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Quantification and kinetic characterization of soluble microbial products from municipal wastewater treatment plants

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A B S T R A C T

Soluble microbial products (SMP) formed by microorganisms in wastewater treatment plants (WWTPs) adversely affect final effluent quality and treatment efficiency. It is difficult to distinguish SMP from residual proteins, lipids and carbohydrates present in the influent that may persist during treatment. No method is currently available to determine quantitatively the extent to which SMP contribute to organic discharges from municipal WWTPs. In this work a modeling approach is presented which allows the SMP fraction of the effluent of a municipal WWTP to be quantified and described. The model is validated, in terms of utilization-associated products, biomass-associated products and extracellular polymeric substances, using influent from a municipal WWTP. SMP was found to account for, on average, 27 mg/L of chemical oxygen demand (COD), or 61% of the total COD in the WWTP effluent. Over 90% of the SMP was comprised of biomass-associated products. Five main factors influencing SMP formation in WWTP were evaluated. Neither wastewater composition nor mixed liquor suspended solids concentration was found to affect SMP production. On the other hand, a positive correlation was observed for SMP formation with both solids retention time and influent COD concentration, and a negative correlation with hydraulic retention time. Thus, operating or designing WWTPs with short solids retention and long hydraulic retention times could be considered as solutions for minimizing SMP production.

1. Introduction

Activated sludge is the most widely used technology to treat municipal wastewater in the world. Biodegradable organic pollutants in wastewater are hereby utilized by microorganisms as substrates for growth, maintenance and others microbial activities (de Silva and Rittmann, 2000; Ni et al., 2011). Soluble microbial products (SMP), which are released by microorganisms during normal metabolism in bioreactors, are composed of macromolecules such as polysaccharides, proteins, humic and fulvic acids and nucleic acids (Magbanua and Bowers, 2006; Ni et al., 2011; Zhang et al., 2008). These soluble organic compounds are present in wastewater treatment plant (WWTP) discharges and represent a significant fraction of the soluble organic carbon content of final effluent due to their refractory characteristics (Barker and Stuckey, 1999; Laspidou and Rittmann, 2002a, b; Wang et al., 2013). They are also distinct from extracellular polymeric substances (EPS), which are more sticky secretions from cells (Ni and Yu, 2012). Additionally, SMP are a major contributor to membrane fouling in membrane bioreactors (MBR) and constrain the application of this promising technology (Jiang et al., 2008; Kimura et al., 2009; Meng et al., 2009). A better understanding of the composition and control of final effluent SMP is therefore required to meet industrial challenges as well as the increasingly stringent limits applied to effluent quality.

Studies characterizing SMP production in biological wastewater treatment systems are almost always carried out at the laboratory scale using well-controlled reactors fed synthetic wastewaters (Jiang et al., 2008; Kimura et al., 2009; Xie et al., 2012). Investigations into SMP production from MBR systems treating real wastewaters have failed to segregate the SMP from un-degraded influent organic components (Drews et al., 2007; Reid et al., 2008). This is because it is impossible to distinguish SMP from any un-degraded influent organic components through simple chemical analyses alone as proteins, carbohydrates, and lipids are

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also the major components of municipal wastewater (Vakondios et al., 2014). There is hence a lack of fundamental understanding about the formation of SMP in full-scale WWTPs. It is additionally difficult to distinguish SMP from any un-degraded influent organic components through simple chemical analyses as proteins, carbohydrates, and lipids are also major components of municipal wastewater (Vakondios et al., 2014). The dependence of WWTP SMP production on process factors, such as influent chemical oxygen demand (COD), hydraulic retention time (HRT), solids retention time (SRT) and mixed liquor suspended solids (MLSS) concentration on SMP production in WWTPs, is currently poorly understood. The means to quantify and control SMP production would allow for further improvements in WWTP effluent quality. Given the difficulties in distinguishing SMP from un-degraded influent organic components, mathematical modeling presents as a feasible option for quantifying effluent SMP from full-scale WWTPs (Gernaey et al., 2004; Ni and Yu, 2012). This would also allow the influence of process parameters on SMP formation in full-scale WWTPs to be evaluated, and subsequent process optimizations.

In this study, the formation of SMP, including both utilization-associated products (UAP, defined as the products of the direct conversion of substrate) and biomass-associated products (BAP, or the products of the endogenous conversion of biomass), in a full-scale WWTP is evaluated using both experimental and modeling approaches. A model is developed to provide greater resolution than the existing descriptions of SMP production, accounting specifically for the different sources of SMP and the mechanisms for SMP degradation. This is in turn fully validated by extensive experimental data collected from studies on actual municipal wastewater. The fraction of SMP in the effluent is calculated and key factors influencing SMP formation analyzed. These results provide a better understanding of SMP formation in activated sludge processes and an efficient tool for quantifying and optimizing SMP production in WWTPs.

2. Materials and methods

2.1. Wastewater characterization and WWTP descriptions

The Zhuzhuanjing WWTP is located in Hefei City, China. It consists of gridirons, primary clarifiers and eight sequencing batch reactors (SBRs). Each SBR has a working volume of 2000 m^3 and is operated in a fill-and-draw mode, which includes: feeding, 30 min; aeration, 120 min; settling, 60 min; and decant, 30 min. The COD, 5-day biochemical oxygen demand (BOD_5), NH_4^+-N, total N and suspended solids (SS) concentrations in the influent are 160 ± 35, 60 ± 23, 20 ± 5, 35 ± 8 and 90 ± 46 mg/L, respectively. The MLSS, mixed liquor volatile suspended solids (MLVSS) and sludge volume index (SVI) of the activated sludge in the SBRs are 4000 ± 760, 2400 ± 510 mg/L and 85 ± 45 mL/g. The SRT and HRT of the WWTP are approximately 15 d and 8 h. The organic content of the wastewater is further classified into soluble readily degradable substrate (S_S), inert soluble organic substance (S_I), inert particulate organic solid (X_I), and slowly degradable substrate (X_S) according to whether it passes through a 0.45-μm membrane and its oxygen uptake rate (OUR) (from Equation (1)):

$$(S_S + X_S)^{*}V_{wastewater} = \frac{\int \Delta OUR^{*}dt^{*}V_{reactor}}{(1 - Y_H)} \quad (1)$$

S_S, S_I, X_I and X_S account for 30.1 ± 3.9%, 10.3 ± 2.3%, 11.0 ± 2.7% and 48.6 ± 3.2% of the total COD, respectively.

2.2. SMP experiments

Fresh activated sludge was taken from the full-scale SBR at the end of the aeration phase, washed with distilled water and added to 2-L reactors. The reactors were operated at temperatures of around 20 °C to enable BAP and UAP to be determined. BAP was calculated by aerating the sludge (MLVSS at 920 mg/L and 3100 mg/L) without substrate addition, whereby BAP dominate SMP as described by Jiang et al. (2008). 30 mL samples were drawn from the reactor and soluble COD (SCOD) and extracellular polymeric substances (EPS) measured at 1 h intervals. The BAP production rate constant was determined from the change in EPS concentration.

UAP experiments were conducted by spiking the sludge with 2 L of ultra-filtered wastewater. Due to the low strength of the WWTP influent COD (e.g., average COD concentration of 160 mg/L) and low fraction of S_S in the influent COD (30.1%), it was difficult to quantify UAP directly. Thus, the municipal wastewater influent was filtered first through a 0.45-μm membrane followed by an ultrafiltration membrane (PLAC cellulosic disks, MWCO, 1000 Da, Millipore Inc., USA) to concentrate the soluble readily degradable substrate. The concentrated retentate was then used to determine the UAP yield coefficients by fitting the measured SCOD data.

OUR was determined as follows: (1) 250 mL of mixed liquor sample were withdrawn from the reactors during aeration phase, (2) DO changes were measured using a dissolved oxygen (DO) electrode (LDO101, HACH Inc., USA); and (3) OUR was then calculated based on the DO depletion rate. SCOD was assessed following 0.45-μm membrane filtration of samples. EPS was extracted from the sludge using the cation-exchange resin technique (Dowex Marathon C, 20–50 mesh, sodium form, Fluka 91973), as described by Frølund et al. (1996). EPS content is described in terms of its total COD content. COD, NH_4^+-N, NO_3^--N, MLSS and MLVSS were measured by Standard Methods (APHA, 1995).

2.3. Model development

Fenu et al. (2010) reviewed the incorporation of SMP and EPS elements into the Activated Sludge Model, specifically with regards to assessing MBR performance. It was concluded that, while UAP formation can be accurately described, mechanisms for BAP formation are still uncertain. Laspidou and Rittmann (2002a, b) proposed a Unified Theory for SMP and EPS production assuming that BAP result only from EPS hydrolysis. Other studies (Aquino and Stuckey, 2008; Jang et al., 2006; Li et al., 2012) suggest that BAP result from both EPS hydrolysis and cell lysis. The extent to which either contributes to BAP formation however, is unknown. In order to reduce the uncertainty of parameters related to SMP production we assumed EPS hydrolysis to be the only source of BAP.

Conflicting mechanisms for SMP degradation have been proposed. In the Unified Theory developed by Laspidou and Rittmann (2002a, b) they assume that SMP are utilized directly by activated sludge. However, Jiang et al. (2008) observed that SMP were high molecular weight (MW) compounds (>20 kDa) and therefore unlikely to pass through cell membranes directly. Hence, they expanded on the existing activated sludge model No. 2d (ASM2d) to ASM2dSMP, to include four additional SMP-related parameters. The model of Jiang et al. (2008) assumes that SMP is hydrolyzed to fermentable COD, which then becomes available for utilization by heterotrophs. However, the model of Jiang et al. (2008) does not consider EPS as a source of BAP production (Laspidou and Rittmann, 2002a, b).

Our work therefore aims to overcome the limitations of existing SMP models by incorporating the latest insights into EPS and SMP production and consumption, in a dynamic biological wastewater treatment model that more accurately describes SMP production in