnant treatment (e.g., chemical coagulation, sedimentation, oxidation and photocatalysis) are cost and/or labour intensive (Spanoghe et al., 2004). 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, in which 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, or a certain amount of treated water may exit at the bottom of the biofilter (if the water retention capacity of the biofilter is exceeded at certain times).

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. In natural soils organic matter and clay are the main soil components contributing to the sorption of pesticides (El Bakouri et al., 2007; Spark and Swift, 2002). Because sorption is one of the main processes reducing the mobility of these chemicals in soils, the addition of exogenous organic matter to soil has been suggested as a possible method to reduce pesticide leaching (Singh, 2003; Si et al., 2011). 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 (Delgado-Moreno et al., 2010; De Wilde et al., 2008; Marín-Benito et al., 2012 and 2014), which improved the sorption and degradation behaviour of the studied pesticides even when the pesticides were added in repeated applications and high dosage. Even if some studies already analyzed the 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 using two bioenergy residues, namely biochar and digestate. Biochar as an anthropogenic pyrogenic solid carbon source has been proven to be good replacement of peat in horticultural media (Tian et al., 2012) and might be therefore also suitable for biopurification systems. The main process induced by 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; Tatarkova et al., 2013). Several studies reported that biochar enhanced the sorption of pesticides by 400-2500 times compared to soils without biochar addition (Yang and Sheng, 2003; Yu et al., 2010), whereby 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 and high specific surface area (Accardi-Dey and Gschwend, 2003). Additionally, the biochar sorption properties primarily depend on the pyrolysis conditions, mostly by production temperature (Keiluweit et al., 2012). For example, high temperature biochar is characterized by highly condensed aromatic structures, which will lead to surface adsorption of the pesticides whereas partitioning into the amorphous carbon and different site specific interactions with functional groups can be the principle adsorption mechanisms for low-temperature biochar (Chun et al., 2004). This indicates that biochar can sorb different compounds which may vary in their polarity and planarity (Chun et al., 2004). Even if high pesticide sorption was reported in several studies Martin et al. (2012) stated that the sorption capacity of the biochar might be reduced over longer incubation time periods (>1 year) due to aging. Additionally, most studies focused on the adsorption processes but did not analyze the desorption mechanism, which is a key process affecting pesticide behavior 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 assessemnt of biochar addition in biopurification systems. Especially, the entrapment of organic compounds in 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 a laboratory experiment. 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 and 0.82% 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,chicken manure,as well as beef and pig urine as feedstock (in a ratio of 60, 4, 20 and 16% on dry mass basis). The main physico-chemical properties of the raw substances and soil biomixtures used for the experiment are listed in Table 1 and 2. It has to be noted that for the experiments already aged soil-biomixtures were used for being more representative for the long-term use of the biopurification matrix. All soil-biomixtures had been stored at room temperature in the dark for 6 months prior the experiments.

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 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 $CaCl_2$ solution. The percentage of solvent in the final pesticide solution was less than 0.1%. The standard stock and working solutions were stored at 4ºC prior to the experiment. An overview of the physico-chemical characteristics of the three compounds is provided in Table 3.

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 $CaCl_2$ 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 5050A equipped with an autosampler ASI-5000A from Shimadzu (Kyoto, Japan) after acidification and purging the samples for 1 min.

UV absorbance at 254 nm (UVA_{254}) 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 ($SUVA_{254}$) (Mukherjee et al., 2016 a and b). The pH of the soil/-biomixtures was determined by equilibrating soil/-biomixture with 10 mM $CaCl_2$ 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 Lüer and Böhmer (2000): In a first step 2.5 g soil was equilibrated with 10 mL 1 M NH_4Cl for 24 h. Subsequently, a folded paper filter (640d, Macherey-Nagel, Düren, Germany) was wetted with 1 M NH_4Cl and placed in a filter funnel. The wet soil was completely transferred to the filter and percolated with 1 M NH_4Cl until a volume of 100 mL percolate was collected. Exchangeable cations (Al^{+3}, Ca^{+2}, K^{+}, Mg^{+2}, Na^{+}) were determined in the filtrate using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Ciros CCD, SPECTRO Analytical Instruments GmbH, Kleve, Germany).

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 based on nitrogen adsorption-desorption isotherms at 77 K within the 0.03-0.3 relative pressure range (AUTOSORB-1, Quanta chrome apparatus).

The measurement of the organic carbon of the soil and biomixtures were performed 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 to the OECD guideline 106 (OECD, 2000). The experiment consisted of five different biomixtures and one reference soil (see Table 2), whereby all combinations were analyzed in triplicates. The blank soil (without any pesticides) was included in the experiments to check for artifacts and matrix effects caused by them in the analytical method. Additionally, control samples 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 on the batch container surfaces, no sorption and no metabolization could be detected in this process.

Pesticide loads were calculated based on 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 each on dry-mass basis and the final volume was filled with 100 mL 10 mM $CaCl_2$. 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. In a preliminary study the sorption equilibrium time for pesticides was investigated. 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 was selected as equilibrium time for obtaining the adsorption isotherms of all pesticide using 1:100 soil/-biomixture solution ratio. After reaching pseudo equilibrium, <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 equilibrium (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 over the equilibration time of 168 h. Based on the dissipation study using the same sorbents indicated (Mukherjee et al., 2016b) that <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:

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

where C_i is the initial and C_e (µg L^{-1}) is the equilibrium pesticide concentration in water phase, respectively. C_s is the amount of sorbed pesticides on the soil/-biomixtures (µg kg^{-1}) as calculated by:

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

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 $CaCl_2$ 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 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. The lower concentrations of the adsorption study were not used for desorption experiment because expected 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 ºC, capillary voltage 3.6 kV, cone voltage 45 V, source temperature 150 ºC. Nitrogen was used as desolvation and cone gas at a flow of 1000 and 150 L h^{-1}, argon was used as collison 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 ($R^2 > 0.99$) were established from 6 concentrations respectively. The limits of quantification (LOQs) and limits of detection (LODs) for the pesticide concentrations were 1 and 0.25 pg mL^{-1} for bentazone, and 5 and 2 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 behavior over the entire concentration range and can be expressed by:

$$C_S = K_d \,.\, C_e \qquad [3]$$

where C_s and C_e are the equilibrium pesticide concentration in the solid (µg kg^{-1}) and liquid phase (µg L^{-1}) and K_d (L kg^{-1}) is the distribution coefficient.

The second model tested was the Freundlich model, which theoretically accounts for heterogeneous binding surfaces and infinite surface coverage (sorption) resulting from extremely strong matrix and/or solute–solute interactions. The Freundlich model can be written as:

$$C_S = K_f \, . \, C_e^{1/n} \qquad [4]$$

where K_f (µg$^{1-1/n}$ L$^{1/n}$ kg^{-1}) is the adsorption coefficients and $1/n$ (-) is the Freundlich exponent. Hereby, K_f refers to the multilayer adsorption capacity and the Freundlich exponent referes to the adsorption intensity (Hussein et al., 2004). In consequence, different K_f values are not directly comparable without taking the $1/n$-values into account. Therefore, 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) assumes monolayer sorption on a set of different localized sorption sites with uniform energies and can be expresssed by:

$$C_S = \frac{C_{S\max}\, K_L\, C_e}{1 + K_L\, C_e} \qquad [5]$$

where C_{Smax} (µg kg^{-1}) is the maximum sorption capacity of the adsorbent, K_L is the Langmuir sorption coefficients (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 influence of the organic matter on the sorption behavior has been discussed in many studies (Correia et al., 2007; Delgado-Moreno et al., 2010). Consequently, 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:

$$K_{OC} = \frac{K_d .100}{\% \ OC} \qquad [6]$$

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 occuring 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. As a consequence the K_{oc} values cannot be generalized and only indicate differences in sorption between substrates normalized to the organic carbon content at a given concentration level. 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:

$$H = \frac{1/n_{des}}{1/n_{ads}} \qquad [7]$$

In general, lower H values indicate increased difficulty of the sorbed pesticide to be desorbed from the matrix (Barriuso et al., 1994; O'Connor et al., 1980).

2.8. Statistical Analysis

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

$$t = \frac{parameter - value}{SD(parameter - value)} \qquad [8]$$

$$type - I\ error\ rate = t - distribution(t, dof, 1) \qquad [9]$$

where, *t* is the empirical t-value, *SD* is the standard deviation of parameter value and *dof* is the degrees 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 $m^2\ g^{-1}$ of all used soil biomixtures, reflecting the high specific surface area of pure biochar (231 $m^2\ g^{-1}$).

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). Digestate based biomixtures showed significantly lower $SUVA_{254}$ values with and higher values without biochar than the biochar/soil biomixtures ($p<0.05$; *t*-test). This means that DOC stemming from digestate based biomixtures is more aromatic compared to the DOC stremming from biochar. This can be explained by the fact that the hydrophobic nature of biochar tends to preferentially bind aromatic fractions of the DOC.

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 time needs to be also longer for bentazone and pyrimethanil and equilibrium reaches 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 quick 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 µg 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 %). According to these results, the ratio of 1:100 was selected for all studied pesticides to have comparable experimental conditions and to facilitate the experimental procedure.

3.3 Equilibrium adsorption isotherms

The sorption (and desorption) behavior as well as the fitted isotherms of all pesticides on each soil-/biomixtures are depicted in Fig. 2-4 and the fitted sorption parameters are listed in Table 4. 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 prelimenary experiments, recording sorption data of all pesticides to the 5 % BC biomixture were not possible due to analytical limitations, and therefore, no sorption-desorption coefficients could be determined for these 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 Tab. 4), 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 (Fig. 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). It was shown that specific interactions dominate at low concentrations, whereas the relative contribution of hydrophobic and van der Waals forces increases with increasing concentrations of sorbates in the solid-solution phase. Khan and Mazurkevich (1974) described that adsorption of polar pesticides on humic acid is mostly governed through physical forces (ionic bonding and charge transfer complexes), such as dipole-ion (cation bridges) or dipole-dipole (hydrogen bonds) bonds due to the coordination of cations on the humic acids, rather than by weak chemical bonds. Hydrophobic interactions were found to be the most vital interaction mechanism for non-polar pesticides (Torrents et al.,1997). Boscalid and pyrimethanil are more hydrophobic pesticides with low water solubility and consequently their affinity for organic matter is higher, which makes these compounds less mobile than more soluble pesticide like bentazone being supported by the differences in their K_{ow} and K_{oc} values listed in Table 3. Consequently, also the adsorption coefficients of boscalid and pyrimethanil ($K_{f\ ads}$ value) in our experiment were higher than for bentazone (seeTable 4). Several other studies already reported that differences in pesticide sorption capacity among different maturity stages of organic residues and a soil depended mainly on the hydrophobic characteristics of the compounds (Marín-Benito et al., 2012 and 2014; Rojas et al., 2013). 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 better described 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 µg 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. Indeed, the slightly smaller SSR values for this fits also point in this direction.

Analyzing the fitted sorption parameters is 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 double 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). To account for the different amounts of organic carbon available for sorption, the K_{OC} was also calculated and indicated that the addition of digestate (5 and 30 %) did not increase normalized sorption capacity compared to reference soil. Contrary,

K_{OC} values dropped by more than three times for the low DG addition and even upto >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. (2012 and 2014), whereby their relationship was more linear with lower DOC and higher 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 and 19.3 L kg^{-1} for boscalid. The stronger sorption of boscalid has been already reported in several studies (Chen and Zhang et al., 2010; Karlsson et al., 2016), and can be explained by the lower water solubility and higher hydrophobicity of this substance (see also Table 3). The changes in normalized K_{OC} values are siginificantly 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 again 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 3). Therefore, the strong sorption of pyrimethanil on these BC-containig substrates cannot be attributed mainly to its high organic carbon content. Other factors, such as the nature of the BC organic matter or its physicochemical characteristics may be crucial here, e.g. by showing a higher molecule-specific affinity for pyrimethanil than for boscalid. In general, it is widely recognized that sorption is also affected by the quality or nature of the soil organic matter (De Wilde et al., 2009; Delgado-Moreno et al., 2010). This is mainly due to aromatic C content, which increased K_{oc} values, and O-alkyl C and alkyl C content which make K_{oc} values usually decrease. These negative correlations may reflect a lower affinity of these carbon types for the studied pesticides, but they may also be due to blocking of higher affinity sites by organic matter constituents rich in these functional groups.

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 3). 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 L kg^{-1} 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.

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 are an indication that different mechanisms of sorption may exist between pesticides and soil components and/or biomixture moieties (Chiou et al., 2000). L, S or C types of isotherm have frequently been found to describe the sorption of other pesticides 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 from a strong competition by the solvent molecules, which explains the high affinity of sorbent for solute at low concentrations (Giles et al., 1960).

Basically, sorption of pesticides on the biomixtures is related also to the DOC content and the specific surface area (SSA) of the biomixtures. The effects of DOC on the sorption of pesticides and hydrophobic compounds on soils were discussed contradictory by previous researchers (Barriuso et al., 1994; Müller et al. 2007). Andrades et al. (2004) reported an increase in the sorption of pesticides if organic soluble compounds from DOC are co-sorbed by soils and give rise to the formation of new hydrophobic surfaces. A decrease in sorption might occur if pesticides interact with the soluble moieties of organic matter in the soil-solution interface (Luo et al. 2009) or when the pesticides compete with the soluble organic molecules for the same sorption sites (Cox et al. 2000). These effects could explain our results, which showed decreased pesticide sorption by the amended soil biomixtures with the highest DOC load (30 % DG biomixture). Additionally, many authors reported on larger portion of smaller pores in organic amendments compared to soil which presumably increased the residence time of pesticides in the immobile water phase (Cañero et al., 2012; Cox et al., 1997) and hence sorption. In our study, micropores proportion was not studied, but BET measurements revealed a SSA of 8.60, 6.90 and 3.30 $m^2 g^{-1}$ for 5 % BC, 5% DG + 5 % BC and 30 % DG respectively (Table 2), which were in agreement with reported values for other highly microporous organic matrices (Méndez et al., 2013; Thinakaran et al., 2008). Basically, biochar consists of highly condensed aromatic carbon, which is known for its high sorption capacity for many organic compounds (Chun et al., 2004; Ahmad et al., 2014). Uchimiya et al. (2012) and Yu et al. (2010) have also doccumented the increase of sorption of pesticides with the increase of the SSA of the biochars added to soils. 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).

3.4 Equilibrium desorption isotherms

The equilibrium desorption isotherms for the different biomixtures and pesticides are plotted in Fig. 2-4. The desorption isotherms were fitted using the Henry (linear) and Freundlich equation [Eq. 3 and 4]. The Henry desorption ($K_{d\ des}$ and $K_{oc\ des}$) and Freundlich coefficients ($K_{f\ des}$ and $1/n_{\ des}$), the coefficient of determination (R^2), the sum of squared residuals (SSR) as well as the hysteresis coefficients (*H*) are listed in Table 5.

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 (Tab. 5) 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 to the adsorption ones 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 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 higher desorption (no hysteresis) for polar compounds due to 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 due to repulsion between negatively charged bentazone molecules and COO^- groups of the DOC derived from biomixtures. On the other hand, mixing biochar into the soil resulted in stronger sorption and in comparison even lower desorption. The reason for the observed strong sorption to digestate/biochar based biomixtures cannot be explained easily. Yet, it can be speculated that adsorption of biomixture derived DOC by biochar could provide additional sorption sites for bentazone, whereas the high surface area of biochar could contribute to a multiplication of sorption sites for bentazone.

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 by pyrimethanil and boscalid when sorbed on digestate and biochar based mixtures. In contrast, for both pesticides, blank soil was the worst adsorbate. Bentazone showed highest adsorption by blended biomixture of digestate and biochar followed by digestate based biomixture. 5 and 30 % digestate combinations showed almost similar sorption capacity for bentazone and pyrimethanil respectively. We conclude that a blended 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.

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