

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

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30

31 **'Conflicts of interest: none'**

32 **Abstract**

33 Under the Industrial Emissions Directive (IED), coke production wastewater must be treated  
34 to produce an effluent characterised by a total nitrogen (TN) <50 mg/L. An anoxic-aerobic  
35 activated sludge pilot-plant (1 m<sup>3</sup>) fed with coke production wastewater was used to  
36 investigate the optimal operational requirements to achieve such an effluent. The loading  
37 rates applied to the pilot-plant varied between 0.198 - 0.418 kg COD/m<sup>3</sup>.day and 0.029 -  
38 0.081 kg TN/m<sup>3</sup>.day, respectively. The ammonia (NH<sub>4</sub><sup>+</sup>-N) removals were maintained at  
39 96%, after alkalinity addition. Under all conditions, phenol and SCN<sup>-</sup> remained stable at 96%  
40 and 100%, respectively with both being utilised as carbon sources during denitrification. The  
41 obtained results showed that influent soluble chemical oxygen demand (sCOD) to TN ratio of  
42 should be maintained at >5.7 to produce an effluent TN <50 mg/L. Furthermore, nitrite  
43 accumulation was observed under all conditions indicating a disturbance to the denitrification  
44 pathway. Overall, the anoxic-aerobic activated sludge process was shown to be a robust and  
45 reliable technology to treat coke making wastewater and achieve the IED requirements.

46 Nevertheless, the influent to the anoxic tank should be monitored to ensure a sCOD:TN ratio  
47 >5.7 or, alternately, the addition of an external carbon source should be considered.

#### 48 **Keywords**

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

#### 51 **1. Introduction**

52 Coke making wastewater is a by-product of the steel industry produced from the quenching  
53 of hot coke masses, washing of ammonia stills, cooling and washing of coke oven gases and  
54 the processing and purification of coke (Pal and Kumar, 2014). World crude steel production  
55 reached 1,620 million tons for the year 2015 (World Steel Association, 2016). Coke making  
56 wastewater is produced in substantial quantities with 1000 tons of coke typically producing  
57 1000 m<sup>3</sup> of wastewater (Pal and Kumar, 2014). Such wastewater is hazardous, containing a  
58 complex mix of harmful and toxic compounds which require treatment prior to their  
59 discharge (Marañón et al., 2008; Wu et al., 2018). Quantities of the individual compounds  
60 vary over both time and space in response to the composition of the coals used and variations  
61 in plant operational conditions and production levels (Marañón et al., 2008). Coke making  
62 wastewater is characterised by high concentrations of ammonia (NH<sub>4</sub><sup>+</sup>-N) (50 - 500 mg/L)  
63 and thiocyanate (SCN<sup>-</sup>) (100 - 400 mg/L) (Marañón et al., 2008; Staib and Lant, 2007;  
64 Vázquez et al., 2006b). Breakdown of SCN<sup>-</sup> results in the formation of NH<sub>4</sub><sup>+</sup>-N (0.24 g  
65 NH<sub>4</sub><sup>+</sup>/g SCN<sup>-</sup>) and therefore increased NH<sub>4</sub><sup>+</sup>-N loading is observed during the treatment  
66 process (Kim et al., 2008). Additional to the high nitrogen loading, the wastewater also  
67 contains other pollutant compounds such as phenol and polycyclic aromatic hydrocarbons  
68 (PAHs) (Vázquez et al., 2006b; Zhang et al., 2012b). Phenol has been reported at  
69 concentrations between 60 - 400 mg/L (Bai et al., 2010; Marañón et al., 2008; Staib and Lant,

70 2007; Vázquez et al., 2006b). Reports on the concentrations of polycyclic aromatic  
71 hydrocarbons (PAHs) are less commonly reported and vary substantially. Burmistrz and  
72 Burmistrz (2013) reported 255-312 µg/L for the sum of 16 PAHs whilst Zhang et al. (2012a)  
73 reported much higher concentrations of  $5470 \pm 907$  µg/L for the sum of 18 PAHs. Raper et  
74 al. (2017) reported the sum of 6 PAHs at  $179 \pm 35$  µg/L therefore being more comparable to  
75 the values reported by Burmistrz and Burmistrz (2013). Trace metals have been reported at  
76 4216 µg/L (Raper et al., 2017).

77

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

92

93 The toxic influence of compounds such as  $\text{SCN}^-$  and phenol on nitrification and  
94 denitrification of coke wastewater treatment has previously been investigated. Vázquez et al.  
95 (2006a) reported that  $\text{SCN}^-$  negatively impacted the removal of ammonia, in a laboratory-  
96 scale ASP, which decreased from  $0.081 \text{ kg NH}_4^+-\text{N}/\text{m}^3/\text{d}$  in the absence of  $\text{SCN}^-$  to ca.  $0.04$   
97  $\text{kg NH}_4^+-\text{N}/\text{m}^3/\text{d}$  when  $\text{SCN}^-$  was increased to  $80 \text{ mg/L}$ . In contrast, Kim et al. (2011)  
98 reported that shock-loading of  $\text{SCN}^-$  did not directly impact nitrification, rather, it impacted  
99 total nitrogen removal. Increased nitrogen loading to the system resulted in higher  
100 concentrations of nitrate and carry over of nitrate into the effluent. Increasing the recycling of  
101 nitrified effluent to the anoxic tank, however, improved removal efficiencies of nitrate and in  
102 turn total removal. The impact of  $\text{SCN}^-$  is therefore controversial. Furthermore, Kim et al.  
103 (2009) highlighted that the supply of inorganic carbon was critical in maintaining nitrogen  
104 removal as a result of the autotrophic nature of the nitrifying bacteria. When nitrification  
105 treatment efficiency declined the residual inorganic carbon in the treated effluent decreased  
106 from  $15$  to  $5 \text{ mg/L}$ , suggesting a shortage. Inlet alkalinity values were not reported. Vázquez  
107 et al. (2006b) reported an alkalinity addition requirement for coke wastewater of at least  $6.5$   
108  $\text{mg CaCO}_3/\text{mg NH}_4^+-\text{N}$  for a 90% removal efficiency.

109

110 Denitrification is impacted by the supply of organic carbon with the removal of  $1 \text{ g}$  of  $\text{NO}_3^--\text{N}$   
111 theoretically requiring  $2.86 \text{ g}$  of COD (Chakraborty and Veeramani, 2006). The actual  
112 requirement, nevertheless, varies in response to both the carbon compound, microorganisms  
113 present and the operational conditions (Carrera et al., 2004; Chakraborty and Veeramani,  
114 2006; Metcalf & Eddy Inc, 2014; Yang et al., 2012). Although phenol was utilised as a form  
115 of carbon in the anoxic reactor, as the loading rates increased removal efficiencies in the  
116 anoxic reactor declined due to the insufficient contact time and supply of nitrate. A loading  
117 rate of  $0.06 \text{ g-phenol/L.d}$  was associated with a 69.5% removal efficiency compared to a

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

122 Many laboratory-scale investigations have considered the inhibitory roles of pollutants  
123 associated with coke making wastewater (Amor et al., 2005; Chakraborty and Veeramani,  
124 2006; Kim et al., 2011, 2009; Kwon et al., 2002; Vázquez et al., 2006a). Ammonia removal  
125 has been investigated through air stripping but this is unable to reduce ammonia sufficiently  
126 to enable compliance with a TN emission limit of 50 mg/L (Marañón et al., 2008). Alkalinity  
127 supply has been suggested as important in maintaining nitrification efficiencies in a  
128 laboratory-scale anoxic-aerobic ASP whilst carbon requirements have been investigated in a  
129 laboratory-scale post-denitrification ASP (Kim et al., 2009; Lee and Park, 1998). Optimal  
130 operational conditions and loading rates for TN removal in an anoxic-aerobic ASP have not  
131 been reported. The aim of this investigation was therefore to investigate TN removal at a  
132 larger scale through a pilot-scale anoxic-aerobic ASP and to identify the operational  
133 conditions required to consistently achieve an effluent TN of <50 mg/L.

134

## 135 **2. Materials and Methods**

### 136 **2.1 Coke making wastewater and activated sludge biomass**

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

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

144

## 145 **2.2 Anoxic-aerobic pilot-plant configuration**

146 A pilot-scale anoxic-aerobic ASP was designed with a 340 L (working volume) anoxic  
147 reactor, a 680 L (working volume) aerobic reactor and a 55 L (working volume) clarifier  
148 (Figure 1). The pollutant loading rates applied to the pilot-plant varied between 0.198 - 0.418  
149 kg COD/m<sup>3</sup>.day and 0.029 - 0.081 kg TN/m<sup>3</sup>.day, respectively, due to adjustments in the  
150 feeding rates (0.32 - 0.55 m<sup>3</sup>/day) as well as the natural variability of pollutants concentration  
151 in the wastewater coming from the full-scale site. Consequently, the total hydraulic retention  
152 time (HRT) also varied from 76.5 - 45 h, which was significantly higher than the HRT of  
153 16.7 h Kim et al. (2008) reported to be necessary to achieve stable nitrification and  
154 denitrification.

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

164

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  $4800 \pm 1600$  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  $\text{CaCO}_3$ . 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

187 to its degradation to  $\text{NH}_4^+\text{-N}$ ). Although TN, is defined as containing organic nitrogen, coke  
188 making wastewaters contain very little organic nitrogen other than  $\text{SCN}^-$  (Vázquez et al.,  
189 2007) and therefore the method used is a good approximation of TN. Nitrite-nitrogen,  $\text{NO}_3^-$ -  
190 N,  $\text{NH}_4^+\text{-N}$  and soluble chemical oxygen demand (sCOD) were analysed using Merck cell  
191 test kits according to the manufacturer's instructions. Thiocyanate was analysed  
192 colourmetrically by complex reaction with thiocyanate and iron oxide at a wavelength of 465  
193 nm, based on The Institute of Gas Engineers analytical method (The Institution of Gas  
194 Engineers, 1971). Mono phenols were analysed by complex reaction with 4-aminoantipyrine  
195 at a wavelength of 510 nm, based on ISO 6439:1990 (ISO, 1990). Both were analysed using a  
196 Jenway 6300 spectrophotometer (Staffordshire, UK). pH was recorded using a Jenway 3540  
197 pH meter (UK). Total suspended solids (TSS), alkalinity and  $\text{BOD}_5$  were analysed according  
198 to standard methods (Eaton, 2005). Data was analysed using a Grubbs' test to identify  
199 outliers. Outliers were subsequently excluded from the data set.

200

### 201 **3. Results and discussion**

202

#### 203 **3.1 Coke making wastewater composition and pilot-plant operation**

204 Over the 5 month period the pilot-plant was operated, the feed coke making wastewater was  
205 subject to the same variation as the full-scale treatment plant (Table 1). Total nitrogen  
206 concentrations averaged at 110 mg/L, varying from 87 to 152 mg/L. Ammonia-nitrogen  
207 averaged at 59 mg/L, varying from 43 to 75 mg/L. Nitrite-nitrogen levels ranged from 6 to 29  
208 mg/L averaging at 13 mg/L whilst  $\text{NO}_3^-$  -N levels were low, at an average of 3.3 mg/L and a  
209 maximum of 6.2 mg/L. Phenol concentrations averaged at 99 mg/L during the pilot-plant  
210 operation, however, concentrations were initially at ca. 166 mg/L, declining to 52 mg/L at the

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

216

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

218

219 During this study, the wastewater was fed to the pilot-plant at a rate between 0.32 - 0.55  
220 m<sup>3</sup>/day corresponding to HRTs from 45 - 76.5 h. Due to the high natural variation of the  
221 wastewater composition, the correlation between HRT and SCN<sup>-</sup>, phenol and TN loading  
222 rates did not follow a linear relationship (Figure 2 ). In the current investigation, the lack of  
223 correlation between the HRT and loading rate was particularly noticeable for the phenol  
224 loading which varied from 0.026 to 0.039 kg/m<sup>3</sup>.d at HRTs 76.5 – 52.5 h. At the shortest  
225 considered HRT, of 45 h, phenol loading rates were at their lowest (0.007 – 0.016 kg/m<sup>3</sup>.d).  
226 Similarly, SCN<sup>-</sup> loading rates did not increase linearly with the decreased HRTs with  
227 observed SCN<sup>-</sup> loading rates of 0.046 – 0.057 kg/m<sup>3</sup>.d, 0.038 – 0.059 kg/m<sup>3</sup>.d and 0.044 –  
228 0.067 kg/m<sup>3</sup>.d at 76.5, 67.5 and 60 h HRT, respectively. Although TN loading rates showed  
229 an overall increase with declining HRT there was still considerable overlaps between the  
230 different HRTs (Figure 2). Traditionally, HRT has been used as an operational parameter,  
231 however, it is not useful for the treatment of industrial wastewaters which have a variable  
232 composition. When influent concentrations vary significantly setting a fixed HRT cannot  
233 guarantee consistent treatment efficiencies as pollutant loading rates can vary significantly

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

236

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

239

### 240 **3.2 Biodegradation of phenol and thiocyanate**

241 Influent to the anoxic-aerobic pilot-plant was characterised by phenol concentrations of 52 to  
242 166 mg/L corresponding to a loading rate of 0.007 to 0.059 kg/m<sup>3</sup>.d. The mass balances  
243 completed, demonstrate that phenol was removed primarily in the anoxic reactor with  
244 removal efficiencies of 82 - 99% (Figure 3 and Figure 4). These results indicate that phenol  
245 was consumed as a carbon source by denitrifying bacteria. Under high loading conditions  
246 (0.059 kg/m<sup>3</sup>.d) some residual phenol passed into the aerobic reactor, but there was enough  
247 capacity in the aerobic reactor to ensure that the remaining phenol was degraded to 0 - 1.7  
248 mg/L, averaging at 0.8 mg/L. Phenol removal efficiencies were consistently greater than  
249 96%, averaging at 99%, similar to those observed by Kim et al. (2009) in laboratory-scale  
250 investigations. Nevertheless, further process optimisation would be required to ensure total  
251 compliance, as phenol emissions exceeded the 0.5 mg/L limit set by the IED. Increasing the  
252 sludge age may allow improved phenol degradation rates whilst the incorporation of other  
253 technologies such as bioaugmentation and activated carbon have also been shown to be  
254 effective at improving phenol removal efficiencies and resilience to shock-loads (Fang et al.,  
255 2013; Vinitnantharat et al., 2001).

256

257 Thiocyanate loading rates varied from 0.038 - 0.101 kg/m<sup>3</sup>.d and removal efficiencies  
258 averaged at 99% resulting in average effluent concentrations of 1.1 mg/L (Figure 3 and  
259 Figure 4) complying with the 4 mg/L emission limit set by the (European Commission, 2013)  
260 (Table 2). Removal efficiencies of SCN<sup>-</sup> were comparable to those reported by Kim et al.  
261 (2011, 2008) in a laboratory-scale anoxic-aerobic ASP. Degradation of SCN<sup>-</sup> has been  
262 reported to be possible by a wide variety of bacteria under a wide range of conditions (Raper  
263 et al., 2018a). Removal of SCN<sup>-</sup> was complete in the anoxic reactor of the pilot-scale anoxic-  
264 aerobic ASP (Figure 3 and Figure 4) showing capability of the bacteria to degrade SCN<sup>-</sup>  
265 under anoxic conditions. This contrasts the findings of Kim et al. (2011, 2008) who reported  
266 that SCN<sup>-</sup> degradation took place in the aerobic reactor of the laboratory-scale anoxic-aerobic  
267 ASP.

268

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

270

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

273

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

276

277 **3.3 Nitrogen removal**

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

### 283 **3.3.1 Effluent nitrogen $<50 \text{ mg/L}$**

284 Mass balances were produced for the anoxic-aerobic ASP pilot-plant to understand the  
285 conditions required to achieve an effluent characterised by TN of  $<50 \text{ mg/L}$  (Figure 3 and  
286 Figure 4). When the effluent had a TN  $<50 \text{ mg/L}$  the wastewater influent concentrations were  
287 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  
288 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  $0.002$   
289  $\text{kg/m}^3 \cdot \text{d NO}_3^- \text{-N}$ . Ammonia-nitrogen was therefore the largest contributor to TN in the  
290 influent. Thiocyanate was present at  $163 \text{ mg/L}$  in the influent and through its degradation it  
291 produced a further  $39 \text{ mg/L}$  of  $\text{NH}_4^+ \text{-N}$  corresponding to an additional  $\text{NH}_4^+ \text{-N}$  loading rate of  
292  $0.018 \text{ kg/m}^3 \cdot \text{d}$ . Total nitrogen concentrations in the influent were  $112 \text{ mg/L}$  giving a loading  
293 rate of  $0.051 \text{ kg/m}^3 \cdot \text{d}$ . Nitrification was stable at 98% with ammonia being removed to below  
294 the detection limit of  $2 \text{ mg/L}$  comparable to other reported nitrification efficiencies (Wu et  
295 al., 2018). As a result of nitrification,  $\text{NO}_3^- \text{-N}$  concentrations increased substantially from an  
296 influent of  $4 \text{ mg/L}$  to a concentration of  $25 \text{ mg/L}$  in the aerobic reactor.

297

298 The concentrations of sCOD and phenol were  $638 \text{ mg/L}$  and  $71 \text{ mg/L}$ , respectively. The feed  
299 wastewater was therefore characterised by a sCOD:TN ratio of 5.7. Combining the influent,  
300 RAS and nitrate recycle, resulted in a sCOD loading rate of  $1.429 \text{ kg/m}^3 \cdot \text{d}$  and a TN loading  
301 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

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

306

### 307 **3.3.2 Effluent TN>50 mg/L**

308 A mass balance was subsequently produced for the anoxic-aerobic reactor when effluent TN  
309 concentrations exceeded the 50 mg/L emission limit (Figure 4). The influent concentrations  
310 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  
311 corresponded to loading rates of 0.036  $\text{kg/m}^3\cdot\text{d}$   $\text{NH}_4^+\text{-N}$ , 0.003  $\text{kg/m}^3\cdot\text{d}$   $\text{NO}_3^-\text{-N}$  and 0.013  
312  $\text{kg/m}^3\cdot\text{d}$  of  $\text{NO}_2^-\text{-N}$ . The influent contained 175 mg/L of  $\text{SCN}^-$  giving a loading rate of 0.093  
313  $\text{kg/m}^3\cdot\text{d}$ . The degradation of  $\text{SCN}^-$  in the anoxic reactor supplied the system with a further 42  
314 mg/L of  $\text{NH}_4^+\text{-N}$  to the system. Ammonia-nitrogen was the main contributor to TN.  
315 Nitrification removal efficiencies were also comparable at 96% with ammonia being removed  
316 to below the detection limit of 2 mg/L. In contrast,  $\text{NO}_3^-\text{-N}$  concentrations increased, as a  
317 result of nitrification, from an influent of 5 mg/L to a concentration of 71 mg/L in the aerobic  
318 reactor.

319

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

324 much lower loading rate of just 0.013 kg/m<sup>3</sup>.d. As a result of higher TN concentrations, the  
325 sCOD:TN ratio of the pilot-plant feed decreased to 5.2.

326

327 Significant differences in treatment efficiencies occurred in the anoxic reactor. Due to the  
328 increased production of NO<sub>3</sub><sup>-</sup>-N in the aerobic reactor, from 25 mg/L to 71 mg/L, the loading  
329 rate of NO<sub>3</sub><sup>-</sup>-N to the anoxic reactor more than tripled from 0.139 to 0.463 kg/m<sup>3</sup>.d. The NO<sub>3</sub><sup>-</sup>  
330 -N specific removal rate increased from 0.081 g/g VSS.d (TN <50 mg/L) to 0.186 g/g VSS.d  
331 (TN >50 mg/L) in response to the increased loading. The sCOD loading increased from 1.429  
332 kg/m<sup>3</sup>.d (TN <50 mg/L) to just 1.619 kg/m<sup>3</sup>.d. Nitrate-nitrogen concentrations in the anoxic  
333 reactor increased from 1 mg/L (TN <50 mg/L) to 22 mg/L. The concentration of NO<sub>2</sub><sup>-</sup>-N was  
334 more than double, at 42 mg/L, with no removal being observed. Consequently, the  
335 denitrification efficiency decreased from 93% to 61%. Total nitrogen removal in the anoxic  
336 reactor declined from 46% to 15%. Decreased nitrogen removals were associated with the  
337 decreased sCOD:TN ratio of influent to the anoxic reactor of 1.4 which was insufficient for  
338 the complete removal of NO<sub>3</sub><sup>-</sup>-N and NO<sub>2</sub><sup>-</sup>-N. Figure 5 shows the impact of the anoxic  
339 sCOD:TN ratio on NO<sub>2</sub><sup>-</sup>-N, NO<sub>3</sub><sup>-</sup>-N and TN concentrations in the anoxic reactor. When the  
340 anoxic sCOD:TN ratio declined below a ratio of 4, NO<sub>2</sub><sup>-</sup>-N concentrations started to increase.  
341 Below an sCOD:TN ratio of 2 concentrations of NO<sub>2</sub><sup>-</sup>-N and NO<sub>3</sub><sup>-</sup>-N increased rapidly.

342

343 **Figure 5: Changing concentrations of □ NO<sub>2</sub><sup>-</sup>-N, ● NO<sub>3</sub><sup>-</sup>-N and ○ TN in the anoxic**  
344 **reactor in response to changes in the anoxic sCOD:TN ratio. Dashed line marks anoxic**  
345 **sCOD:TN ratio below which nitrogen rapidly accumulates.**

346

347 As a result of the poor performance of the anoxic reactor under carbon limited conditions the  
348 anoxic-aerobic ASP effluent TN increased substantially to 89 mg/L greatly exceeding the 50  
349 mg/L IED emission limit. With effluent concentrations of 67 mg/L of  $\text{NO}_3^-$ -N the emission  
350 limit was exceeded by  $\text{NO}_3^-$ -N concentrations alone. Whilst the decline in the sCOD:TN ratio  
351 of the influent appeared relatively small, declining from 5.7 to 5.2, the increased TN loading  
352 had a much more significant impact on the sCOD:TN ratio observed in the anoxic reactor  
353 which declined from 3.9 to 1.4. The sCOD:TN ratio of the anoxic reactor is therefore a more  
354 accurate indication of TN removal potential. Liu et al. (1996) reported that the carbon  
355 requirement was best represented by the influent COD:TN ratio during the treatment of coal  
356 gasification and coke plant wastewater, however, comparability needs to recognise the  
357 different treatment configuration which consisted of the use of a submerged biofilm in the  
358 anoxic cell and also the use of total COD rather than soluble COD. Furthermore, an influent  
359 sCOD:TN ratio of 5.7 in the current investigation resulted in TN removal efficiencies of 57%,  
360 much lower than the 83% removal efficiency observed by Liu et al.(1996) at a COD:TN  
361 ratio of 5.

362

### 363 **3.3.3 Nitrite removal in the anoxic-aerobic reactor**

364

365 A notable characteristic of the anoxic-aerobic ASP was the poor removal of  $\text{NO}_2^-$ -N (Figure  
366 6). The presence of  $\text{NO}_2^-$ -N can be indicative of a disturbance or limitation within the  
367 nitrification and or denitrification step process (Philips et al., 2002). Several factors have  
368 been associated with the accumulation of  $\text{NO}_2^-$ -N during the denitrification process including  
369 the type of carbon (Rocher et al., 2015), reactor pH (Cao et al., 2013), the rate of  $\text{NO}_3^-$ -N and  
370  $\text{NO}_2^-$ -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<sub>2</sub><sup>-</sup>-N/g NO<sub>3</sub><sup>-</sup>-N whilst alcohols such as methanol, ethanol or glycerol resulted in lower accumulations of 0.05 - 0.1 g NO<sub>2</sub><sup>-</sup>-N/g NO<sub>3</sub><sup>-</sup>-N (Rocher et al., 2015). A high pH may result in the accumulation of NO<sub>2</sub><sup>-</sup>-N as the NO<sub>2</sub><sup>-</sup>-N reduction rate decreases with increased pH (Cao et al., 2013). The abundance of species present in the mixed liquor can also impact NO<sub>2</sub><sup>-</sup>-N accumulation due to the relative numbers of true denitrifying bacteria (complete both NO<sub>3</sub><sup>-</sup>-N and NO<sub>2</sub><sup>-</sup>-N reduction) and incomplete denitrifiers/nitrate-respiring bacteria (complete NO<sub>3</sub><sup>-</sup>-N reduction but are unable to reduce NO<sub>2</sub><sup>-</sup>-N) (Philips et al., 2002).

379

**Figure 6: Variation of nitrite-nitrogen (NO<sub>2</sub><sup>-</sup>-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 - □.**

383

When effluent TN concentrations were <50 mg/L, NO<sub>2</sub><sup>-</sup>-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<sub>2</sub><sup>-</sup>-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<sub>2</sub><sup>-</sup>-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<sub>2</sub><sup>-</sup>-N, representing a 55% increase in NO<sub>2</sub><sup>-</sup>-N concentrations. Under carbon limited conditions, the pH was suitable for denitrification and therefore species abundance may be responsible for the increased NO<sub>2</sub><sup>-</sup>-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*

395 (*Rhodanobacter denitrificans*) have been associated with complete denitrification (Prakash et  
396 al., 2012) others (*Rhodanobacter thiooxidans*) have been characterised as capable of  $\text{NO}_3^-$ -N  
397 reduction but not  $\text{NO}_2^-$ -N reduction (Lee et al., 2007). Under carbon limited conditions,  
398 competition for electron donors becomes more intense which has been reported to favour  
399  $\text{NO}_3^-$ -N reduction (Oh and Silverstein, 1999). The competitive conditions can therefore lead  
400 to a further increase the numbers of incomplete denitrifiers/nitrate-respiring bacteria.  
401 Consequently, the high loading of  $\text{NO}_3^-$ -N to the anoxic reactor observed when the effluent  
402 TN >50 mg/L, would result in reduced  $\text{NO}_2^-$ -N removal efficiencies further exacerbating  
403  $\text{NO}_2^-$ -N accumulation. Any accumulation of  $\text{NO}_2^-$ -N is undesirable due to the resulting  
404 impact on the ability to reach ever tightening nitrogen emission limits and its higher toxicity  
405 relative to other nitrogen compounds. Consequently, a clear indication of the pathways  
406 leading to  $\text{NO}_2^-$ -N accumulation requires more investigation.

407

#### 408 **4. Conclusion**

409 The anoxic-aerobic ASP pilot-plant was capable of removing  $\text{SCN}^-$  and phenol under all  
410 loading rates to 100% and 96% respectively. Nitrification remained stable at >96% under all  
411 conditions. Both phenol and  $\text{SCN}^-$  were utilised as carbon sources during denitrification.  
412 Organic carbon availability was a critical parameter in nitrogen removal. Influent to the  
413 anoxic-aerobic ASP required an sCOD:TN ratio of 5.7 to enable an effluent characterised by  
414 a TN concentration <50 mg/L. At an sCOD:TN ratio of 5.2 the emission limit was exceeded  
415 (89 mg/L) as  $\text{NO}_3^-$ -N removal efficiencies in the anoxic reactor decreased from 93% to 61%.  
416 Hence, to achieve the IED requirements is recommended that the sCOD:TN ratio in the fed  
417 wastewater to the ASP is kept >5.7, and an external carbon should be considered together  
418 with alkalinity dosing. The presence of  $\text{NO}_2^-$ -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

422 **Acknowledgements**

423 This work was supported by Tata Steel and the Natural Environment Research Council [grant  
424 number NE/K007424/1]. We wish to express our gratitude to John Spooner, Tata Steel, and  
425 his team for their supporting role in the pilot plant commission and operation. Our thanks are  
426 expressed to Central Laboratories, Tata Steel, for the completion of suspended solids  
427 analysis. We would also like to thank James Taylor for his support to the pilot plant.

428

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

535

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

\*After alkalinity dosing (523 mg/L as CaCO<sub>3</sub>)

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

536

537

538

539

540

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

542

---

**Industrial Emission Directive emission limit (mg/L)**

---

COD: < 220

BOD<sub>5</sub>: <20

SCN: < 4

PAHs\*: 0.05

Phenols: 0.5

TN: <15-50

---

Figure 1

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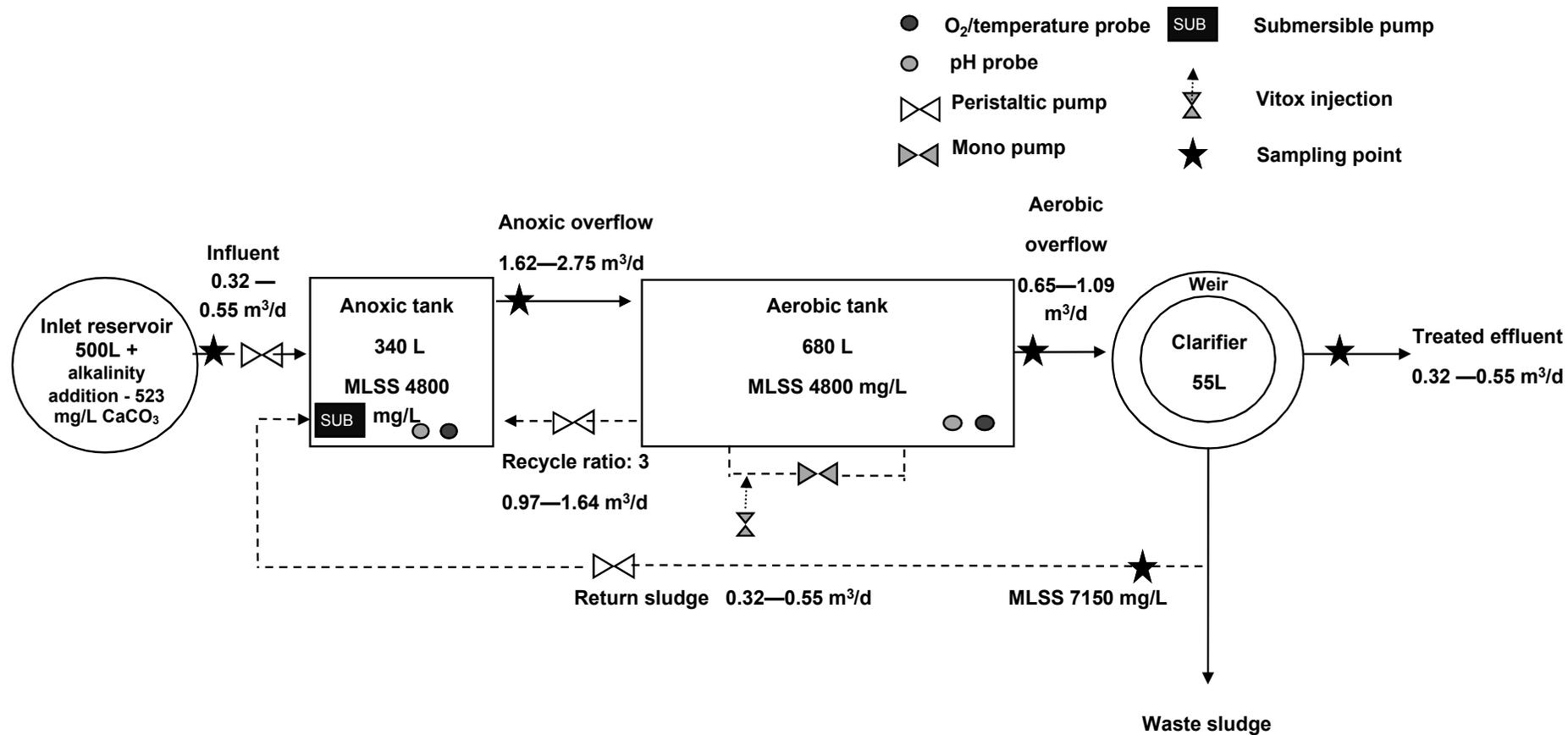
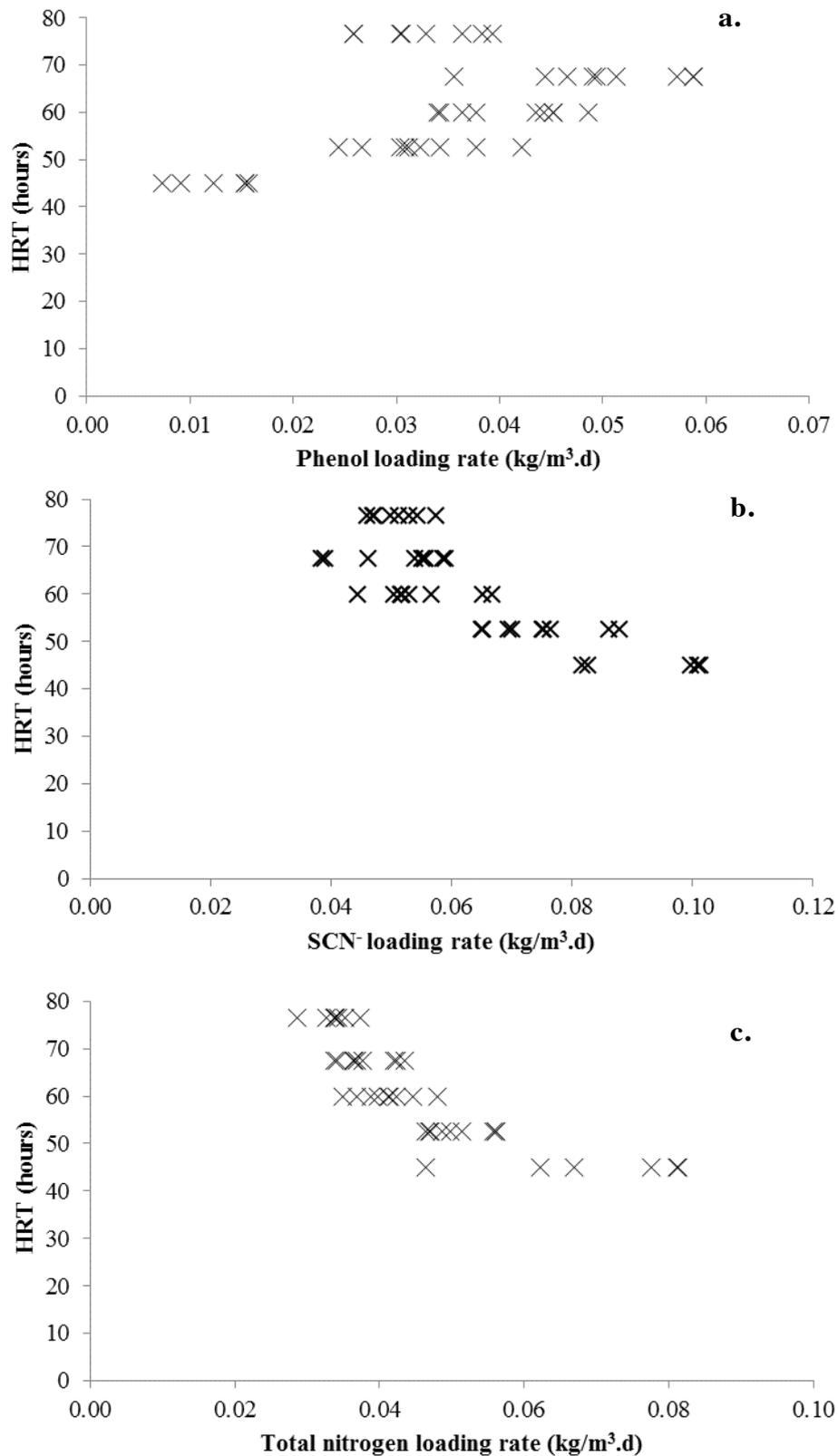


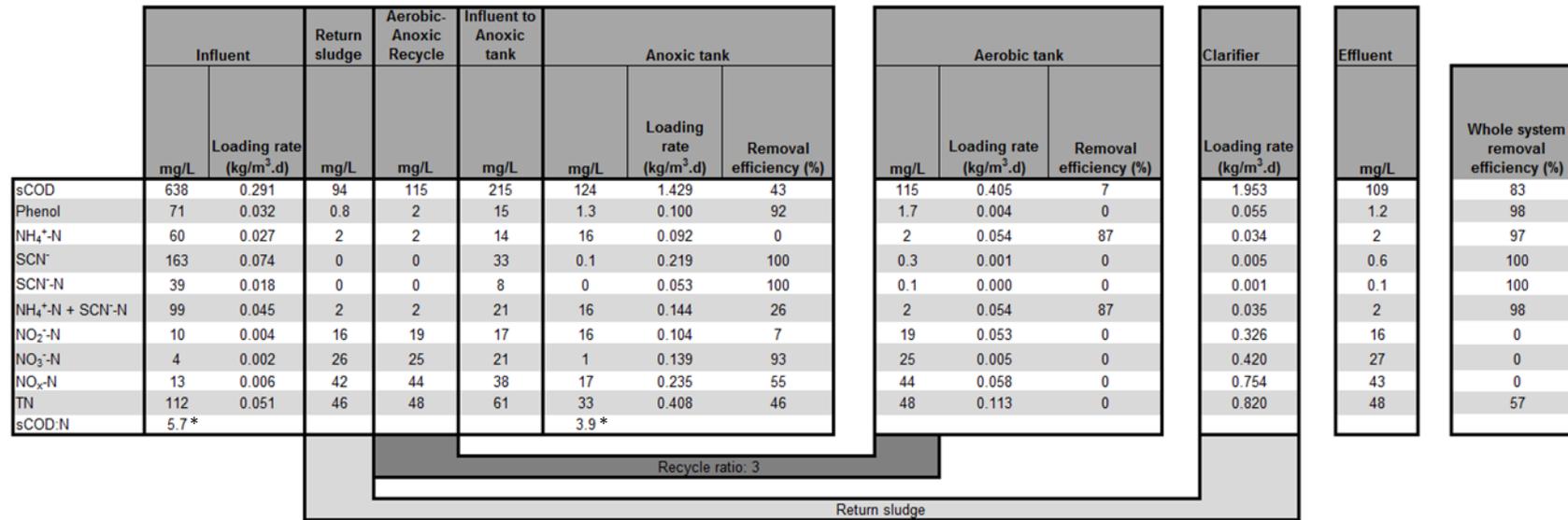
Figure 1: Pilot-scale anoxic-aerobic ASP configuration, operational conditions and sampling locations.



**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)

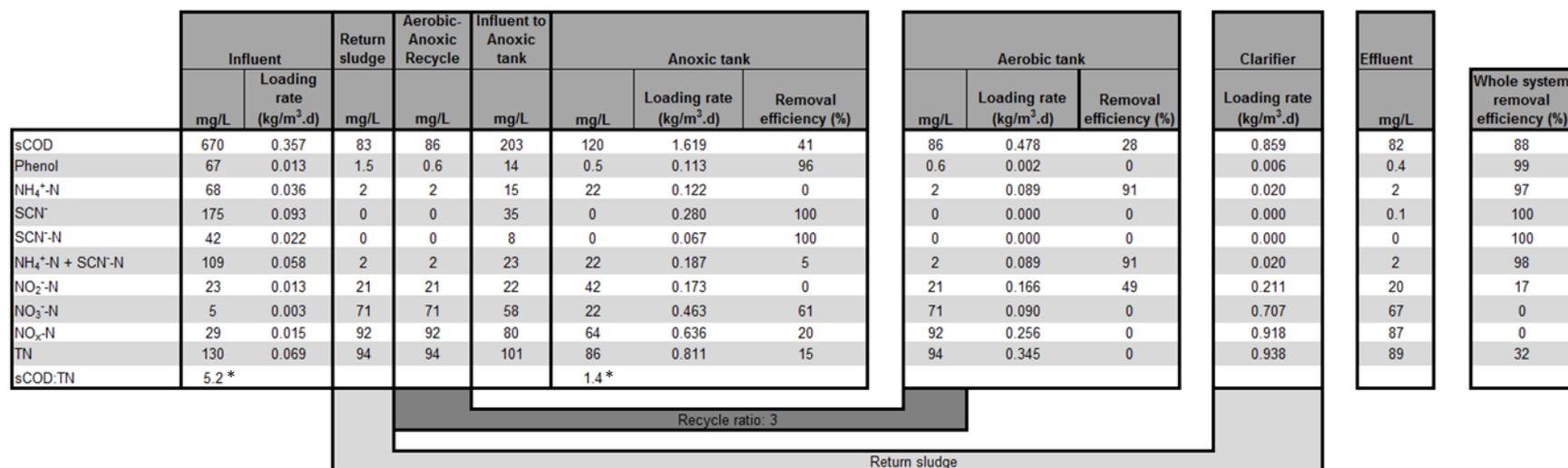
Influent loading rate = (influent flow (m<sup>3</sup>/d) x concentration of pollutant in influent (kg/m<sup>3</sup>) / total reactor volume (1.02 m<sup>3</sup>)

Anoxic loading rate = (anoxic influent flow (m<sup>3</sup>/d) x concentration of pollutant at influent of anoxic reactor (kg/m<sup>3</sup>) / volume of anoxic reactor (0.34 m<sup>3</sup>)

Aerobic loading rate = (aerobic influent flow (m<sup>3</sup>/d) x concentration of pollutant at influent of aerobic reactor (kg/m<sup>3</sup>) / volume of aerobic reactor (0.68 m<sup>3</sup>)

**Figure 4**

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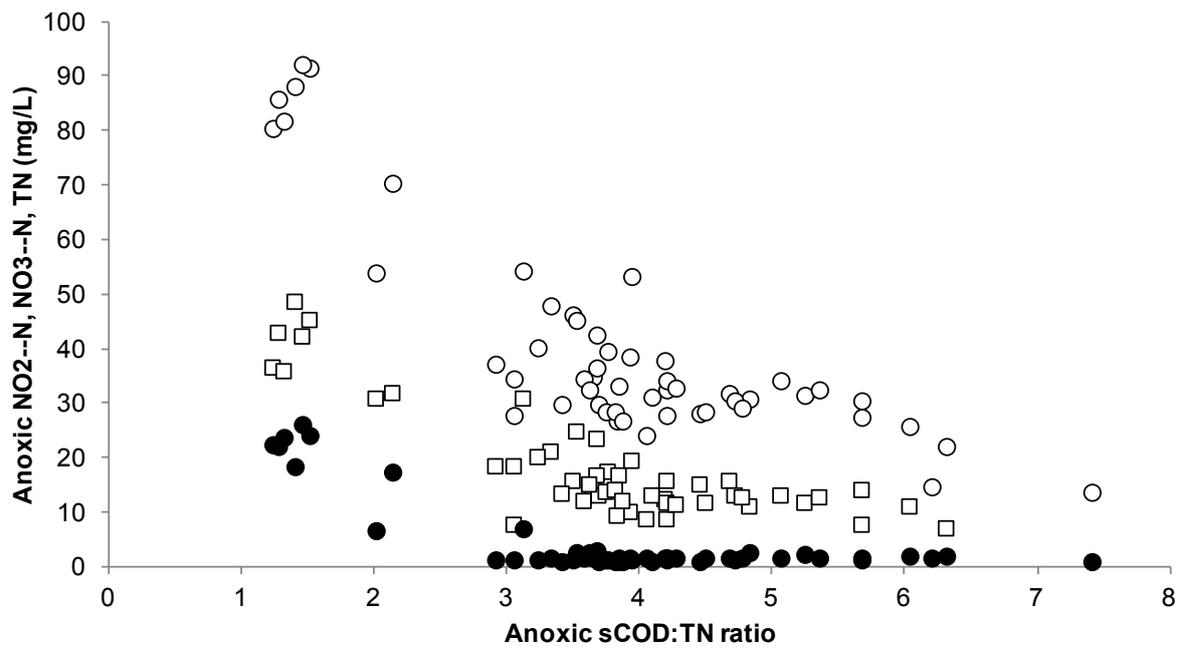
**Figure 4: Mass balance for anoxic-aerobic pilot-plant characterised by an effluent >50 mg/L TN.**

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

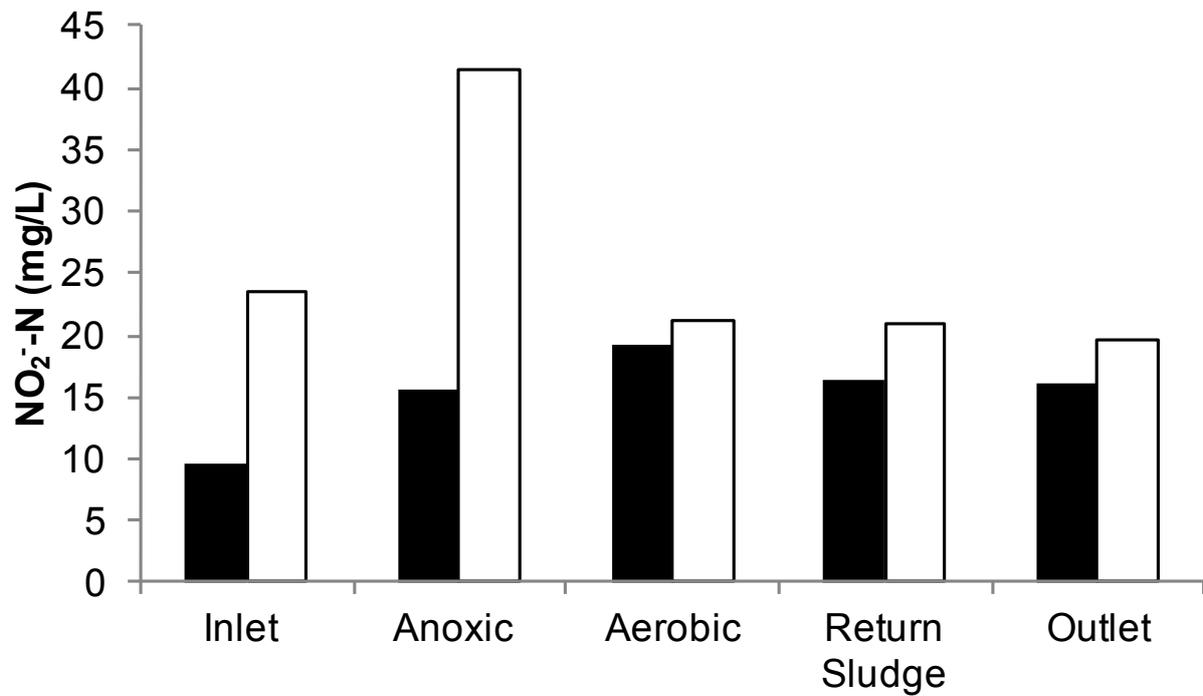
Influent loading rate = (influent flow (m<sup>3</sup>/d) x concentration of pollutant in influent (kg/m<sup>3</sup>) / total reactor volume (1.02 m<sup>3</sup>)

Anoxic loading rate = (anoxic influent flow (m<sup>3</sup>/d) x concentration of pollutant at influent of anoxic reactor (kg/m<sup>3</sup>) / volume of anoxic reactor (0.34 m<sup>3</sup>)

Aerobic loading rate = (aerobic influent flow (m<sup>3</sup>/d) x concentration of pollutant at influent of aerobic reactor (kg/m<sup>3</sup>) / volume of aerobic reactor (0.68 m<sup>3</sup>)



**Figure 5: Changing concentrations of □ NO<sub>2</sub><sup>-</sup>-N, ● NO<sub>3</sub><sup>-</sup>-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.**



**Figure 6: Variation of nitrite-nitrogen ( $\text{NO}_2^-$ -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

2019-02-14

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E Raper, R Fisher, DR Anderson, et al., (2019) Nitrogen removal from coke making wastewater through a pre-denitrification activated sludge process. *Science of The Total Environment*, Volume 666, May 2019, pp. 31-38

<https://doi.org/10.1016/j.scitotenv.2019.02.196>

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