

Nitrogen removal from coke making wastewater through a pre-denitrification activated sludge process.

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Abstract

Under the Industrial Emissions Directive (IED), coke production wastewater must be treated to produce an effluent characterised by a total nitrogen (TN) <50 mg/L. An anoxic-aerobic activated sludge pilot-plant (1 m³) fed with coke production wastewater was used to investigate the optimal operational requirements to achieve such an effluent. The loading rates applied to the pilot-plant varied between 0.198 - 0.418 kg COD/m³.day and 0.029 - 0.081 kg TN/m³.day, respectively. The ammonia (NH₄⁺-N) removals were maintained at 96%, after alkalinity addition. Under all conditions, phenol and SCN⁻ remained stable at 96% and 100%, respectively with both being utilised as carbon sources during denitrification. The obtained results showed that influent soluble chemical oxygen demand (sCOD) to TN ratio of should be maintained at >5.7 to produce an effluent TN <50 mg/L. Furthermore, nitrite accumulation was observed under all conditions indicating a disturbance to the denitrification pathway. Overall, the anoxic-aerobic activated sludge process was shown to be a robust and reliable technology to treat coke making wastewater and achieve the IED requirements.

Nevertheless, the influent to the anoxic tank should be monitored to ensure a sCOD:TN ratio >5.7 or, alternately, the addition of an external carbon source should be considered.

Keywords

Coke making wastewater, nitrification, denitrification, sCOD:TN ratio, nitrate-respiring bacteria.

1. Introduction

Coke making wastewater is a by-product of the steel industry produced from the quenching of hot coke masses, washing of ammonia stills, cooling and washing of coke oven gases and the processing and purification of coke (Pal and Kumar, 2014). World crude steel production reached 1,620 million tons for the year 2015 (World Steel Association, 2016). Coke making wastewater is produced in substantial quantities with 1000 tons of coke typically producing 1000 m³ of wastewater (Pal and Kumar, 2014). Such wastewater is hazardous, containing a complex mix of harmful and toxic compounds which require treatment prior to their discharge (Marañón et al., 2008; Wu et al., 2018). Quantities of the individual compounds vary over both time and space in response to the composition of the coals used and variations in plant operational conditions and production levels (Marañón et al., 2008). Coke making wastewater is characterised by high concentrations of ammonia (NH₄⁺-N) (50 - 500 mg/L) and thiocyanate (SCN⁻) (100 - 400 mg/L) (Marañón et al., 2008; Staib and Lant, 2007; Vázquez et al., 2006b). Breakdown of SCN⁻ results in the formation of NH₄⁺-N (0.24 g NH₄⁺/g SCN⁻) and therefore increased NH₄⁺-N loading is observed during the treatment process (Kim et al., 2008). Additional to the high nitrogen loading, the wastewater also contains other pollutant compounds such as phenol and polycyclic aromatic hydrocarbons (PAHs) (Vázquez et al., 2006b; Zhang et al., 2012b). Phenol has been reported at concentrations between 60 - 400 mg/L (Bai et al., 2010; Marañón et al., 2008; Staib and Lant,

2007; Vázquez et al., 2006b). Reports on the concentrations of polycyclic aromatic hydrocarbons (PAHs) are less commonly reported and vary substantially. Burmistrz and Burmistrz (2013) reported 255-312 µg/L for the sum of 16 PAHs whilst Zhang et al. (2012a) reported much higher concentrations of 5470 ± 907 µg/L for the sum of 18 PAHs. Raper et al. (2017) reported the sum of 6 PAHs at 179 ± 35 µg/L therefore being more comparable to the values reported by Burmistrz and Burmistrz (2013). Trace metals have been reported at 4216 µg/L (Raper et al., 2017).

Coke making wastewaters are regulated under the Industrial Emissions Directive (IED). Emission limits, introduced in 2016, require the reduction of total nitrogen (TN), the sum of ammonia-nitrogen ($\text{NH}_4^+\text{-N}$), nitrate nitrogen ($\text{NO}_3^-\text{-N}$) and nitrite-nitrogen ($\text{NO}_2^-\text{-N}$), to <50 mg/L (European Commission, 2013). Due to the high nitrogen content of coke making wastewaters it is therefore essential for current treatment processes to combine both nitrification and denitrification processes. Coke making wastewaters are typically treated through an activated sludge process (ASP) (European Commission, 2013). A pre-denitrification configuration i.e. anoxic-aerobic ASP, enables the use of organic matter in the wastewater, reducing the need for an external carbon source, as well as lowering the aeration demand in the nitrification reactor, both resulting in operational savings (Kim et al., 2008; Soares et al., 2010). The treatment of shock-loadings of pollutants in coke wastewater was previously investigated through a laboratory-scale anoxic-aerobic ASP to determine the cause of an observed treatment loss (Kim et al., 2009). Despite this, there has been no consideration of the optimal conditions for TN removal.

The toxic influence of compounds such as SCN^- and phenol on nitrification and denitrification of coke wastewater treatment has previously been investigated. Vázquez et al. (2006a) reported that SCN^- negatively impacted the removal of ammonia, in a laboratory-scale ASP, which decreased from $0.081 \text{ kg NH}_4^+-\text{N}/\text{m}^3/\text{d}$ in the absence of SCN^- to ca. $0.04 \text{ kg NH}_4^+-\text{N}/\text{m}^3/\text{d}$ when SCN^- was increased to 80 mg/L . In contrast, Kim et al. (2011) reported that shock-loading of SCN^- did not directly impact nitrification, rather, it impacted total nitrogen removal. Increased nitrogen loading to the system resulted in higher concentrations of nitrate and carry over of nitrate into the effluent. Increasing the recycling of nitrified effluent to the anoxic tank, however, improved removal efficiencies of nitrate and in turn total removal. The impact of SCN^- is therefore controversial. Furthermore, Kim et al. (2009) highlighted that the supply of inorganic carbon was critical in maintaining nitrogen removal as a result of the autotrophic nature of the nitrifying bacteria. When nitrification treatment efficiency declined the residual inorganic carbon in the treated effluent decreased from 15 to 5 mg/L , suggesting a shortage. Inlet alkalinity values were not reported. Vázquez et al. (2006b) reported an alkalinity addition requirement for coke wastewater of at least $6.5 \text{ mg CaCO}_3/\text{mg NH}_4^+-\text{N}$ for a 90% removal efficiency.

Denitrification is impacted by the supply of organic carbon with the removal of 1 g of NO_3^--N theoretically requiring 2.86 g of COD (Chakraborty and Veeramani, 2006). The actual requirement, nevertheless, varies in response to both the carbon compound, microorganisms present and the operational conditions (Carrera et al., 2004; Chakraborty and Veeramani, 2006; Metcalf & Eddy Inc, 2014; Yang et al., 2012). Although phenol was utilised as a form of carbon in the anoxic reactor, as the loading rates increased removal efficiencies in the anoxic reactor declined due to the insufficient contact time and supply of nitrate. A loading rate of $0.06 \text{ g-phenol/L.d}$ was associated with a 69.5% removal efficiency compared to a

removal efficiency of 32.1% at a loading rate of 0.25 g-phenol/L.d. Residual phenol was, however, degraded in the aerobic reactor. Despite this, it was highlighted that sudden increases in phenol in the aerobic reactor may result in a sudden proliferation of heterotrophic bacteria which could potentially out-number slower growing nitrifying bacteria.

Many laboratory-scale investigations have considered the inhibitory roles of pollutants associated with coke making wastewater (Amor et al., 2005; Chakraborty and Veeramani, 2006; Kim et al., 2011, 2009; Kwon et al., 2002; Vázquez et al., 2006a). Ammonia removal has been investigated through air stripping but this is unable to reduce ammonia sufficiently to enable compliance with a TN emission limit of 50 mg/L (Marañón et al., 2008). Alkalinity supply has been suggested as important in maintaining nitrification efficiencies in a laboratory-scale anoxic-aerobic ASP whilst carbon requirements have been investigated in a laboratory-scale post-denitrification ASP (Kim et al., 2009; Lee and Park, 1998). Optimal operational conditions and loading rates for TN removal in an anoxic-aerobic ASP have not been reported. The aim of this investigation was therefore to investigate TN removal at a larger scale through a pilot-scale anoxic-aerobic ASP and to identify the operational conditions required to consistently achieve an effluent TN of <50 mg/L.

2. Materials and Methods

2.1 Coke making wastewater and activated sludge biomass

The coke making wastewater used in this study was produced from a full-scale steelworks in the UK after primary treatment. During the long-term operation of the pilot-plant, the coke making wastewater was subject to the same variability as the full-scale site. The pilot-plant was seeded with activated sludge biomass taken from the return activated sludge (RAS) line

of the full-scale wastewater treatment system that operated an aerobic ASP with a hydraulic retention time (HRT) of 21 hours and a sludge retention time (SRT) of approximately 38 days.

2.2 Anoxic-aerobic pilot-plant configuration

A pilot-scale anoxic-aerobic ASP was designed with a 340 L (working volume) anoxic reactor, a 680 L (working volume) aerobic reactor and a 55 L (working volume) clarifier (Figure 1). The pollutant loading rates applied to the pilot-plant varied between 0.198 - 0.418 kg COD/m³.day and 0.029 - 0.081 kg TN/m³.day, respectively, due to adjustments in the feeding rates (0.32 - 0.55 m³/day) as well as the natural variability of pollutants concentration in the wastewater coming from the full-scale site. Consequently, the total hydraulic retention time (HRT) also varied from 76.5 - 45 h, which was significantly higher than the HRT of 16.7 h Kim et al. (2008) reported to be necessary to achieve stable nitrification and denitrification.

Return activated sludge was fed back into the anoxic reactor at a flow rate of 0.32 - 0.55 m³/d and was characterised by a mixed liquor suspended solids (MLSS) of 7150 mg/L. The sludge age was maintained at approximately 80 days through sludge wasting. Other studies, have investigated the nitrate recycle ratios (between the aerobic and anoxic reactors) from 1 to 5 (Chakraborty and Veeramani, 2006; Kim et al., 2008). Chakraborty and Veeramani (2006) reported a 75% removal of total nitrogen at a recycle ratio of 3. In this study, the recycle ratio was therefore kept at 3, to promote high removals whilst maintaining reasonable costs for the pumping requirement. A recycle ratio of 3 corresponded to a flow rate of 0.97- 1.65 m³/d.

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165 Temperature was maintained at $\sim 28^{\circ}\text{C}$ through the use of heaters in both the anoxic and
166 aerobic reactors. Dissolved oxygen (DO) in the anoxic reactor was maintained below 0.3
167 mg/L whilst Vitox oxygen injection maintained the DO in the aeration reactor between the set
168 points of 2 - 4 mg/L. Mixed liquor suspended solids were maintained at 4800 ± 1600 mg/L and
169 were kept in suspension through the use of a submersible pump in the anoxic reactor and
170 through the action of the Vitox oxygen injection in the aeration reactor.

171 The addition of sodium carbonate was previously established in coke wastewater samples
172 taken from the full-scale steelworks, as critical for successful nitrification of coke making
173 wastewater through the provision of inorganic carbon for nitrifying bacteria and pH buffering
174 (Raper et al., 2018b). The influent wastewater was therefore dosed with the optimised
175 concentration of sodium carbonate of 523 mg/L as CaCO_3 . The pH averaged at 7.9 and 7.2 in
176 the anoxic and aerobic reactors, respectively. The higher pH in the anoxic reactor was
177 associated with the alkalinity dosing of the influent.

178

179 **Figure 1: Pilot-scale anoxic-aerobic ASP configuration, operational conditions and**
180 **sampling locations.**

181

182 **2.3 Analytical methods**

183 Duplicate daily samples were taken from the inlet reactor, anoxic reactor overflow, aerobic
184 reactor overflow, return sludge feed and system outlet (Figure 1). Samples were filtered
185 through $0.45\ \mu\text{m}$ filters and refrigerated at $2 - 5^{\circ}\text{C}$ before analysis. Total nitrogen (TN) was
186 calculated through the measurement of $\text{NO}_2^{-}\text{-N}$, $\text{NO}_3^{-}\text{-N}$, $\text{NH}_4^{+}\text{-N}$ and $\text{SCN}^{-}\text{-N}$ (included due

to its degradation to $\text{NH}_4^+\text{-N}$). Although TN, is defined as containing organic nitrogen, coke making wastewaters contain very little organic nitrogen other than SCN^- (Vázquez et al., 2007) and therefore the method used is a good approximation of TN. Nitrite-nitrogen, NO_3^- -N, $\text{NH}_4^+\text{-N}$ and soluble chemical oxygen demand (sCOD) were analysed using Merck cell test kits according to the manufacturer's instructions. Thiocyanate was analysed colourmetrically by complex reaction with thiocyanate and iron oxide at a wavelength of 465 nm, based on The Institute of Gas Engineers analytical method (The Institution of Gas Engineers, 1971). Mono phenols were analysed by complex reaction with 4-aminoantipyrine at a wavelength of 510 nm, based on ISO 6439:1990 (ISO, 1990). Both were analysed using a Jenway 6300 spectrophotometer (Staffordshire, UK). pH was recorded using a Jenway 3540 pH meter (UK). Total suspended solids (TSS), alkalinity and BOD_5 were analysed according to standard methods (Eaton, 2005). Data was analysed using a Grubbs' test to identify outliers. Outliers were subsequently excluded from the data set.

3. Results and discussion

3.1 Coke making wastewater composition and pilot-plant operation

Over the 5 month period the pilot-plant was operated, the feed coke making wastewater was subject to the same variation as the full-scale treatment plant (Table 1). Total nitrogen concentrations averaged at 110 mg/L, varying from 87 to 152 mg/L. Ammonia-nitrogen averaged at 59 mg/L, varying from 43 to 75 mg/L. Nitrite-nitrogen levels ranged from 6 to 29 mg/L averaging at 13 mg/L whilst NO_3^- -N levels were low, at an average of 3.3 mg/L and a maximum of 6.2 mg/L. Phenol concentrations averaged at 99 mg/L during the pilot-plant operation, however, concentrations were initially at ca. 166 mg/L, declining to 52 mg/L at the

end. Phenol concentrations were more variable than previous reports (Raper et al., 2017). Thiocyanate was comparable to previous reports averaging at 154 mg/L (Raper et al., 2017). Soluble chemical oxygen demand averaged at 710 mg/L, ranging from 528 to 906 mg/L. Pollutant concentrations observed in the wastewater were therefore within the lower end of the ranges reported in the literature and lower than those observed by Kim et al. (2008).

Table 1: Characterisation of coke wastewater composition feed to the pilot-plant.

During this study, the wastewater was fed to the pilot-plant at a rate between 0.32 - 0.55 m³/day corresponding to HRTs from 45 - 76.5 h. Due to the high natural variation of the wastewater composition, the correlation between HRT and SCN⁻, phenol and TN loading rates did not follow a linear relationship (Figure 2). In the current investigation, the lack of correlation between the HRT and loading rate was particularly noticeable for the phenol loading which varied from 0.026 to 0.039 kg/m³.d at HRTs 76.5 – 52.5 h. At the shortest considered HRT, of 45 h, phenol loading rates were at their lowest (0.007 – 0.016 kg/m³.d). Similarly, SCN⁻ loading rates did not increase linearly with the decreased HRTs with observed SCN⁻ loading rates of 0.046 – 0.057 kg/m³.d, 0.038 – 0.059 kg/m³.d and 0.044 – 0.067 kg/m³.d at 76.5, 67.5 and 60 h HRT, respectively. Although TN loading rates showed an overall increase with declining HRT there was still considerable overlaps between the different HRTs (Figure 2). Traditionally, HRT has been used as an operational parameter, however, it is not useful for the treatment of industrial wastewaters which have a variable composition. When influent concentrations vary significantly setting a fixed HRT cannot guarantee consistent treatment efficiencies as pollutant loading rates can vary significantly

which may result in an insufficient contact time between the degrading microorganisms and pollutant.

Figure 2: Correlation between HRT and a. phenol loading rate b. thiocyanate loading rate c. total nitrogen loading rate.

3.2 Biodegradation of phenol and thiocyanate

Influent to the anoxic-aerobic pilot-plant was characterised by phenol concentrations of 52 to 166 mg/L corresponding to a loading rate of 0.007 to 0.059 kg/m³.d. The mass balances completed, demonstrate that phenol was removed primarily in the anoxic reactor with removal efficiencies of 82 - 99% (Figure 3 and Figure 4). These results indicate that phenol was consumed as a carbon source by denitrifying bacteria. Under high loading conditions (0.059 kg/m³.d) some residual phenol passed into the aerobic reactor, but there was enough capacity in the aerobic reactor to ensure that the remaining phenol was degraded to 0 - 1.7 mg/L, averaging at 0.8 mg/L. Phenol removal efficiencies were consistently greater than 96%, averaging at 99%, similar to those observed by Kim et al. (2009) in laboratory-scale investigations. Nevertheless, further process optimisation would be required to ensure total compliance, as phenol emissions exceeded the 0.5 mg/L limit set by the IED. Increasing the sludge age may allow improved phenol degradation rates whilst the incorporation of other technologies such as bioaugmentation and activated carbon have also been shown to be effective at improving phenol removal efficiencies and resilience to shock-loads (Fang et al., 2013; Vinitnantharat et al., 2001).

Thiocyanate loading rates varied from 0.038 - 0.101 kg/m³.d and removal efficiencies averaged at 99% resulting in average effluent concentrations of 1.1 mg/L (Figure 3 and Figure 4) complying with the 4 mg/L emission limit set by the (European Commission, 2013) (Table 2). Removal efficiencies of SCN⁻ were comparable to those reported by Kim et al. (2011, 2008) in a laboratory-scale anoxic-aerobic ASP. Degradation of SCN⁻ has been reported to be possible by a wide variety of bacteria under a wide range of conditions (Raper et al., 2018a). Removal of SCN⁻ was complete in the anoxic reactor of the pilot-scale anoxic-aerobic ASP (Figure 3 and Figure 4) showing capability of the bacteria to degrade SCN⁻ under anoxic conditions. This contrasts the findings of Kim et al. (2011, 2008) who reported that SCN⁻ degradation took place in the aerobic reactor of the laboratory-scale anoxic-aerobic ASP.

Table 2 Industrial Emission Directive emission limits for coke wastewaters.

Figure 3: Mass balance for anoxic-aerobic pilot-plant characterised by an effluent <50 mg/L TN.

Figure 4: Mass balance for anoxic-aerobic pilot-plant characterised by an effluent >50 mg/L TN.

3.3 Nitrogen removal

During the operation of the ASP pilot-plant, TN removal was observed by the combination of denitrification and nitrification. The wastewater natural variability in composition resulted in variable SCN^- , phenol and TN in the feed wastewater, that together with changes in operational loading rates, resulted into 2 different phases of operation that could be grouped in effluent TN concentrations $<50 \text{ mg/L}$ and $> 50 \text{ mg/L}$.

3.3.1 Effluent nitrogen $<50 \text{ mg/L}$

Mass balances were produced for the anoxic-aerobic ASP pilot-plant to understand the conditions required to achieve an effluent characterised by TN of $<50 \text{ mg/L}$ (Figure 3 and Figure 4). When the effluent had a TN $<50 \text{ mg/L}$ the wastewater influent concentrations were characterised by: $60 \text{ mg/L NH}_4^+ \text{-N}$, $10 \text{ mg/L NO}_2^- \text{-N}$ and $4 \text{ mg/L NO}_3^- \text{-N}$ (Figure 3). This corresponded to loading rates of $0.027 \text{ kg/m}^3 \cdot \text{d NH}_4^+ \text{-N}$, $0.004 \text{ kg/m}^3 \cdot \text{d NO}_2^- \text{-N}$ and $0.002 \text{ kg/m}^3 \cdot \text{d NO}_3^- \text{-N}$. Ammonia-nitrogen was therefore the largest contributor to TN in the influent. Thiocyanate was present at 163 mg/L in the influent and through its degradation it produced a further 39 mg/L of $\text{NH}_4^+ \text{-N}$ corresponding to an additional $\text{NH}_4^+ \text{-N}$ loading rate of $0.018 \text{ kg/m}^3 \cdot \text{d}$. Total nitrogen concentrations in the influent were 112 mg/L giving a loading rate of $0.051 \text{ kg/m}^3 \cdot \text{d}$. Nitrification was stable at 98% with ammonia being removed to below the detection limit of 2 mg/L comparable to other reported nitrification efficiencies (Wu et al., 2018). As a result of nitrification, $\text{NO}_3^- \text{-N}$ concentrations increased substantially from an influent of 4 mg/L to a concentration of 25 mg/L in the aerobic reactor.

The concentrations of sCOD and phenol were 638 mg/L and 71 mg/L , respectively. The feed wastewater was therefore characterised by a sCOD:TN ratio of 5.7. Combining the influent, RAS and nitrate recycle, resulted in a sCOD loading rate of $1.429 \text{ kg/m}^3 \cdot \text{d}$ and a TN loading rate of $0.408 \text{ kg/m}^3 \cdot \text{d}$ resulting in a sCOD:TN ratio of 3.9 fed to the anoxic reactor. Nitrate

was reduced in the anoxic reactor resulting in a 46% TN removal efficiency. The consumption of carbon for denitrification led to a 43% removal of sCOD and a 92% removal efficiency for phenol. As a result of the nitrogen removal, effluent from the anoxic-aerobic ASP was characterised by a TN of 48 mg/L meeting the IED 50 mg/L emission limit.

3.3.2 Effluent TN>50 mg/L

A mass balance was subsequently produced for the anoxic-aerobic reactor when effluent TN concentrations exceeded the 50 mg/L emission limit (Figure 4). The influent concentrations were characterised by: 68 mg/L of $\text{NH}_4^+\text{-N}$, 23 mg/L $\text{NO}_3^-\text{-N}$ and 5 mg/L $\text{NO}_2^-\text{-N}$. This corresponded to loading rates of 0.036 $\text{kg/m}^3\text{.d}$ $\text{NH}_4^+\text{-N}$, 0.003 $\text{kg/m}^3\text{.d}$ $\text{NO}_3^-\text{-N}$ and 0.013 $\text{kg/m}^3\text{.d}$ of $\text{NO}_2^-\text{-N}$. The influent contained 175 mg/L of SCN^- giving a loading rate of 0.093 $\text{kg/m}^3\text{.d}$. The degradation of SCN^- in the anoxic reactor supplied the system with a further 42 mg/L of $\text{NH}_4^+\text{-N}$ to the system. Ammonia-nitrogen was the main contributor to TN. Nitrification removal efficiencies were also comparable at 96% with ammonia being removed to below the detection limit of 2 mg/L. In contrast, $\text{NO}_3^-\text{-N}$ concentrations increased, as a result of nitrification, from an influent of 5 mg/L to a concentration of 71 mg/L in the aerobic reactor.

Overall, the system was characterized by a TN loading rate of 0.069 $\text{kg/m}^3\text{.d}$, an increase on that observed when the anoxic-aerobic reactor was operating within the TN 50 mg/L emission limit (0.051 $\text{kg/m}^3\text{.d}$). Influent sCOD concentrations were 670 mg/L giving a higher loading rate of 0.357 $\text{kg/m}^3\text{.d}$. Phenol concentrations of 67 mg/L contributed to a

much lower loading rate of just 0.013 kg/m³.d. As a result of higher TN concentrations, the sCOD:TN ratio of the pilot-plant feed decreased to 5.2.

Significant differences in treatment efficiencies occurred in the anoxic reactor. Due to the increased production of NO₃⁻-N in the aerobic reactor, from 25 mg/L to 71 mg/L, the loading rate of NO₃⁻-N to the anoxic reactor more than tripled from 0.139 to 0.463 kg/m³.d. The NO₃⁻-N specific removal rate increased from 0.081 g/g VSS.d (TN <50 mg/L) to 0.186 g/g VSS.d (TN >50 mg/L) in response to the increased loading. The sCOD loading increased from 1.429 kg/m³.d (TN <50 mg/L) to just 1.619 kg/m³.d. Nitrate-nitrogen concentrations in the anoxic reactor increased from 1 mg/L (TN <50 mg/L) to 22 mg/L. The concentration of NO₂⁻-N was more than double, at 42 mg/L, with no removal being observed. Consequently, the denitrification efficiency decreased from 93% to 61%. Total nitrogen removal in the anoxic reactor declined from 46% to 15%. Decreased nitrogen removals were associated with the decreased sCOD:TN ratio of influent to the anoxic reactor of 1.4 which was insufficient for the complete removal of NO₃⁻-N and NO₂⁻-N. Figure 5 shows the impact of the anoxic sCOD:TN ratio on NO₂⁻-N, NO₃⁻-N and TN concentrations in the anoxic reactor. When the anoxic sCOD:TN ratio declined below a ratio of 4, NO₂⁻-N concentrations started to increase. Below an sCOD:TN ratio of 2 concentrations of NO₂⁻-N and NO₃⁻-N increased rapidly.

Figure 5: Changing concentrations of □ NO₂⁻-N, ● NO₃⁻-N and ○ TN in the anoxic reactor in response to changes in the anoxic sCOD:TN ratio. Dashed line marks anoxic sCOD:TN ratio below which nitrogen rapidly accumulates.

As a result of the poor performance of the anoxic reactor under carbon limited conditions the anoxic-aerobic ASP effluent TN increased substantially to 89 mg/L greatly exceeding the 50 mg/L IED emission limit. With effluent concentrations of 67 mg/L of NO_3^- -N the emission limit was exceeded by NO_3^- -N concentrations alone. Whilst the decline in the sCOD:TN ratio of the influent appeared relatively small, declining from 5.7 to 5.2, the increased TN loading had a much more significant impact on the sCOD:TN ratio observed in the anoxic reactor which declined from 3.9 to 1.4. The sCOD:TN ratio of the anoxic reactor is therefore a more accurate indication of TN removal potential. Liu et al. (1996) reported that the carbon requirement was best represented by the influent COD:TN ratio during the treatment of coal gasification and coke plant wastewater, however, comparability needs to recognise the different treatment configuration which consisted of the use of a submerged biofilm in the anoxic cell and also the use of total COD rather than soluble COD. Furthermore, an influent sCOD:TN ratio of 5.7 in the current investigation resulted in TN removal efficiencies of 57%, much lower than the 83% removal efficiency observed by Liu et al.(1996) at a COD:TN ratio of 5.

3.3.3 Nitrite removal in the anoxic-aerobic reactor

A notable characteristic of the anoxic-aerobic ASP was the poor removal of NO_2^- -N (Figure 6). The presence of NO_2^- -N can be indicative of a disturbance or limitation within the nitrification and or denitrification step process (Philips et al., 2002). Several factors have been associated with the accumulation of NO_2^- -N during the denitrification process including the type of carbon (Rocher et al., 2015), reactor pH (Cao et al., 2013), the rate of NO_3^- -N and NO_2^- -N reduction (Philips et al., 2002) and the abundance of species present (Philips et al.,

2002). Carbohydrates and organic acids have been reported to result in the accumulation of 0.2 - 0.3 g NO_2^- -N/g NO_3^- -N whilst alcohols such as methanol, ethanol or glycerol resulted in lower accumulations of 0.05 - 0.1 g NO_2^- -N/g NO_3^- -N (Rocher et al., 2015). A high pH may result in the accumulation of NO_2^- -N as the NO_2^- -N reduction rate decreases with increased pH (Cao et al., 2013). The abundance of species present in the mixed liquor can also impact NO_2^- -N accumulation due to the relative numbers of true denitrifying bacteria (complete both NO_3^- -N and NO_2^- -N reduction) and incomplete denitrifiers/nitrate-respiring bacteria (complete NO_3^- -N reduction but are unable to reduce NO_2^- -N) (Philips et al., 2002).

Figure 6: Variation of nitrite-nitrogen (NO_2^- -N) concentration at different stages of the anoxic-aerobic ASP pilot-plant when effluent concentration was $\text{TN} < 50 \text{ mg/L}$ - ■ and at $\text{TN} > 50 \text{ mg/L}$ - □.

When effluent TN concentrations were $< 50 \text{ mg/L}$, NO_2^- -N accumulated from 10 mg/L in the influent to 16 mg/L in the effluent. Under carbon-limiting conditions when the effluent TN exceeded 50 mg/L, NO_2^- -N concentrations were observed to increase significantly in the anoxic reactor suggesting that the main disturbance was associated with the denitrification and the reduction of NO_2^- -N to nitrogen gas. Nitrite-nitrogen entered the anoxic reactor at 22 mg/L whilst effluent from the anoxic reactor contained 42 mg/L of NO_2^- -N, representing a 55% increase in NO_2^- -N concentrations. Under carbon limited conditions, the pH was suitable for denitrification and therefore species abundance may be responsible for the increased NO_2^- -N accumulation. Species of *Rhodanobacter* genus have previously been identified as representing a significant abundance (11%) in the bacterial composition of the activated sludge used in this study (Raper et al., 2018a). Whilst some species of *Rhodanobacter*

(*Rhodanobacter denitrificans*) have been associated with complete denitrification (Prakash et al., 2012) others (*Rhodanobacter thiooxidans*) have been characterised as capable of NO_3^- -N reduction but not NO_2^- -N reduction (Lee et al., 2007). Under carbon limited conditions, competition for electron donors becomes more intense which has been reported to favour NO_3^- -N reduction (Oh and Silverstein, 1999). The competitive conditions can therefore lead to a further increase the numbers of incomplete denitrifiers/nitrate-respiring bacteria. Consequently, the high loading of NO_3^- -N to the anoxic reactor observed when the effluent TN >50 mg/L, would result in reduced NO_2^- -N removal efficiencies further exacerbating NO_2^- -N accumulation. Any accumulation of NO_2^- -N is undesirable due to the resulting impact on the ability to reach ever tightening nitrogen emission limits and its higher toxicity relative to other nitrogen compounds. Consequently, a clear indication of the pathways leading to NO_2^- -N accumulation requires more investigation.

4. Conclusion

The anoxic-aerobic ASP pilot-plant was capable of removing SCN^- and phenol under all loading rates to 100% and 96% respectively. Nitrification remained stable at >96% under all conditions. Both phenol and SCN^- were utilised as carbon sources during denitrification. Organic carbon availability was a critical parameter in nitrogen removal. Influent to the anoxic-aerobic ASP required an sCOD:TN ratio of 5.7 to enable an effluent characterised by a TN concentration <50 mg/L. At an sCOD:TN ratio of 5.2 the emission limit was exceeded (89 mg/L) as NO_3^- -N removal efficiencies in the anoxic reactor decreased from 93% to 61%. Hence, to achieve the IED requirements is recommended that the sCOD:TN ratio in the fed wastewater to the ASP is kept >5.7, and an external carbon should be considered together with alkalinity dosing. The presence of NO_2^- -N in the anoxic reactor under all conditions

419 indicates a disturbance to the denitrification process which may be attributed to the bacterial
420 speciation and was exacerbated under carbon limited conditions.

421

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Table I: Characterisation of coke wastewater composition feed to the pilot-plant.

Average and standard deviation (mg/L)	
BOD	390 ± 60
sCOD	710 ± 110
NO ₂ ⁻ -N	13 ± 6
NO ₃ ⁻ -N	3 ± 1
NH ₄ ⁺ -N	59 ± 9
TN	113 ± 15
SCN	154 ± 22
SCN ⁻ -N	37 ± 5
Phenol (mono)	99 ± 31
SS	40 ± 20
pH*	9.4 ± 0.2
Trace metals (µg/L)**	149 ± 21

*After alkalinity dosing (523 mg/L as CaCO₃)

** Sum of Cr, Ni, Cu, Zn, As, Cd and Pb.

541 **Table 2: Industrial Emission Directive emission limits for coke wastewaters .**

542

Industrial Emission Directive emission limit (mg/L)

COD: < 220

BOD₅: <20

SCN: < 4

PAHs*: 0.05

Phenols: 0.5

TN: <15-50

Figure 1
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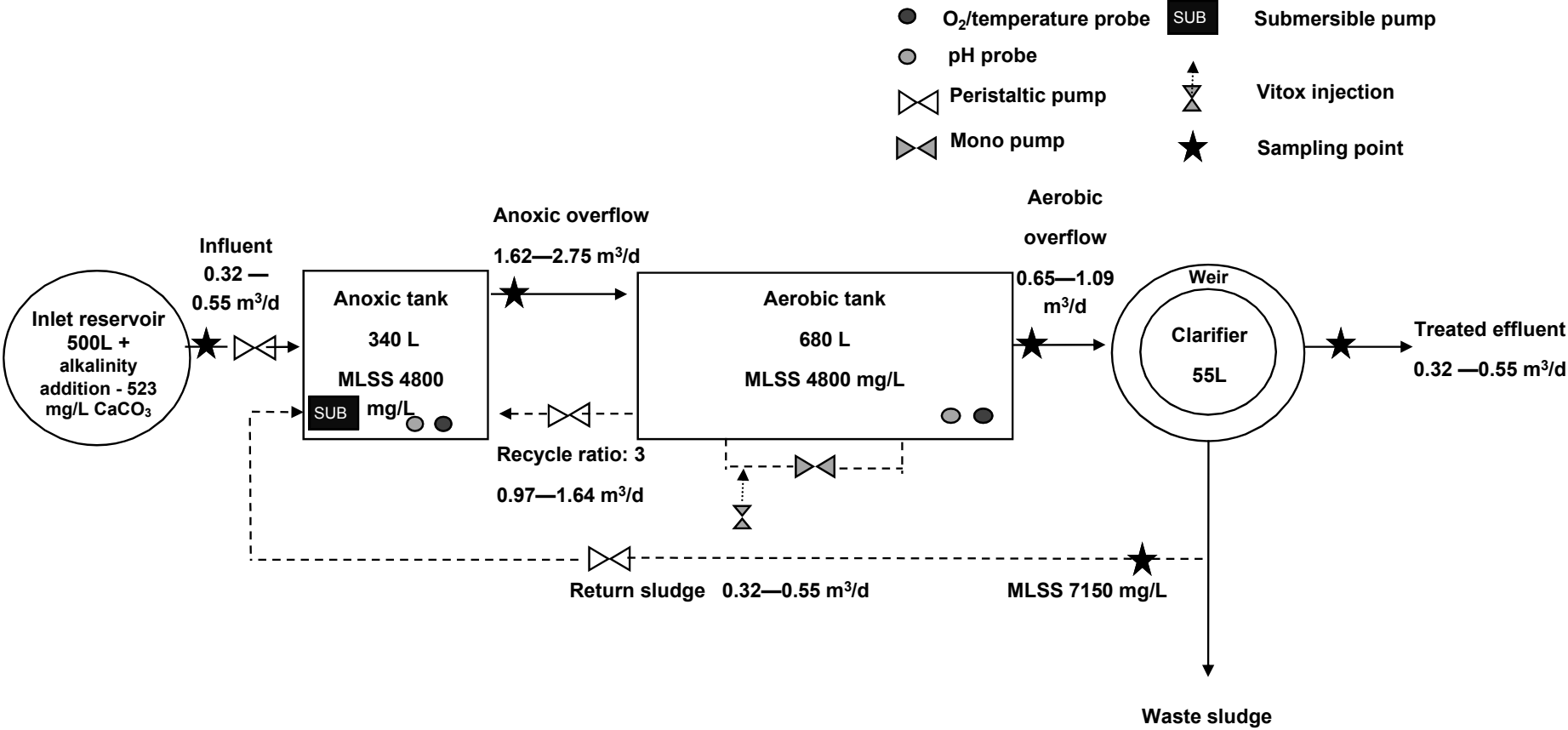


Figure 1: Pilot-scale anoxic-aerobic ASP configuration, operational conditions and sampling locations.

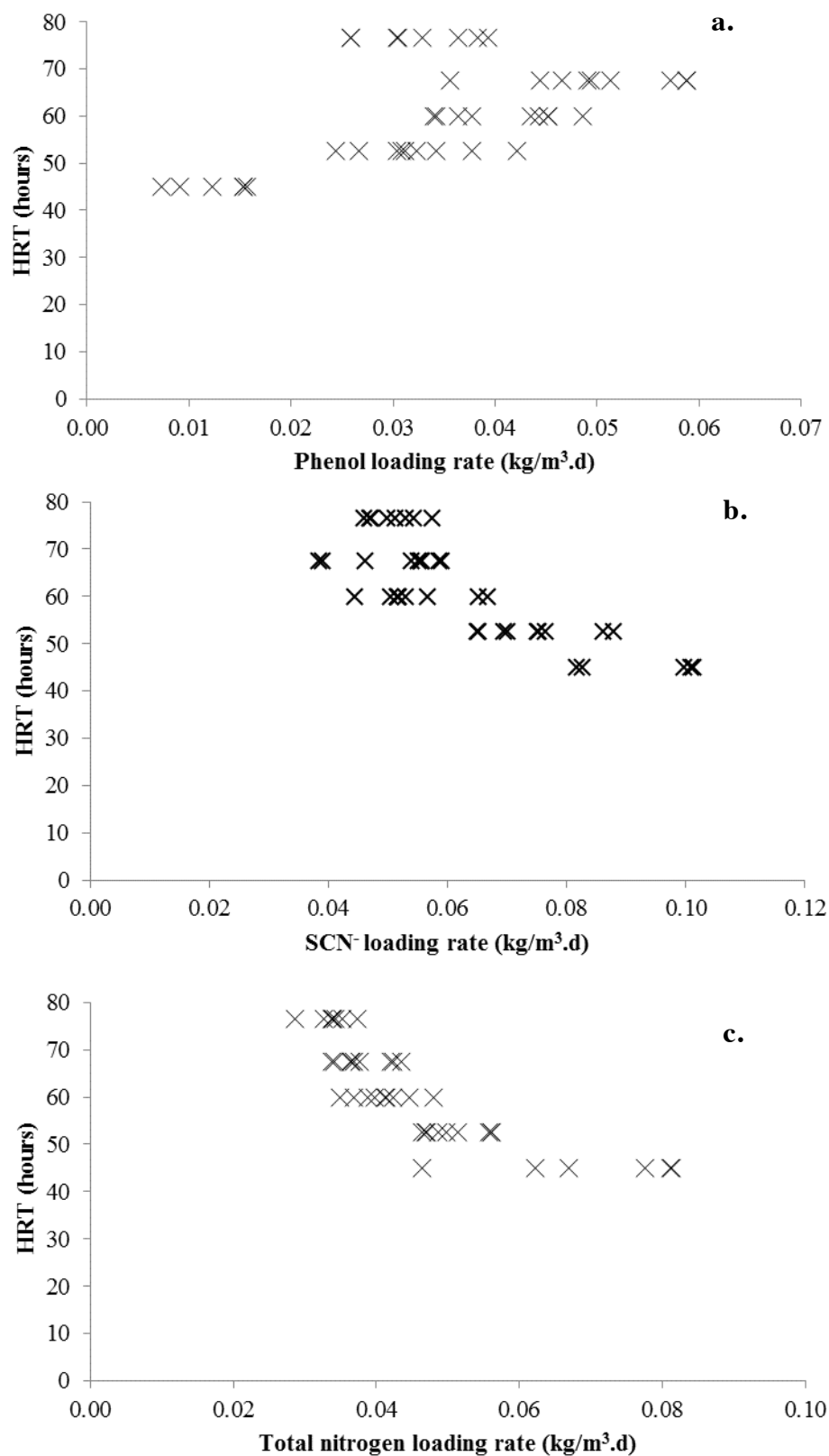


Figure 2: Correlation between HRT and a. phenol loading rate b. thiocyanate loading rate c. total nitrogen loading rate.

Figure 3
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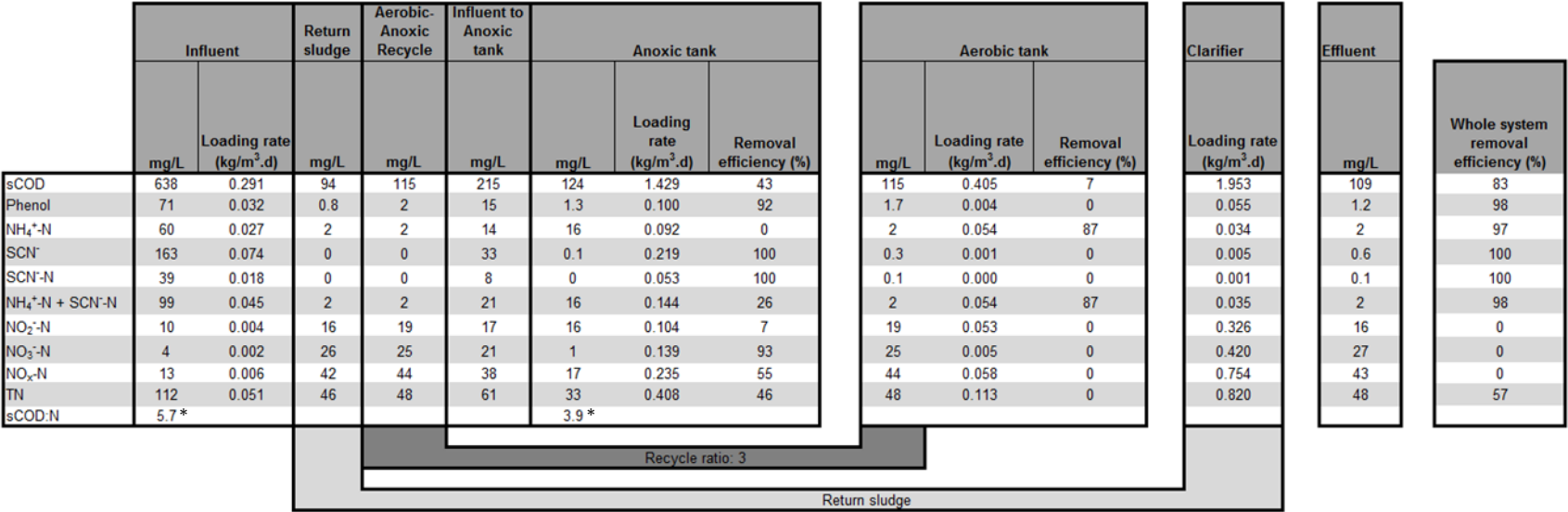


Figure 3: Mass balance for anoxic-aerobic pilot-plant characterised by an effluent <50 mg/L TN.

*dimensionless (mg sCOD/L / mg TN/L)

Influent loading rate = (influent flow (m³/d) x concentration of pollutant in influent (kg/m³) / total reactor volume (1.02 m³)

Anoxic loading rate = (anoxic influent flow (m³/d) x concentration of pollutant at influent of anoxic reactor (kg/m³) / volume of anoxic reactor (0.34 m³)

Aerobic loading rate = (aerobic influent flow (m³/d) x concentration of pollutant at influent of aerobic reactor (kg/m³) / volume of aerobic reactor (0.68 m³)

Figure 4

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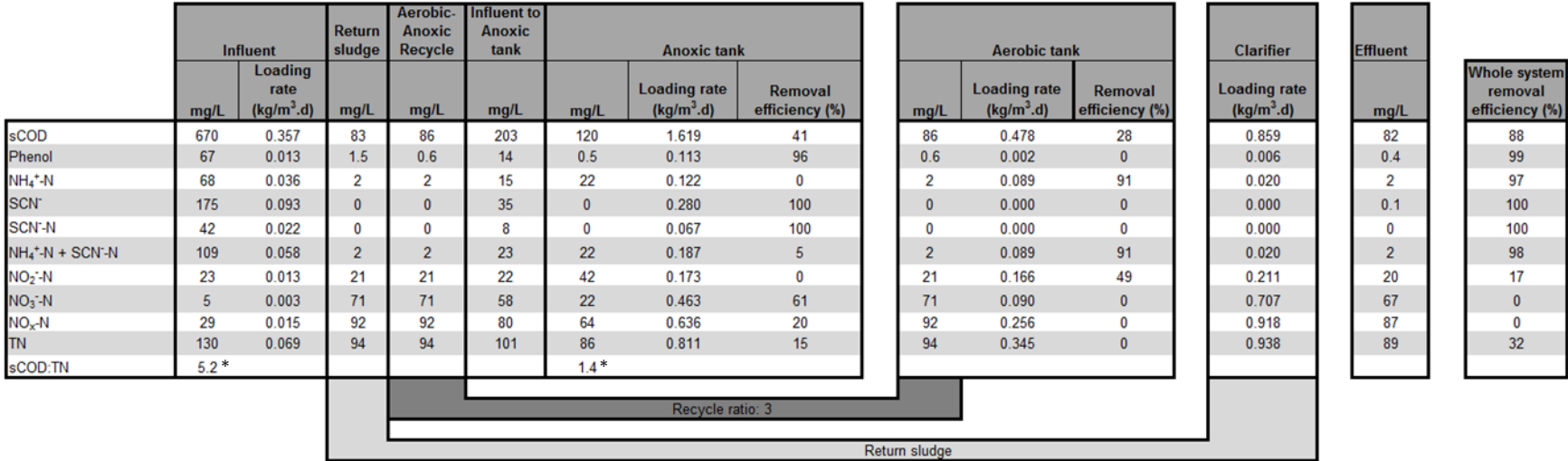


Figure 4: Mass balance for anoxic-aerobic pilot-plant characterised by an effluent >50 mg/L TN.

*Dimensionless (mg sCOD/L / mg TN/L)

Influent loading rate = (influent flow (m³/d) x concentration of pollutant in influent (kg/m³) / total reactor volume (1.02 m³)

Anoxic loading rate = (anoxic influent flow (m³/d) x concentration of pollutant at influent of anoxic reactor (kg/m³) / volume of anoxic reactor (0.34 m³)

Aerobic loading rate = (aerobic influent flow (m³/d) x concentration of pollutant at influent of aerobic reactor (kg/m³) / volume of aerobic reactor (0.68 m³)

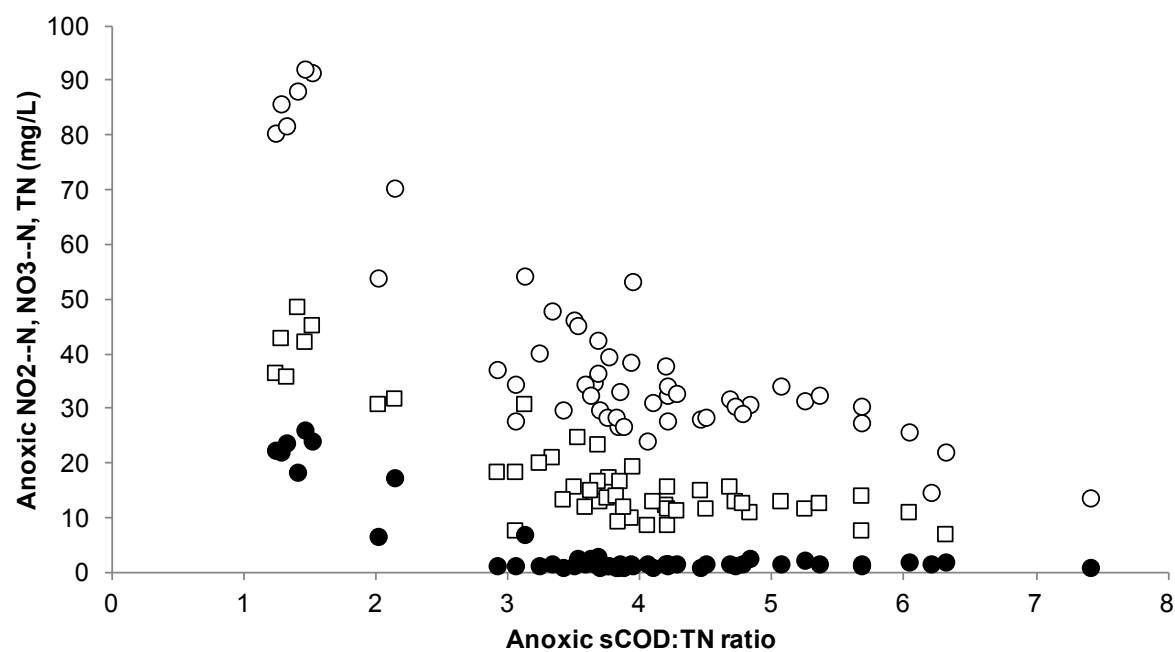


Figure 5: Changing concentrations of \square NO_2^- -N, \bullet NO_3^- -N and \circ TN in the anoxic reactor in response to changes in the anoxic sCOD:TN ratio. Dashed line marks anoxic sCOD:TN ratio below which nitrogen rapidly accumulates.

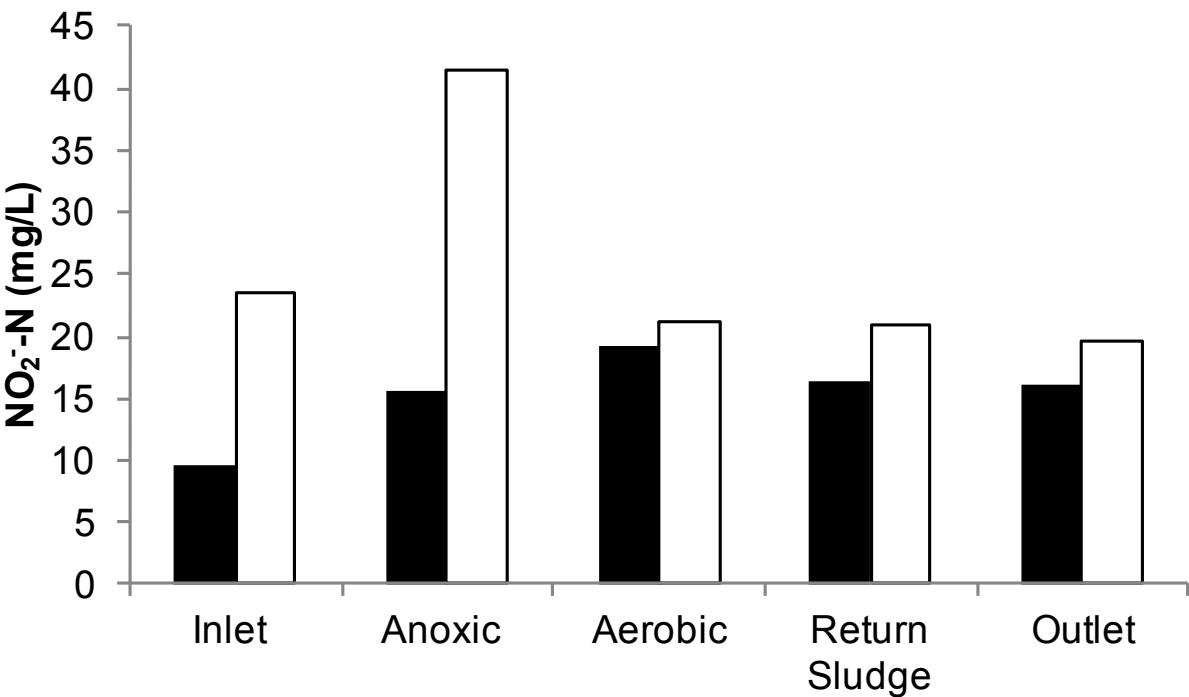


Figure 6: Variation of nitrite-nitrogen (NO_2^- -N) concentration at different stages of the anoxic-aerobic ASP pilot-plant when effluent concentration was TN <50 mg/L - ■ and at TN >50 mg/L - □.

Nitrogen removal from coke making wastewater through a pre-denitrification activated sludge process

Raper, Eleanor

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