Sludge settling enhancement in petrochemical activated sludge systems focused on organic matter removal

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In agreement with the current tendencies, the recently approved version of the Best Available Techniques Reference Document for Wastewater Treatment in the Chemical Sector (UE 2016/902) recommends more stringent allowed emission levels to water. Consequently, the existing wastewater treatment processes need to be upgraded, in order to meet future regulations. Particularly, petrochemical activated sludge systems focused on organic matter removal must face two frequent issues, which difficult sludge settling: (i) Filamentous bulking caused by a low food-to-microorganism ratio (F/M) (Cardete *et al*., 2017a) (ii) undesired nitrification in the biological reactor, which results in denitrification with rising sludge in the clarifier (Cardete *et al*., 2017 a,b). The literature refers the implementation of selectors in several industrial sectors as a solution to the low F/M filamentous bulking (Al-Mutairi, 2009, Ferreira *et al*., 2014) . The present research has complemented the existing bibliography by experiencing with selectors in petrochemical activated sludge systems (Cardete *et al*., 2017 a,b, Cardete *et al*., 2018). With regard to nitrification control, conventional solutions deal with adjusting operational parameters (Flores-alsina *et al*., 2010, EPA, 2018) or implementing investments, such as intermediate denitrification steps. However, these possibilities may not be convenient because of process limitations, cost or site constraints. Therefore, an alternative strategy is suggested, by supplying folic acid to the biological reactor. As a vitaminic supplement, it has been reported to improve biological treatments (Burgess *et al*., 2000). Also, its nitrogen heterocyclic structure reminds of a group of effective nitrification inhibitors used in soils (McCarty and Bremmer, 1989).

Pilot-scale tests with real petrochemical substrate and inoculum have been conducted to assess about the effectiveness of aerobic and anoxic selectors to enhance sludge settling. Eventually, the design parameters of the aerobic selector have been optimized, as well as the operational parameters of the activated sludge system including the selector. The control of undesired nitrification by folic acid addition, as a novel strategy, has been bench-scale tested. Folic acid cost-effective concentrations of 0.4 and 0.9 mg g^{-1} VSS d^{-1} have been supplemented to respective petrochemical bioreactors, in comparison to a control. The effect of folic acid on nitrification patterns was assessed during and after the vitamin addition. Also, aiming to evaluate its full-scale implementation, the effect of folic acid on the heterotrophic operational parameters was evaluated.

The experimentation began operating the pilot plant as a petrochemical continuous stirred tank reactor (CSTR) to confirm the tendency of such systems to develop low F/M filamentous bulking and undesired nitrification. Sludge volumetric index (SVI) values higher than 350 mL g^{-1}, corresponding to abundant, cross-linked filaments inside and outside the floc were obtained (Cardete *et al*., 2017a). Also, nitrite and nitrate concentrations around 250 mg NO_x^--N L^{-1}were produced, with a tendency to increase while reducing the F/M ratio(Cardete *et al*., 2017a). The SVI in the petrochemical CSTR could only be slightly improved by increasing the F/M (up to 0.4 g COD g^{-1} VSS d^{-1}) (Cardete *et al*., 2017a) and by working at the optimum range of the mixed liquor parameters, such as dissolved oxygen (DO> 2 mg L^{-1}), ammonia concentration (> 2 mg L^{-1}), and sludge retention time (SRT) (< 19 d) (Cardete *et al*., 2018). However, the filamentous bulking was not definitively solved until a selector was implemented in the pilot activated sludge system. The experimental work demonstrated that aerobic and anoxic selectors improved the biomass quality. Nevertheless, when comparing both, the aerobic selector obtained a more reliable performance and lower SVI results (average 45 in front of 80 mL g^{-1}) (Cardete *et al*., 2017a). The inclusion of the aerobic selector was effective to improve the biomass quality, provided two conditions were accomplished (Cardete *et al*., 2017b): (i) guarantee a DO concentration greater than 2 mg L^{-1} in the main reactor (ii) operate the selector at its optimum parameters in order to obtain a high COD removal efficiency to establish the feed-starve cycle with the reactor (Henze *et al*., 2008), while keeping also a high substrate equilibrium concentration in the selector to enhance floc formers (Eckenfelder and Cleary, 2013). Hence, the optimum F/M and hydraulic retention time for the petrochemical aerobic selector were characterized at 35 g COD g^{-1} VSS d^{-1} and 30 min, respectively, to obtain average COD and BOD removal efficiencies in the selector of 35% and 95%, respectively. The optimum substrate equilibrium concentration in the selector was determined at 2.5 g COD L^{-1} (Cardete *et al*., 2017b). The best substrate for the selector to enhance sludge settling was a high biodegradable and low particulate content one. Therefore, while sludge settling ability in the CSTR was statistically ($p<0.05$) affected by F/M, SRT and ammonia nitrogen concentration, the effect of these variables was no longer significant with the inclusion of a selector. Otherwise, other parameters, such as suspended solids, pH, temperature and conductivity continued to have a key role on sludge settling even with the implementation of a selector. Hence, whereas an increase in mixed liquor suspended solid concentration (from 2.3 to 16 mg L^{-1}) or in conductivity (from 20 to 60 mS cm^{-1}) provided a poorer sludge settling, increasing pH (from 8.0 to 9.0) or temperature (from 30 to 38 ºC) enhanced sludge settling. While pH and temperature determined the ability of bacteria for bioflocculation, conductivity and temperature affected water properties with an effect on sludge settling, such as density and viscosity (Cardete *et al*., 2018). As a drawback, the inclusion of a selector in the activated sludge system resulted in an older sludge, which enhanced undesired nitrification in the biological reactor (increased in a 48% compared to the CSTR) (Cardete *et al*., 2017a). Therefore, the control of biological nitrification acquired more relevance with the inclusion of a selector in the activated sludge system. The supply of the lower folic acid concentration to the bench-scale bioreactor provided satisfactory results regarding to nitrification reduction (93.6%) and also an improvement of the sludge volumetric index compared to control (17.4 in front of 67.3 mL g^{-1}). However, its feasibility to be full-scale implemented is conditioned to the availability of spare aeration capacity, since oxygen demand increased in a 85.7%, probably due to an older sludge age (71.4% reduction in observed sludge yield). Reductions up to 97.1% in nitrification rates were obtained during and 60 days after the dosage of the higher vitamin concentration. Despite other advantages, such as increasing the organic matter removal efficiency (60.0%) and reducing oxygen demand (14.7%) relative to control, the high dosed reactor exhibited a worse sludge settling (93.1 mL g^{-1}) and more sludge production (57.1% increase in observed sludge yield). This scenario suggests an alternative strategy to explore in future research, to dosify discontinuous doses of 0.9 mg g^{-1} VSS d^{-1}.

To conclude, this research suggests the implementation of an aerobic selector in full-scale petrochemical activated sludge systems in order to overcome frequent low F/M filamentous bulkings. Rules for the design and operation of aerobic selectors in such systems are provided. Despite using petrochemical effluents, the methodology and conclusions could be extrapolated to other industrial sectors with a similar wastewater's composition. Complementarily to the inclusion of a selector, it is recommended to limit undesired nitrification in activated sludge systems focused on organic matter removal. As a novel strategy, this research suggests dosing 0.4 mg g^{-1}VSS d^{-1} of folic acid to the biological reactor, although other dosing strategies could also be pilot-tested. The behaviour patterns of the ammonia oxidizing bacteria have been reported, during and after folic acid addition, which could serve as background for future research, aiming to find a mechanism of action of nitrogen heterocyclic compounds. The last finding is also of interest for the agricultural sector, where nitrification is the main responsible for nitrogen losses and nitrogen oxides emissions.

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