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Analytical indicators to characterize Particulate Organic Matter (POM) and its evolution in French Vertical Flow Constructed Wetlands (VFCWs)

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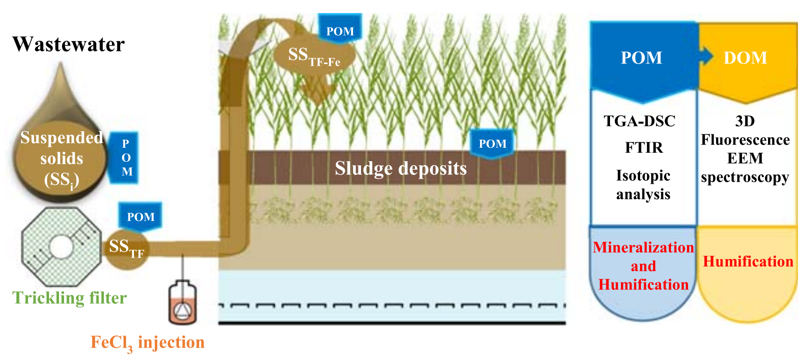
HIGHLIGHTS

- POM in inlet wastewater contains predominantly readily biodegradable compounds
- Along the treatment chain, POM is hydrolyzed and partially mineralized, and the residual fraction is progressively humified
- Thermal analyses provide relevant information on POM mineralization
- 3D fluorescence EEM spectroscopy is relevant to assess humification but requires a preliminary step of extraction
- Isotopic ratios, notably $\delta^{15}N$, are good indicators of biological processes of POM evolutions

GRAPHICAL ABSTRACT



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ABSTRACT

The design of French VFCWs leads to the formation of a sludge layer at the surface of the first filters due to the retention of suspended solids from the percolation of unsettled wastewater. This layer plays a major role in the system but still little is known on its characteristics and evolutions. In this study, suspended solids and sludge deposits sampled from two French VFCW plants were analyzed by different methods in the objective to assess the evolution of particulate organic matter (POM) along the treatment chain and within the sludge layer, and identify relevant analytical indicators of these phenomena. The treatment chain included an aerobic trickling filter followed by $FeCl_3$ injection and two successive stages of filters.

Thermal analyses showed that OM contents of suspended solids decreased along the treatment chain. POM in inflow suspended solids was predominantly composed of reactive, biodegradable compounds which were partly hydrolyzed and mineralized notably at the trickling filter stage. 3D fluorescence spectra collected from aqueous POM extracts confirmed the evolution of organic matter from low-molecular reactive compounds to more complex and stable structures such as humic-like substances. FTIR confirmed the mineralization of POM's reactive constituents along the treatment chain by the decrease in the intensities of the characteristics bands of aliphatic compounds or proteins, and its humification in the sludge deposits through the relative increase of the bands at 1634 cm^{-1} ($\nu_{C=O}$) and 1238 cm^{-1} ($\delta_{C=O}$ and/or δ_{OH}). Isotopic ratios $\delta^2H/^1H$ and $\delta^{15}N/^{14}N$ were found to be good indicators of POM evolutions. The higher values of $\delta^2H/^1H$ and $\delta^{15}N/^{14}N$ ratios measured in sludge deposits

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as compared to inflow suspended solids were related to POM humification and to microbial processes of POM hydrolysis and mineralization, respectively.

1. Introduction

Constructed wetlands have become over the last decade the number-one technology used by small communities in France for the treatment of domestic wastewaters. The so-called "French system" composed of two successive stages of vertical-flow filters fed with unsettled wastewater is by far predominant in France. The first-stage filter usually comprises three cells which are alternatively fed for a week and rested for two weeks. Suspended solids are thereby progressively accumulated by filtration at the surface of the first-stage filter cells in the form of a sludge layer. This phenomenon is often considered as a risk to reduce permeability and induce clogging (Knowles et al., 2011; Nivala et al., 2012). Some studies however have more recently revealed positive roles of the surface sludge layer in the retention of suspended solids and the sorption or degradation of dissolved trace pollutants (Kim et al., 2013; Kim et al., 2015a; Molle, 2014). Fu et al., 2015, showed that spreading at the surface of a newly installed constructed wetland filter, sludge deposits taken from a mature constructed wetland first-stage filter improved greatly the startup performance of the new constructed wetland. The benefits were attributed to the presence in the old sludge of active microbial communities and complex organic matter which helped prevent clogging by contributing to the porous structure of the layer. Another advantage may also be the release of soluble organic compounds from sludge OM hydrolysis which are leached to the bottom of the filter where they provide a good carbon supply to support denitrification (McCarty and Bremner, 1992; Van Oostrom and Russell, 1994).

Published work related to the sludge layer reported mostly quantitative parameters such as thickness, humidity and organic matter contents (Kania et al., 2017; Kim and Forquet, 2016; Nivala et al., 2012). Compositional and structural parameters have rarely been considered, both in practice and in scientific publications, although they might have strong influence on performance issues.

The objectives of our study were to analyze more specifically the characteristics of wastewater particulate organic matter (POM) in French VFCW systems and assess its evolution in the treatment chain and within the sludge layer. Two municipal vertical flow constructed wetland units based on the French system were selected for the study. Suspended solids were sampled from wastewater at different stages along the treatment chain and sludge deposits were sampled from the sludge layer at the surface of the first-stage filters. The samples were analyzed using several complementary methods including thermogravimetric analysis (TGA), Fourier-transform infrared (FT-IR) spectroscopy, 3D fluorescence excitation/emission (EEM) spectroscopy, and nuclear magnetic resonance (NMR) (Chen et al., 2003; Gomez et al., 2007; Gomez et al., 2005; Sheng and Yu, 2006; Wei et al., 2016; Zahra El Ouaqoudi et al., 2015).

2. Materials and methods

2.1. Origins of the samples

Particulate organic materials were taken from two French VFCW plants of similar sizes (around 1000 population equivalent) and with the same treatment stages, receiving mostly domestic wastewater. The plants were located in the middle-eastern part of France, respectively in Vercia (Jura) and Cormatin (Saône-et-Loire), and referenced here as VER and COR. Both plants were designed and operated according to the AZOE-NP® process patented by the French company SCIRPE in 2003 and illustrated in Fig. 1. This process comprised all the treatment stages of the classical French VFCW design, including gridding operations on inflow raw wastewater to remove coarse debris and particles. However it differed from the classical design by the implementation, ahead of the filter stages, of an aerobic trickling filter to improve organic load treatment and nitrification, followed by the injection of $FeCl_3$ solution to precipitate phosphates. Consequently, the suspended solids received by the first-stage filters in the AZOE-NP® process studied here were composed of a mix of (i) particulate materials from the wastewater influent, (ii) biofilm fragments detached from the aerobic trickling filter, and (iii) flocs coagulated by the action of $FeCl_3$. Following the trickling filter stage and $FeCl_3$ injection, the process included, as in the classical French system, two successive filter stages respectively made of three and two cells alternatively fed one week and rested for two or one week(s) respectively. In the AZOE-NP® process, the levels of water-saturation in the filter-cells was adjustable to allow nitrification in the upper, unsaturated zone, and denitrification in the lower, saturated zone.

The major difference between the two selected plants was in their number of years of operation. Vercia plant (VER) was started in 2004 as the first AZOE-NP® plant put in operation, whereas Cormatin (COR) was started in 2015.

2.2. Sampling and samples preparation

Inflow suspended solids, denoted SS_i, were collected from the inlet wastewater of each plant (spot (A) in Fig. 1) and also at different stages along the process line in COR as shown in Fig.1. This was not technically feasible in VER plant. Suspended solids denoted SS_{TF} were collected from the outlet of the trickling filter (spot B), and solids $SS_{TF\text{-}Fe}$ were collected from the wastewater spread at the surface of the first-stage filters (i.e. after $FeCl_3$ injection, spot C in Fig.1). Large volumes of suspensions were sieved to recover the suspended solids. The concentrated sieved suspensions were then poured into analytical-grade plastic flasks and the sieves washed with a small volume of the solution of origin in order to recover the totality of the sieved particles. The flasks were then taken to the laboratory where the suspensions were centrifuged and filtered at 0.45 μm on cellulose acetate filters.

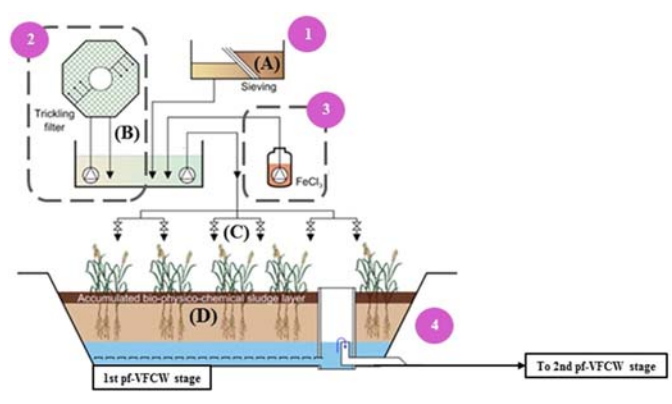

Fig. 1. Simplified diagram of AZOE-NP® process in the selected French VFCW plants (adapted from Kim et al., 2013). The numbers show the successive stages of the treatment line: [1] gridding/sieving; [2] aerobic biological trickling filter; [3] $FeCl_3$ injection, and [4] first stage filter cells. The letters show the locations of the sampling spots, as explained in Table 1.