Science of the Total Environment 650 (2019) 267–276

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Cork as a sustainable carbon source for nature-based solutions treating hydroponic wastewaters – Preliminary batch studies

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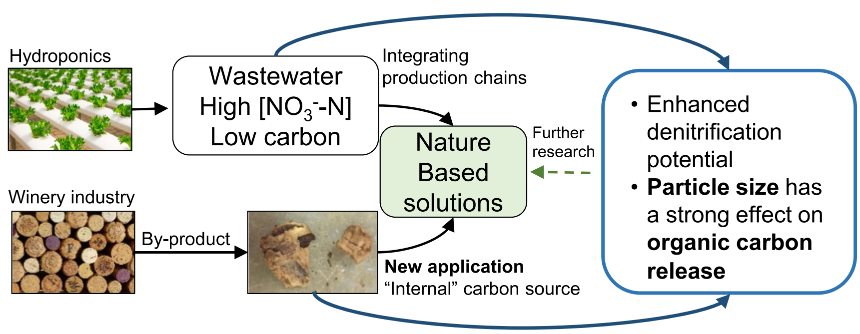
HIGHLIGHTS

- The reuse of local by-products like cork allows preservation of natural capital.
- Cork has the potential to enhance denitrification in nature-based solutions.
- As particle size increases, the release of carbon becomes slower along time.
- Estimations showed that 1.8 m^3–3.9 m^3 of hydroponic wastewater could be treated.
- Cork particle size is a key parameter to design natural denitrification solutions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 June 2018
Received in revised form 22 August 2018
Accepted 25 August 2018
Available online 27 August 2018

Keywords:
Wastewater
Denitrification
Reusing
By-products
Particle size
Contact time

ABSTRACT

Reusing by-products is an important strategy to ensure the preservation of natural capital and climate change mitigation. This study aimed at evaluating the potential of cork granulates, a by-product of winery industry, as an organic carbon (OC) source for the treatment of hydroponic wastewaters. First, chemical characterization was performed and discussed. Secondly, batch studies were performed using synthetic hydroponic wastewater to understand the role of particle size (PS), pH and contact time (CT) on the release of OC. The suberin is the major compound, representing >50%. It was noticed that a variance on the content of suberin across species, within the same species and depending on the extraction part (belly, cork and back) could be expected. >60% of the sample is composed by carbon while <1% was nitrogen (high C:N ratio), indicating a low risk of releasing organic nitrogen. The statistical results suggested that the main effect of PS on the release of OC is greater than both, CT and pH. The chemical release of OC gets slower with time, being this effect greater as the PS increase. Moreover, estimations showed that using the 4 mm PS, the amount of water treated would be twice the amount if the 8 mm PS had been used. The PS seems to play an important role at design nature-based solutions (NBS) focused on denitrification. The surface response methodology indicates a significant negative interaction between CT and PS suggesting that the mathematical model could be used for further optimization studies. The reuse of organic by-products as filter media seems to be an economic and environmentally friendly alternative to enhance

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https://doi.org/10.1016/j.scitotenv.2018.08.365
0048-9697/

denitrification in NBS, while preserving natural capital. However, further real scale and long-term experiments are needed to validate cork's potential as an "internal" OC source for NBS.

1. Introduction

In the past years, the use of urban and soilless agriculture is becoming more common to supply the ever-increasing food demand and to deal with water and land scarcity, increasing the risk of water pollution. Wastewater from soilless agriculture, besides having high concentration of nitrates and phosphates is usually drained and discharged to the environment without proper treatment (Prystay and Lo, 2001). The leaching of N and P causes several environmental impacts such as, groundwater pollution, eutrophication of surface waters and ecosystem biodiversity losses. Therefore, the treatment of wastewaters generated by soilless agriculture is a must as it may play an important future role, with regards of ensuring food security, sustainable management of water resources and environmental protection, once this type of agriculture is implemented, both in urban and rural environments.

Conventional treatments such as reverse osmosis and ion exchange membranes were highly efficient, although have high maintenance and operation costs (Koide and Satta, 2004; Gagnon et al., 2010; Park et al., 2015). Therefore, NBS, namely, constructed wetlands (CWs) and biofilters, may represent a sustainable and low-cost alternative for the removal of nitrogen from hydroponic wastewaters before discharge (Park et al., 2008; Gagnon et al., 2010; Abbassi et al., 2011; Park et al., 2015).

However, nitrogen removal from hydroponic wastewaters by NBS can be a challenge, since this water is known to have high concentration of nitrates and, at the same time, low carbon content (Prystay and Lo, 2001). The availability of carbon is one of the main limiting factors regarding the efficiency of biological denitrification (Vymazal, 2007; Mutsvangwa and Matope, 2017). According to Mutsvangwa and Matope (2017) wastewaters with low carbon to nitrogen ratio, usually require an external carbon source to achieve denitrification. However, the use of external carbon sources such as, methanol, ethanol, acetic acid and fructose besides increasing operational costs can cause negative environmental impacts (Park et al., 2008).

Therefore, alternative organic materials such as, plant biomass (Wen et al., 2010; Zhang et al., 2014), flower straws (Chang et al., 2016) and plant pruning (Park et al., 2008) have been proposed as external carbon sources to enhance denitrification in NBS, mainly because of their low cost, availability and renewable biomass. In addition, in the past 5 years, authors have shown the potential of roots exudates as a carbon source for denitrification in CWs (Zhai et al., 2013; Chen et al., 2016; Wu et al., 2017).

Moreover, some authors have suggested the use of organic filter media to enhance denitrification, such as, woodchip bioreactors (Nordström and Herbert, 2017), green walls built with coconut fibber and light expanded clay (Masi et al., 2016) and green walls with Coco coir (Prodanovic et al., 2017). Results of Prodanovic et al. (2017) indicated that biological processes are enhanced by the addition of organic filter media. The use of coco coir increased the retention time and the availability of OC, enhancing the microbiological removal process. On the other hand, the use of organic substrates can lead to an accumulation of total nitrogen in the effluent. The study of Masi et al. (2016) showed an increment of total Kjeldahl nitrogen when using coconut fibber and light expanded clay mixed, possibly due to the increment of retention time, which favours the release of organic compounds, such as organic nitrogen.

Nevertheless, reusing organic by-products, as filter media transforms, what was once an external source, into an integrated part of the system, reducing operational costs while preserving natural capital. In this regard, cork granulated seems to have potential to be used as a sustainable "internal" organic source for the treatment of hydroponic wastewaters.

Cork granulates by-product is generated from several operations of wine industry and is considered as a natural, renewable and biodegradable raw material (Olivella et al., 2011a; Sierra-Pérez et al., 2016). The cork oak trees are planted, the bark is stripped for the first time when tree is 20 to 25 years old. The next stripping is carried out every 9 to 12 years, with an expected productive life from 100 to 300 years depending on the tree's health (Jové et al., 2011; Olivella et al., 2013a). >80% of the world's cork is produced in Europe, being the annual production about 340.000 ton (Olivella et al., 2011a). However, the cork waste generated is around 50.000 ton (Olivella et al., 2011a), which represents approximately 15% of waste in relation to the total cork extracted.

Moreover, several researchers have shown the potential of cork to remove emergent pollutants such as, polycyclic aromatic hydrocarbons (Olivella et al., 2011a, 2011b, 2013a), phenanthrene (Olivella et al., 2013b), methyl orange (Krika and Benlahbib, 2015), ofloxacin (Crespo-Alonso et al., 2013), Biphentrin (Domingues et al., 2005) ibuprofen, carbamazepine and clofibric acid (Dordio et al., 2011) or heavy metals (Pintor et al., 2012). On the other hand, not much is known about the behaviour of cork regarding the release of OC and its potential to enhance denitrification in NBS.

The main goal of this paper was to investigate the potential of granulated cork as an OC source. The chemical release of OC can play an important role regarding the establishment of biofilm in natural wastewater treatments. Moreover, the chemical OC released by the substrate can enhance denitrification process while reducing the use of external carbon sources and thus, ensuring a long-term performance on pollutant removal, reducing operation costs and environmental hazard. The granulated cork was characterized (PZC, FTIR, chemical and elemental constitution) and batch studies were performed using synthetic hydroponic wastewater in order to understand the role of PS, pH and CT on the release of OC.

2. Materials and methods

2.1. Synthetic hydroponic wastewater

The composition of hydroponic wastewaters varies depending on the crops, type of fertilizers used for the nutritive solution, frequency of application, time of the year and type of system (closed or open). A literature research was made to establish a reliable range of contaminants to guide the preparation of synthetic hydroponic water (Table 1). The compounds used to prepare the solution were potassium Nitrate (KNO_3), calcium chloride dihydrate ($CaCl_2 * 2H_2O$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), sodium hydroxide (NaOH), magnesium sulphate heptahydrate ($MgSO_4$ ∗ 7H2O) and zinc sulphate heptahydrate ($ZnSO_4 * 7H_20$). The hygroscopic compounds were dried at 105 °C for 4 h and all compounds were mixed with tap water. When it was necessary, the water was stored in a freezer at 10 °C in order to avoid losses of N-ammoniacal by volatilization. However, the water was not stored for >3 days. The wastewater was prepared five times during the experiment to provide the same initial concentrations of contaminants for all the treatments. All data and the standard deviation can be seen in Table 1.