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Preliminary assessment on the application of biochar and spectral induced polarization for wastewater treatment

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Abstract

In this work we explore the use of biochar as a remediation agent, and the sensitivity of the spectral induced polarization (SIP) method as a remediation monitoring aid. Biochar amended columns were fully saturated with industrial wastewater (olive oil mill waste) with very high concentration of phenols (~2485 mg/L) and other substances. The biochar amended columns achieved very high removal rates of phenols compared to the control (sand only). Geophysical monitoring over the duration of the experiment (10 days) showed changes in the SIP signal (imaginary conductivity) consistent with phenol removal as confirmed with geochemical monitoring. This experiment confirmed the utility of biochar as a remediation agent. Furthermore, SIP can serve as long term, high resolution, monitoring aid in organic contaminant degradation processes.

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1. Introduction

As the world population increases, so does the production of agro-based products necessary for supporting its nutritional needs. As a result, the quantities of agricultural waste increase steadily, both at local and global level. These wastes are commonly utilized in the animal feed industry and/or in composting. However, large quantities remain unexploited and are either combusted in the open, for volume reduction, or end up in landfills. Both these pathways are environmentally and economically unsustainable due to greenhouse gas emissions, pollution of the subsurface and groundwater and landfill lifetime reduction (Dai et al., 2018; Ibrahimoglu and Yilmazoglu, 2018). Therefore, research and development of technologically viable and environmentally friendly management options is ongoing.

The exploitation of agricultural waste for the production of added-value materials with environmental applications is one of the basic axes of circular economy (Toop et al., 2017). One such example is biochar, which is the solid product of lignocellulosic biomass pyrolysis. Biochar is a porous, carbonaceous material with a wide range of environmental applications. Its properties depend on the initial feedstock, as well as the temperature, duration and type of pyrolysis (Chavda and Pandya, 2014; Tang et al., 2013). Biochar has been mostly applied in nutrient-deficient soils as a bio-fertilizer (often in combination with compost) and as an adsorbent in soils contaminated with heavy metals/organics (Agrafioti et al., 2014; Fan et al., 2016; Nautiyal et al., 2016). Other emerging applications include the use of biochar as a catalyst support for the degradation of contaminants in wastewaters (Kalderis et al., 2018; Agrafioti et al., 2014; Mohan et al., 2014), as a composite in building materials (Gupta and Kua, 2017) and as an additive in fodder for the reduction of greenhouse gas emissions from cattle and other livestock (Bachmann et al., 2016; Ippolito et al., 2012; Meyer et al., 2011).

Although the physical and chemical properties of various biochars have been well investigated and correlated to production conditions, the electrical properties remain largely unstudied. Until now, the only application that has been developed through the manipulation of electrical conductivity (EC) of biochar, is their use as supercapacitors (Gabhi et al., 2017; Zhang et al., 2014). Highly carbonized biochars (>80 wt% of carbon) with a graphite-like structure have considerable chemical

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stability and high mechanical strength, which are favorable properties for energy storage applications (Gabhi et al., 2017). Domingues et al. studied the electrical conductivities of biochars from various feedstocks and concluded that the concentration of soluble minerals in the initial biomass was the determining factor of electrical conductivity (EC) of biochars (Domingues et al., 2017). These minerals become an inherent part of the biochar surface groups, i.e. the charged chemical substances connected to the biochars surface, and play an important role in soil remediation and wastewater treatment processes.

Several researchers have confirmed the pH-dependent, electrostatic interactions between biochar's surface groups and ionizable organic contaminants during adsorption (Kalderis et al., 2017). Fourier-transform infrared (FTIR) spectroscopy can provide direct information of the functional groups present on the surface of biochars and is widely used for the characterization and monitoring of biochar formation (Fan et al., 2016; Guo et al., 2016). Recently, Ocampo-Perez et al. (2019) and Jung et al. (2019) concluded that the removal of pharmaceuticals from wastewaters largely depend on hydrogen bonding, electrostatic interactions and surface complexation between charged groups on the biochar surface and moieties of the substance (Ocampo-Perez et al. 2019; Jung et al. 2019). Similar conclusions were drawn by other researchers, who used biochars from different feedstocks to treat a range of organic pollutants (Wang et al. 2018; Wei et al. 2018). In all cases, conventional chemical analyses on the residual wastewater were performed, at the end of each experimental run. This bears the risk of underestimating the adsorption efficiency of the adsorbent, since desorption of the contaminant may occur before analysis. Additionally, the structural stability of certain substances depends on the solution pH, temperature and laboratory conditions (e.g. light intensity), which may lead to further generation of errors. As a result, there is a need for real-time monitoring of the properties of biochar during wastewater treatment; electrical geophysical methods can serve in this role. The monitoring of key electrical properties, indicative of biochar surface properties change, during soil or wastewater treatment processes, could provide valuable information in real time, thus reducing the need for delayed, complex and time-consuming chemical analyses.

Geophysical methods offer non-invasive, and high resolution (spatial and temporal) monitoring of a certain physical property that could be related / linked to the properties of the material under investigation. Indeed, geophysical methods are gaining traction as long term, efficient, monitoring tools for environmental projects (Heenan et al., 2014; Kimak et al., 2019; Ntarlagiannis et al., 2016; Power et al., 2015). In biochar containing media, geophysical methods can be used to characterize biochar concentration and / or monitor biochar related processes. High surface area, porosity and surface adsorption are some of the unique properties of biochar rendering it a promising remediation material; the same properties are typically associated with spectral induced polarization (SIP) signal sources, suggesting that SIP can be used in biochar related studies (Kemna et al., 2012). The link between the SIP method and biochar was originally established and presented by Haegel et

al. (2013). Gao et al. demonstrated one application of the proposed SIP method in the detection and characterization of biochar in sand samples (Gao et al., 2017). Recent research explored the SIP method as a monitoring tool in biochar based remediation processes with very promising results (Kirmizakis, 2016; Kirmizakis et al., 2016; Ntarlagiannis et al., 2016; Ntarlagiannis et al., 2017).

Olive oil production generates large volume of residual wastewater. Olive mill wastewater (OMW) is characterized by a dark brown colour and unpleasant odor, consisting mainly of organic compounds (mainly phenols and polyphenols) and metals such as potassium and phosphorus. The main effects of olive mill wastes on natural water bodies are related to their concentration, composition and seasonal production. The most visible effect of OMW pollution is the discolouring of the receiving water bodies. This change in colour is due to the oxidation and subsequent polymerization of tannins giving darkly coloured polyphenols, which are difficult to remove from the effluent (Kalderis and Diamadopoulos, 2010). The lipids in OMW form an impenetrable film on the surface of water, which blocks out sunlight and oxygen to microorganisms in the receiving water, leading to a reduction in plant growth and increasing erosion (Kavvadias et al., 2014). Other deteriorating effects include eutrophication due to the high phosphorus content and toxicity to aquatic species.

In this work, we present a novel approach for the monitoring of biochar-based wastewater treatment utilizing the sensitivity of the SIP method on the interfacial conductivity and adsorption properties of biochar. Biochar filled columns, saturated with OMW used to assess whether the SIP method can help monitor or aid the design of wastewater treatment strategies. Therefore, the objectives of this study are two fold: (a) to investigate the efficiency of biochar to reduce the contaminant load of OMW, and (b) to identify any links between the treatment process and SIP signatures.

2. Materials and methods

2.1 Materials

The biochar used in this study was obtained from Sonnenerde GmbH (Riedlingsdorf, Austria). It was prepared through pyrolysis 500°C and 1 hr residence time, from a 50:50 mixture of paper sludge/wheat husks (Bachmann et al. 2016). It was then sieved to a particle size between 1 mm and 500 µm (18 and 35 mesh) as more compatible with the Ottawa sand grains and was used without any modifications. The physical and chemical properties of the sample are shown in Table 1. Ottawa

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sand (841-595 μm particle size distribution) was obtained from Fisher Scientific (Fisher Scientific). OMW was collected from a local olive mill waste evaporation pond in Chania, Crete (Southern Greece) and was used as is, without any pre-treatment (Ntarlagiannis et al., 2016). The properties of OMW were determined using conventional laboratory methods and are shown in Table 2. All experiments were conducted in laboratory-scale [acrylic] columns (50 mm diameter and 250 mm length), fitted with Ag-AgCl electrodes for SIP measurements (Ustra et al., 2012; Vanhala and Soininen, 1995).

2.2 Spectral Induced Polarization

The capacitive and conductive properties of porous media, in the low frequency range (below 1 kHz), can be described in terms of complex conductivity (σ^*) (complex resistivity or permittivity can be equally used):

$$\sigma^* = \sigma' + i\sigma'' \quad (\text{eq. 1})$$

$$|\sigma^*| = \sqrt{\sigma'^2 + \sigma''^2} \quad (\text{eq. 2})$$

where σ' and σ'' are the real and imaginary components of σ^* and $i^2 = -1$. The real and imaginary components can be calculated from the measured parameters magnitude ($|\sigma|$) and phase (ϕ):

$$\phi = \tan^{-1} \left(\frac{\sigma''}{\sigma'} \right) \quad (\text{eq. 3})$$

$$\sigma' = |\sigma| \cos(\phi) \quad (\text{eq. 4})$$

$$\sigma'' = |\sigma| \sin(\phi) \quad (\text{eq. 5})$$

The real component σ' is an electromigration term, representing ohmic conduction, and the imaginary one, σ'' , is a charge storage term describing polarization (Binley and Kemna, 2005; Kemna et al., 2012; Merriam, 2007; Placencia-Gómez et al., 2013; Slater and Lesmes, 2002).

In most common cases, where metallic minerals are absent, current transfer in porous media can be described via two principal mechanisms, electrolytic (σ_{ele}) and surface (σ_{surf}) conduction. The former describes ionic charge transport through the saturated interconnected pore space, while the latter occurs within the electrical double layer (EDL) at the mineral-fluid interface (Binley and Kemna, 2005). σ_{ele} is the electromigration term, primarily controlled by pore fluid electrical properties and σ_{surf} on the other hand is a complex term, controlled by processes on the mineral grain interface and dependent, to a lesser degree, on fluid properties. The observed IP signal is the result of mineral grain surface and electrolyte electrochemical polarization processes.

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Briefly, the main IP mechanisms are: the Maxwell-Wagner polarization, EDL polarization, both of the diffuse and Stern layers, and membrane polarization (Kemna et al., 2012; Revil and Cosenza, 2010) (Figure 1). In our experimental configuration and the frequency range of interest (1 mHz – 1 kHz), the most relevant mechanisms are the stern layer and membrane polarization since Maxwell Wagner becomes significant >1 kHz, and the tight nature of the porous media diminishes the diffuse layer polarization (Kemna et al., 2012; Revil and Cosenza, 2010). In metal free earth media, the application of an electric field will force the ions, in the grain's EDL, to move. This tangential to the grain surface movement (Leroy and Revil, 2009) is the source of the complex surface conductivity (σ^*) and is directly dependent on the grain surface properties (area, charge density and ionic mobility) (Lesmes and Frye, 2001). In addition to EDL polarization, in the presence of pore constrictions, the imbalance of current carried by ions can result in the so-called membrane polarization mechanism (Figure 1). This imbalance can increase the cloud of ions on one side of the pore constriction, while decreasing it on the opposite, aligned the applied electric field. These zones of varying salinities can create a diffusion of ions from the high-salinity to the low-salinity zone (Kemna et al., 2012). Detailed discussion on EDL and membrane polarization models can be found elsewhere (e.g. Kemna et al., 2012; Revil and Cosenza, 2010; Revil and Florsch, 2010).

However, for biochar related studies it is worth mentioning IP contributions in the presence of metals, or at least grains that behave like metals, since biochar has been shown to resemble the electrical properties of conductors or semi-conductors (Gao et al., 2017). The presence of disseminated metallic particles in electrolytically conductive porous media will impact both the real and imaginary components of complex conductivity. Continuous metals, or interconnected metallic particles, will impact the real component (Ntarlagiannis et al., 2005a; Placencia-Gómez et al., 2013). The imaginary component can be affected by the strong EDL polarization of the metallic grains associated with interfacial electrochemical reactions (Placencia-Gómez et al., 2013; Wong, 1979). Different electrochemical polarization models have been described in the literature, mostly on the electrode polarization mechanism, but we find that the model described by Placencia et al. (2013) might be suitable for biochar studies. This model recognizes the impact on real component, and describes the IP response based on adsorbed ions on the grain surface and diffusion gradients based active ions engaging in charge transfer with the metallic grain (Placencia-Gómez, 2015) (Figure 1). Although the surface reactions (metals vs biochars) are probably not the same, we believe that charge transfer processes on the biochar surface (Li et al., 2017) could significantly impact the polarization signatures and are worth investigating.

2.3 Experimental methods

Column construction

Three biochar amended columns (5%, 10% and 25% by weight (BW) biochar in Ottawa sand) and one control column (pure Ottawa sand) were dry packed (Dingenen, 1998) and saturated with OMW (Table 3) from the bottom to the top until full saturation. After saturation, the inflow valve was shut off and the experiment was performed under no flow (static conditions) for a duration of 10 days. The duration of 10 days was selected on the basis of commonly used aerobic and anaerobic treatment technologies for partial degradation of the organic load of OMW (Khadija et al., 2019; Paraskeva and Diamadopoulos, 2006). The columns were outfitted with electrodes for SIP measurements, following previous laboratory designs (Heenan et al., 2013; Ntarlagiannis and Ferguson, 2009), with the Ag-AgCl current electrodes placed at the end caps and the potential electrodes symmetrically placed at the center of the column body (Figure 2). The potential Ag-AgCl electrodes were placed at the outer edge of the column body, outside of the current pathway, in electrolytic contact with the column to minimize any unwanted polarization effects (Vanhala and Soininen, 1995).

Before the experiment fluid solutions (KCl) of known conductivity were used to verify the performance of the experimental set up and accurately estimate the geometric factor of each experimental column. Phase errors were <0.1 mrad, consistent with the SIP system [Portable Spectral Induced Polarization (PSIP) system (Ontash & Ermac)] characteristics and columns optimized for SIP measurements (Kimak et al., 2019; Ntarlagiannis et al., 2005b; Ntarlagiannis and Slater, 2014). All experiments were performed in a controlled laboratory environment, at a temperature of $23.5 \pm 2^\circ\text{C}$.

OMW monitoring

Geophysical monitoring involved SIP measurements in the frequency range of 0.01 Hz - 10 kHz, collecting 5 measurements per logarithmic decade. Measurements between electrodes P1 - P5 and P2 - P4 (Figure 2) were obtained. The duration of each SIP sweep was ~ 20 minutes. Before each data acquisition run, the electrode contact resistance between all electrodes was measured to identify, and remedy, any contact resistance issues.

At the end of the 10th day, the 'treated' OMW was removed and collected from the drainage valves at the bottom of all experimental columns for further chemical analysis. Due to the different biochar content the experimental columns had different pore space that was saturated with OMW; the collected volume from each experimental column showed that the variations in pore fluid recovery are similar for all columns containing biochar. Indeed, in previous research sandy soils containing 5% - 20% biochar resulted in very similar water holding capacities (Verheijen et al., 2019; Yu et al., 2013). The treated OMW, along with untreated OMW samples, were characterized for the following

common geochemical parameters (Table 2): pH, electrical conductivity (EC), phenols, soluble chemical oxygen demand (COD), NO_3^- , P, total dissolved solids (TDS).

Destructive analysis

After the 10-day monitoring experiment, the porous media from all columns was collected; the biochar samples were separated from the sand through sieving, air-dried and stored at 4°C before collective samples send for analysis. The surface morphology of biochar (original and the sample from the 10% column) was recorded using scanning electron microscopy (SEM) Zeiss Supra 55 field emission (Germany). SEM provides high-resolution imaging useful for evaluation various materials for surface fractures with a focused beam of electrons. The samples were coated with platinum (Pt) by electrodeposition under vacuum prior to analysis to enhance the surface conductivity. Infra-red spectroscopy measurements were performed in a Perkin-Elmer spectrophotometer to investigate any permanent chemical changes on the biochar surface during the remediation process. Absorbance spectra were recorded from 4000 to 450 cm^{-1} at a resolution of 1 cm^{-1} , with some radiation absorbed and some passed through. The absorbed radiation converted into rotational and/or vibrational energy by the sample molecules. The resulting signal at the detector presents as a spectrum, representing a molecular fingerprint of the samples. Each molecule or chemical structure produced a unique spectral fingerprint.

3. Results and discussion

The control column, with only Ottawa sand without biochar, did not have any significant impact on the pH, electrical conductivity, COD and total dissolved solids (Table 2). However, it retained approximately 22% of phenols, 62% of nitrates and 15% of phosphorus. Total phenols, COD, nitrates and phosphorus were reduced in all biochar-amended columns to a greater extent, thus establishing the efficiency of biochar in treating OMW. The 10% biochar column performed better for contaminant removal than all other treatments, lowering phenols, COD, nitrate and phosphorus content by 87.4, 56.1, 85.7, 84.7%, respectively. It is interesting to note that treatment with the 25% biochar column was not as efficient. A higher biochar percentage probably reduced the uniform dispersion of biochar in Ottawa sand and promoted agglomeration of biochar particles beyond a threshold value (Figure 8). If adsorption is the sole mechanism occurring during treatment, a higher degree of agglomeration would reduce the total number of active sites available for interaction with the wastewater constituents. Previous reports have highlighted that dissolved organic material (abundantly present in the OMW as shown in the COD value) can enhance the colloidal stability of biochars particles and therefore promote agglomeration (Song et al., 2019; Yang et al., 2019). Both

of these studies agreed that at acidic pHs (as was the pH in the 25% column in this study), the formation of stable suspensions of biochars particles is further increased.

The pH of the effluent peaked at a value of 8 at the 10% biochar column, an indication that a significant number of biochar surface groups were dissolved in OMW during the 10-day treatment. However, it only reached to 5.9 at the 25% biochar column. This result further supports the agglomeration hypothesis mentioned earlier. The acidic OMW could not possibly interact sufficiently with the agglomerated biochar particles and dissolve adequate alkaline surface groups, thus maintaining a pH value close to the initial. The total dissolved solids values were practically the same as the initial OMW, with the exception of the 25% w/w biochar column, where a 23% raise was observed. This indicates that there were significant quantities of leachable inorganic compounds (such as metal salts and/or oxides) from the biochar. The high ash content of this particular type of biochar (34.78%) and the long treatment period of 10 days (well beyond the optimum leaching time of 24 h) support this conclusion (Lokeshappa and Dikshit, 2012).

At the end of the 10-day treatment, the dismantling of the biochar-amended columns released a strong odour of methane. Although no gas sampling and analysis was performed during treatment, this is an indication of some degree of anaerobic degradation. It has been reported that the addition of biochar in anaerobic treatment reactors increases the maximum production rates of hydrogen and methane, improves hydrogen and methane yield and shortens the lag period between the different anaerobic processes (González et al., 2018). Biochar addition also enhances volatile fatty acid generation during hydrogen production (Cooney et al., 2016; Mumme et al., 2014; Sunyoto et al., 2016). These studies concluded that the role of biochar is to provide a porous substrate to support microbial metabolism and growth and promotes the methanogenic biofilm formation in the methane production stage. The monitoring of any potential anaerobic treatment phases (through the frequent measurement of volatile fatty acids, dissolved oxygen, hydrogen and methane) was beyond the scope of this study, however it may have acted synergistically to adsorption and is worthy of further investigation.

The FTIR spectra of original, 5, 10 and 25% w/w biochar samples are shown in Figure 3. Analysis of the FTIR peaks indicate the biochar surface moieties responsible for interacting with the substances present in OMW. The broad band at 3300 cm^{-1} is due to the presence of hydroxyl groups ($-\text{OH}$). The aromatic $-\text{C}=\text{C}-$ or the $-\text{COO}-$ group is attributed to the peak at 1625 cm^{-1} . The absorbance band at $\sim 1450\text{ cm}^{-1}$ indicates the $-\text{C}=\text{O}$ (carbonyl) stretching vibration. The carbonyl and hydroxyl groups are responsible for the basic and anionic properties, respectively. Therefore, potentially both anionic and cationic substances can be adsorbed onto the biochar's surface (Nautiyal et al., 2016). The intense absorbance peak at $\sim 1100\text{ cm}^{-1}$ (due to the stretching of ether linkage $-\text{C}-\text{O}-\text{C}-$) shows the

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largest variation among the 4 samples. This indicates the participation of the –C-O-C- linkage in adsorption. Oxygen containing functional groups often play a significant role in the adsorption or binding process (Fan et al., 2016). The bands below 800 cm^{-1} correspond to Fe–O bond deformations. A comparison of the absorbance levels between the biochars from the 3 columns, clearly show that the lowest absorbance – and therefore the highest interaction of the surface groups with the OMW components - was obtained from the sample in the 10% column. This observation confirms the earlier conclusion that this column was the most successful in treating OMW. Since we are dealing with a multi-component wastewater, it is practically impossible to allocate spectral changes to individual OMW compounds. Therefore, what we observe is the sum interaction of various contaminants or classes of contaminants (such as phenols) with biochar. Comparing the four spectra, no disappearance of certain bands and appearance of others can be observed. This indicates that breaking of chemical bonds and the formation of new ones did not occur between substances in the OMW and surface groups present on biochar. It is highly likely that biochar reduced the organic and inorganic load of OMW only through physical sorption in the pores, a hypothesis supported by the earlier observations.

Scanning electron images shows significant changes on the biochar surface before, and after, treatment (Figure 4). The background biochar appears to be smoother, while in the treated biochar surface we observe adsorbed materials (not previously present), presumably OMW components. The presence of these adsorbed components could alter the surface properties of biochar, that could impact the EDL leading to measurable SIP changes, expressed primarily as changes in the imaginary component (Figure 6).

SIP response provided very interesting results, with the real and imaginary components behaving differently (Figure 6 & Figure 7). Looking at the data in day 1, before any adsorption processes take place, the SIP signals can offer insight on the material characteristics. The imaginary component shows the impact of biochar content in each column, clearly differentiating between 5 %, 10 % and 25 % biochar concentrations (Figure 6, closed symbols). This behaviour is expected and consistent with recent literature (Gao et al., 2017), strengthening our hypothesis that the SIP method is suitable for characterization of biochar containing soils. Interestingly enough the real component does not show the same trend (Figure 6, closed symbols). The 2 columns with 5 % and 10 % biochar have almost identical values, with only the 25 % showing increased conductivity values. The OWM used to saturate the column has very high EC (Table 2) and it appears that it dominates the real component response for the columns with lower biochar content; the increase in the 25 % biochar column could be explained by the contribution of biochar in the real part. As discussed earlier such behaviour is observed in metallic mineral containing soils when the metals form interconnected, continuous bodies (Ntarlagiannis et al., 2005a; Placencia-Gómez et al., 2013). It seems that the 25% content in biochar, along with the presence of organic content at acidic pH (Song et al., 2019; Yang et al., 2019),

promoted the formation of continuous biochar 'vein' like structures that enabled electronic conduction, contributing to the overall real conductivity. This observation is in direct agreement with previous research suggesting that biochars behave as conductors (Gao et al., 2017).

For the duration of the experiment both monitoring SIP pairs (1-5, 2-4) showed similar results; for brevity we present only the results from pair 1-5 which is more representative of the mixture (largest measured volume). The real conductivity for columns with 5% and 25% biochar barely changed over the duration of the experiment, showing a small increase at day 10; the control column showed similar behaviour. The 10% biochar column behaved differently showing conductivity decrease at day 10 (Figure 6 & Figure 7). The real conductivity results were consistent with the OMW effluent geochemical monitoring and the electrical conductivity (EC) measured (Figure 5). All BC treated effluent showed slightly elevated EC values compared to the background, except the 10% which showed a decrease; the same trend is observed in the real conductivity results. Minor discrepancies on the observed between EC and real conductivity can be attributed to contributions of surface, and potentially electronic, conductivity of biochar. The important observation is that real conductivity appeared to be heavily influenced by the OMW EC as expected suggesting that electrical resistivity measurements alone (i.e. without IP) are not optimized for characterizing and monitoring biochar properties and processes.

In all active columns (biochar >0%) we observe a similar imaginary conductivity trend. The imaginary component clearly increased over the duration of the experiment (Figure 6 & Figure 7) for all biochar columns; the increase shows similar behaviour for all biochar amended columns, with the initial rate of increase followed by a steeper increase at day 4-6, depending on the column, until the end of the experiment. The same trend on all active columns suggests similar SIP signal sources (i.e. OMW components adsorbed on biochar surface – (Figure 8)). On the contrary, the control column (0% BC) showed no change over the duration of the experiment.

Changes in imaginary conductivity are apparently linked to the presence of biochar in the system. The geochemical monitoring suggested that the primary mode of interaction between biochar and OMW is adsorption, a process that is expected to alter the surface properties of biochar and consequently the imaginary component of complex conductivity (Kemna et al., 2012; Knight et al., 2010; Lesmes and Frye, 2001) (Figure 1 & Figure 8). Adsorption of OMW ions on the biochar surface is expected to alter EDL polarization, and enhance membrane polarization mechanisms (Figure 1 & Figure 8). Adsorption processes are expected to create mobile ligands, and increase polarization consistent with our results; similar behaviour has been observed with sodium sorption on silica (Hao et al., 2015; Vaudelet et al., 2011).

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The polarization increase could also be attributed to membrane polarization commonly exhibited in porous media with pore constrictions and high cation exchange capacity (CEC) (Marshall and Madden, 1959; Merriam, 2007; Titov et al., 2002; Vinegar and Waxman, 1984); the biochar amended columns have both characteristics since biochar is known to have high CEC and mixing biochar in sand creates pore constrictions, due the grain size and shape variations. The cation adsorption on biochar surface should further impede the flow of ions through the pore constrictions, enhancing the observed polarization (Marshall and Madden, 1959; Merriam, 2007; Titov et al., 2002; Vinegar and Waxman, 1984).

Looking the 10 Hz data (Figure 7) for the 10% column closely, the rate of increase in imaginary conductivity occurs after day 5, right when we observed a drop in the real conductivity. This supports our proposed adsorption model, with OMW ions removed from solution (lowering real conductivity) due to adsorption on biochar surface (increased imaginary conductivity). The same behaviour is observed for the other 2 columns, but is not as clear. Geochemical monitoring showed some removal of phenols in the control column, but we recorded no imaginary conductivity changes. Adsorption on sand grains might occur that could cause weak changes in EDL polarization; any imaginary conductivity changes are masked due to the dominant electrolytic conductivity (high EC of OMW) in our system. Biochar grains though, with an already strong background EDL polarization (metal like behaviour) and high adsorption capacity, exhibit strong imaginary conductivity changes that can be recorded despite the high conductivity background.

The observed changes in pH might have contributed to the observed SIP signals. In theory SIP should be affected by the pH of the saturating fluid since it can impact the mineral surface charge properties (Hördt et al., 2016; Lesmes and Frye, 2001). Limited research on this topic suggests a decrease in the SIP parameters with decreasing pH ($\text{pH} > \text{pzc}^1$) (Hördt et al., 2016; Lesmes and Frye, 2001; Zhang et al., 2012). Although our data follow this general trend, we do not believe pH is a dominant signal source in our system. Previous experimental and theoretical work studied only simple systems (single porous media, solutions of a single electrolyte such as NaCl) and showed small changes in the SIP parameters, smaller than the observed in this experiment. Furthermore, the changes should be more pronounced in the real component, and the rate of increase should be higher for the BC 10% columns; both not true for our data (Figure 7).

¹ pzc: point of zero charge

Conceivably the SIP response can be used to assess biochar remediation performance based on imaginary conductivity changes (Figure 7). The bimodal imaginary conductivity trend (Figure 7) might indicate the change of the function group that controls sorption. Li et al. (2017) discusses the different sorption mechanisms on biochars (Figure 8); although they are focused on metals, the concept applies to any function group (Li et al., 2017). The surface charge of biochar particle will change in response to sorption mechanism/contaminant; as processes change, the surface charge will be changing, leading to changes in the imaginary conductivity response (Figure 8).

Further investigation is required to explore any links between sorption processes and the SIP response; the very similar trend observed in biochar amended columns might hold information on sorption processes and provide insight on which mechanism is dominant. This, in turn, will have direct implication for remediation efficiency.

4. Conclusions

In this multidisciplinary study, a porous adsorbent derived from residual biomass was used as a filter to reduce the contaminant load in olive mill wastewater, under static conditions. The process was monitored in real-time through SIP geophysical measurements in a purpose-made experimental set-up. The addition of biochar to sand considerably improved the quality of the wastewater. At the optimum biochar to sand ratio of 10%, phenols, COD, nitrate and phosphorus content were lowered by 87.4, 56.1, 85.7 and 84.7%, respectively, after a 10-day treatment. The pH and the total dissolved solids fell within the limits set by the European Union for discharge of effluents in water bodies. Although the final contaminant values exceeded those allowed in industrial effluents, treatment with biochar showed that it can act as a pre-treatment phase before application of the main remediation technology. The SIP method appears to be a very promising method for characterization on biochar amended porous media and biochar driven degradation processes. The magnitude of the imaginary component of SIP is directly related to the amount of biochar present in the system. Furthermore, the degradation of the organic contaminant through sorption processes impacts the imaginary conductivity. The rate of imaginary conductivity change might be related on the adsorption mechanism (e.g. function group) or even in the contribution of multiple polarization mechanisms such as EDL and membrane polarization; the latter might become significant later in the adsorption process. The process should be further investigated in terms of other detoxification processes (such as aerobic or anaerobic degradation) that may run in parallel to adsorption in the biochar pores. Furthermore, biochars produced from various biomasses and under different

pyrolysis conditions should be tested, in order to determine the exact mechanisms of interaction with the wastewater.

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Figure Captions

Figure 1 Common polarization mechanisms relevant to biochar related processes. Electrical double layer (EDL) polarization associated with mineral grains; membrane polarization associated with mineral and pore constrictions (modified from Kemna et al., 2012)); and possibly surface charge transfer similar to metallic mineral grains (from Placencia-Gómez, 2015).

Figure 2 Schematic and photograph of the column used (all columns were identical).

Figure 3 FTIR absorption spectrum of biochar samples data.

Figure 4 Scanning electron microscopic images of (a) initial biochar and (b) biochar from the 10% column after the 10 days treatment indicating the after effect of the process.

Figure 5 Total phenol concentration and electrical conductivity of the processed OMW in each of the 4 columns after the 10 day period. Geochemical monitoring of the inflow OMW and treated OMW for all the experimental columns, for phenols (red) and electrical conductivity (blue). Biochar (BC) amended columns significantly reduced the phenol content of OMW, while the sand only (0% BC) column had a minimal impact. EC did not vary significantly for any column. Both Phenols concentration and EC are plotted in log scale, over one logarithmic decade, for direct comparison.

Figure 6 Spectral induced polarization data for the biochar amended columns. Data over a broad frequency range (0.01 – 10000 Hz), for the first and last day of the experiment, are shown. [a] Real conductivity data, and [b] Imaginary conductivity data; in the inset imaginary frequency data over one logarithmic decade for direct comparison with the real conductivity data.

Figure 7 Real (top) and imaginary (bottom) conductivity changes over the course of the experiment (10 Hz). Both graphs are plotted on log y scale (one logarithmic decade) for comparison. Imaginary conductivity for the control column (0% biochar) is truncated since it is order of magnitude lower ($\sim 10^{-7}$).

Figure 8 Conceptual schematic of the biochar impact on electrical properties. A-D distribution differences based on biochar concentration (A control, B 5%, C 10%, 25%) ;after a certain concentration biochar could form continuous ‘vein’ like structures; since biochar behaves as a conductor (Gao et al., 2017) such structures should increase the real component of complex conductivity. E biochar has a stronger EDL polarization, compared to sand grains, with direct implications on the SIP signature; the IP signature can be the result of EDL polarization and/or membrane polarization mechanisms. Adsorption mechanisms on biochar (as described by Li et al. (2017) can have a profound effect on SIP signatures.

Table Captions**Table 1** Biochar characteristics.

Production temperature/°C	500
Residence time/min	20
Total C (%)	50.5
H (%)	1.55
N (%)	1.29
O (%)	6.4
S (%)	0.14
O/C ratio	0.126
Ash content (%)	40.2
P (mg kg ⁻¹)	6610
K (mg kg ⁻¹)	16800
Na (mg kg ⁻¹)	910
Mg (mg kg ⁻¹)	4530
Mn (mg kg ⁻¹)	127
Ca (mg kg ⁻¹)	89200
Fe (mg kg ⁻¹)	2780
pH	9.3
Conductivity (μS cm ⁻¹)	759
Surface area (m ² g ⁻¹)	63.8

Table 2 Chemical analysis to the initial OMW and the outflows after the 10 days treatment.

	Initial OMW	0%	5%	10%	25%
		Biochar	Biochar	Biochar	Biochar
		After 10 days			
pH	4.88	4.92	6.57	8	5.9
Electrical Conductivity, mS/cm	9.4	9.6	10.9	9.1	12.5
Phenols, mg/L	2485	1921.6	850.7	310.9	1059.6
Soluble COD, mg/L	37600	36500	27100	16500	30600
NO ₃ ⁻ , mg/L	98	37	28	14	33
P, mg/L	194	164	106	29.5	120
Total Dissolved Solids, mg/L	4.8	4.84	5.5	4.57	6.26

Table 3 Composition of the porous media in the experimental columns saturated with OMW. The mixture of Ottawa and biochar was homogeneous inside the columns with no buffer zones present. The permeability was measured by using the constant-head method prior the 10 days' treatment.

	Porous media	Permeability
Column 1	Ottawa sand + 0 % w/w biochar	4.27×10^{-4} m/sec
Column 2	Ottawa sand + 5 % w/w biochar	4.13×10^{-4} m/sec
Column 3	Ottawa sand + 10 % w/w biochar	3.73×10^{-4} m/sec
Column 4	Ottawa sand + 25 % w/w biochar	3.04×10^{-4} m/sec

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