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New insights into the effects of support matrix on the removal of organic micro-pollutants and the microbial community in constructed wetlands☆

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ABSTRACT

Constructed wetlands (CWs) are an eco-friendly and cost-effective technology to remove organic micro-pollutants (OMPs) from wastewater. The support matrix is an important component in CWs as it has a primary role in the growth and development of plants and microbes. However, the roles of the support matrix in CWs in removing OMPs have not been systematically studied. Therefore, in this study, six common materials (sand, zeolite, blast iron slag, petcoke, polonite and crushed autoclaved aerated concrete (CAAC)) as support matrixes were firstly investigated by batch tests to explore their adsorption capacities to selected OMPs (ibuprofen, iohexol, tebuconazole and imazalil). Results showed that the adsorption capacities of the materials were low (at the level of μg/g) compared to well-known sorbents (at the level of mg/g), such as activated carbon and carbon nanotubes. Columns packed with the six materials, respectively, were then built up to study the effects of different materials on microbial community. In the medium-term study (66 days), the removal of four OMPs in all the columns increased by 2–58% from day 25 to day 66, and was mainly attributed to microbial degradation. Furthermore, Community-level physiological profiling (CLPP) analysis indicates that material presence shaped the microbial community metabolic function not only in the interstitial water but also in the biofilm. Overall, all the findings demonstrate that although the adsorption capacities of the common materials are low, they may be a driver to improve the removal of OMPs by altering microbial community function in CWs.

1. Introduction

Constructed wetlands (CWs) as an eco-friendly and cost-effective biotechnology for wastewater treatment, have been demonstrated to have potential for removing organic micro-pollutants (OMPs) from wastewater (Verlicchi and Zambello, 2014). The removal of OMPs in CWs is typically attributed to substrate sorption, plant uptake and biodegradation processes together (Dordio and Carvalho, 2013). Among these processes, biodegradation has been pointed to be a major process for OMP removal in CWs (Hijosa-Valsero et al., 2010; Zhang et al., 2017a; Lyu et al., 2018). Plant uptake and biodegradation have been more studied (Carvalho et al., 2014; Zhang et al., 2017a), but the role of the support matrix (CW substrate) in removing OMPs has not been fully addressed.

The support matrix is an important component in CWs as it has a primary role as physical support for the growth and development of plants and biofilm (Dordio and Carvalho, 2013). The material used as support matrix may influence the removal of OMPs by affecting the microbial community structures in CWs. To date, the effects of different support matrixes on microbial community structures in CWs have not been elucidated yet. In addition, the support matrix can also directly interact with OMPs by sorption processes, depending on the materials employed. These interactions could highly influence the performance of CW systems.

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Thus, an appropriate selection of support matrix may be a determining step to improve the removal of OMPs in CWs.

Some well-known good sorbents are generally high priced, limiting their wide application as CW media. Due to the low-cost/low-tech approach used by CW practitioners, the cheaply and locally available materials from natural sources, industrial by-products and man-made products have been mostly used (Dordio and Carvalho, 2013). In fact, for the last decade, large efforts have been made in identifying low cost materials with potential for enhanced phosphorus removal, such as sand (Arias et al., 2001), gravel (Vohla et al., 2011), polonite (Hylander et al., 2006), light expanded clay aggregates (LECA) (Dordio and Carvalho, 2013), crushed autoclaved aerated concrete (CAAC) (Berg et al., 2006), fly ash (Chen et al., 2007) and slags from steel and power plants (Hylander et al., 2006) etc. However, concerning OMPs, the sorption capacities of different materials have not been well documented. Although some works have reported the sorption of OMPs (pharmaceuticals, pesticides and phenolic compounds, etc.) by materials, such as activated carbon (Marinović et al., 2005; Salman and Hameed, 2010), clay-based materials (Boyd et al., 2001; Wang et al., 2009), zeolites and other siliceous materials (Huttenloch et al., 2001; Tahar et al., 2014) and industrial and agricultural wastes and by-products (Sharma et al., 2008; Nielsen et al., 2015), there are still a number of common materials used in CWs that need to be studied. Furthermore, only a preliminary indication of the efficiency or kinetics of the sorption processes can be provided as most work consisted of batch sorption studies at much higher OMP concentration than that observed in untreated or treated wastewater (Dordio and Carvalho, 2013). The sorption capacities of common materials (CW substrates) at typical concentration ranges of OMPs in real wastewater (ng to μg/L) are still unknown.

Filling the knowledge gaps on the sorption capacities of different materials for OMPs, as well as the effects of materials on microbial community, and consequently biodegradation, will allow to better understand the mechanisms behind OMP removal in CWs. As such, a range of substrates typically used in CWs is presently selected: natural materials (sand, zeolite and polonite), industrial by-products (blast iron slag, petroleum coke (petcoke) and man-made products (crushed autoclaved aerated concrete (CAAC)). Sand is one of the most common media used in CWs. Zeolite is a low-cost and readily available material, generally used for treating ammonium-containing wastewater (Copcia et al., 2010; Yang et al., 2017). Blast-iron slag, polonite and CAAC are often employed for the removal of phosphorus (Berg et al., 2006; Hylander et al., 2006). Petcoke is a carbonaceous hydrophobic black solid material that is delivered from the refinery coker units of crude oil. It is the precursor material for activated carbon preparation (Torrellas et al., 2015).

Two pharmaceuticals (ibuprofen and iohexol) and two pesticides (tebuconazole and imazalil) were used as the target compounds. Ibuprofen and iohexol, widely used in our daily life and hospital respectively, are frequently detected in environmental samples (Joss et al., 2006). The pesticides tebuconazole and imazalil are relevant in the agricultural setting but also commonly occur in storm water or surface water from urban settings (Bollmann et al., 2014; Gamba et al., 2015). Physico-chemical properties of the four OMPs are summarized in Table S1.

Therefore, we aimed to study the aforementioned four model OMPs: (a) adsorption to the selected materials by short-term isotherm experiments; (b) sorption and biodegradation in packed columns under medium-term operation (66 days) with spiked real wastewater. In addition, the similarity/dissimilarity of the microbial community function in the columns was studied using community level physiological profiling (CLPP) analysis. CLPP is an easy, accurate and rapid biotechnology, and has been widely used for investigating the functionality of microbial community in CWs (Zhao et al., 2010; Weber and Legge, 2011; Zhang et al., 2018).

2. Materials and methods

2.1. Chemicals

Methanol (>99.9%) and formic acid (98%, reagent ACS) were purchased from Merck (Darmstadt, Germany). In the batch adsorption tests, analytical quality standards of ibuprofen (98% purity), iohexol (95% purity), tebuconazole (99.3% purity) and imazalil (99.8% purity) were supplied by Sigma-Aldrich (Munich, Germany). In the packed column experiment, commercial products of the same compounds were purchased in local stores. The exact concentrations of the four compounds in the commercial products were determined before conducting the study to calculate the adequate dosage of the compounds in the wastewater.

2.2. Batch adsorption experiment

Adsorption isotherms were investigated by batch tests at 20 °C for the six selected materials (sand, zeolite, blast iron slag, petcoke, polonite and CAAC) (Fig. S1). These materials were purchased from Vestergård (Denmark), Silkem (Slovenia), HACO (Norway), Carbomax (Sweden), Ecofiltration (Sweden), Silikazit (Belgium), respectively. The physical and chemical characteristics of the six materials are presented in Table 1. Equilibrium isotherm experiments were performed (n = 2) using sealed aliquots of 500 mL of tap water with 30 g of sand, 5 g of zeolite, petcoke, polonite or CAAC and 10 g of blast iron slag, in brown glass bottles continuously agitated in a shaker (100 rpm) for 24 h. Each model compound was studied separately by spiking 10 different concentrations (0, 10, 30, 60 μg/L, 0.1, 0.25, 0.5, 1, 5, 10 mg/L). At the end of the equilibrium period (24 h), the bottles were placed on a desk for 4 h to allow settling of materials before aliquots of the supernatant were collected for further analysis. Bottles without any adsorbents were used as blanks to monitor the loss of adsorbates during the experiment. The amount of model compounds adsorbed onto materials, q_t (μg/g) was calculated by mass-balance relationship (Eq. (1)). Two common non-linear isothermal models to describe the adsorption process, namely Freundlich (Eq. (2)) and Langmuir (Eq. (3)) isotherm models were presently applied.

$$q_t = (C_0 - C_t)\frac{V}{W} \quad (1)$$

where C_0 and C_t are the liquid-phase concentrations of the model compounds (μg/L) at initial and time t, respectively, V is the solution volume (L) and W is the weight of the dry materials used (g).

$$q_e = K_f C_E^{1/N} \quad (2)$$

$$q_e = \frac{q_m k_l C_e}{1 + k_l C_e} \quad (3)$$

where, q_e is the mass of adsorbate per mass unit of adsorbent at equilibrium (μg/g), C_e is the equilibrium adsorbate concentration (mg/L), K_f is the Freundlich adsorption constant ($1/(\mu g/L)^N$), N is the degree of non-linearity, q_m is the maximum mass adsorbed at saturation conditions per mass unit of adsorbent (μg/g) and K_l is the Langmuir affinity coefficient, respectively.