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Complete Autotrophic Process for Nitrogen Removal from Ink-jet Printing Wastewater

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Lab-scale results on the treatability of ammonium-rich wastewater from textile digital printing highlight the feasibility of an innovative biological process, based on purely autotrophic bacterial populations: ammonium oxidising bacteria (AOB) and anaerobic ammonium oxidisers (AAO). Activity of AOB has been measured through pH/DO-stat titration and that of AAO has been assessed through manometric tests, on raw mixed wastewater coming from textile-print factories (0.5 to 0-6 gN/L as ammonium nitrogen). AOB activity showed a reduction of 20-40% if compared with maximum activity on a synthetic medium. AAO activity tests showed a residual specific maximum anammox activity (SAA) of 0.1-0.4 gN_2-N/gVSS/d, 40-60% of the control values obtained with synthetic wastewater. Activity tests confirmed treatability of the textile wastewater by AAO. Tests have been performed also on concentrated wastewater (2 to 3 gN/L as ammonium nitrogen) from the first rinsing bath. In this case, strong inhibition (between 80 and 100%) of anammox activity was observed. Careful operation of a continuous-flow completely mixed bioreactor can overcome this drawback, as pH and effluent ammonium concentration in the reactor are controlled.

1. Introduction

Digital (or ink-jet) textile printing is gradually replacing traditional serigraphic printing. Although its present market share is about 3% of the world printing textile business, ink-jet printing is growing at a 25% annual rate (Global Analyst Inc., 2014). At this pace, ink-jet printing will cover more than 80% of all printing factories in the silk district of Como (Italy) by 2017. Compared to conventional printing processes, digital printing processes produce lower volumes of wastewater characterized by considerably higher concentration of urea and ammonium. Typical nitrogen concentration in the discharged wastewater ranges from 150 to 600 mgN/L with a COD/N ratio around 2:1. Conventional nitrogen removal processes would require high investment and operational costs and would reduce the benefits of digital textile printing.

The anaerobic ammonium oxidation (anammox) process is a cost-effective nitrogen removal process for treating ammonium-rich wastewater, and is getting rapidly introduced in practice worldwide (Hu et al., 2013). The responsible microorganisms (anaerobic ammonium oxidisers, AAO) grow on ammonium with nitrite as electron acceptor resulting in the production of dinitrogen gas (Figure 1).

The completely autotrophic nitrogen removal process combines conversion of part of ammonium nitrogen to nitrous nitrogen with Ammonium Oxidising Bacteria (AOB) with anammox process, which converts the remaining ammonium nitrogen and nitrous nitrogen into dinitrogen gas and water. The combination of the two processes requires no organic carbon and lower oxygen input if compared with conventional activated sludge nitrification– denitrification processes, resulting in a more cost effective and environmentally friendly alternative.

Anammox based technologies have been applied for the treatment of sewage sludge digester liquids as well as of several types of industrial waste water (Lackner et al. 2014) but, to the best of authors' knowledge, no results on applications of anammox processes to digital printing effluents (not even to traditional serigraphic industry) are present in literature yet. More specifically, possible inhibiting/limiting effects of these effluents on anammox activity are still unknown.

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The aim of this research is to evaluate the feasibility of applying autotrophic N removal processes (partial nitritation + anammox) to wastewater from digital printing factories (sampled from equalized tank and concentrated fluxes from first washing steps).
In this paper, some lab-scale results will be presented: short-term activity batch tests (manometric) have been carried out to assess anammox activity on (i) raw samples coming from the equalization tank of 3 textile-print factories, (ii) same samples after a high-load aerobic treatment (iii) raw samples of the concentrate fluxes and (iv) after membrane pre-treatment.

Figure 1 – Biological transformations of nitrogen

2. Material and methods

2.1 Origin of the industrial wastewaters

The industrial dyes used in the digital printing processes vary according to the textile to be printed. All factories that provided the wastewater samples print on silk, cotton, viscose (rayon), wool, nylon (polyamide), polyester, and linen. Emulsions for impregnating and dyeing are made of urea; ludigol, a mild oxidizing agent that helps to prevent fibre reactive dyes from decomposing and allows more dye to react with the fabric; sodium bicarbonate; thickening agents (mainly starch and alginates) that may vary with the textile to be printed. Other components may be present such as self-emulsifying urethane resins. Dyes used for ink-jet printing are made of reactive dyes (cotton, linen and viscose), acid dyes (for silk and nylons) and, to a minor extent, metal-complex dyes. Samples did not show the presence of quaternary ammonium compounds.
No factories apply any treatment. Wastewater is discharged into a public combined sewer system and collected to a centralized wastewater treatment plant operating with conventional activated sludge processes for carbon and nitrogen removal, followed by finishing treatments (filtration and disinfection, in one case final effluent ozonation is also included). Batch samples (V = 10 L) or raw equalized wastewater were taken from 3 textile industries and maintained at 4°C till use. Batch samples of first rinsing bath (V = 10 L) were taken from the same industries and maintained at 4° C till use.

2.2 Pretreatment of concentrated wastewaters by membrane filtration

Membrane filtration has been applied as pretreatment of raw concentrate sample to check whether potential inhibitors of AAO may be removed prior to the N removal process.
A continuous filtration device (SEPA CF II, GE Infrastructure) operating in cross-flow mode was used, operating at a transmembrane pressure (TMP) of 65 bar. A flat sheet membrane of 12,000 Daltons (12 kD) cut-off, in polyethersulfone material and 258 cm^2 square area was used.
Membrane was conditioned with total recirculation of both permeate and concentrate for 10 minutes, after which, operation was switched to a "feed and bleed" mode, i.e.: continuous permeate collection and recirculation of the concentrate. To simulate the conditions of operation of a real scale plant it is employed a concentration ratio of feed to concentrate equal to 3. Out of 9 litres of feed, 6 litres of permeate were collected in six 1-litre bottles and 3 litres of concentrate were collected in three 1-litre bottle.
From each bottle of permeate 0.5 litres were collected and used as the substrate for treatability tests with anammox biomass.

2.3 Fed-batch aerobic pre-treatment

The procedure includes addition of 1 M HCl to adjust the pH of textile wastewater samples to values around 7.5. Then nitrifying activated sludge with a concentration of suspended solids of 4 g/L is mixed with the wastewater sample and reach a food-to-microorganism ratio F/M = 0.12 gCOD/gSST. 0.6 l have been added over six cycles of four hours each, totalling 3.6 L per day. The volume of the activated sludge used in each fed-batch test is determined according to the concentration of COD in the wastewater, to keep the specified F/M ratio. The corresponding sludge loading rate was 0.73 gCOD/gSST/d.

2.4 Respirometric test

Respirometric tests have been used to assess the specific AOB activity. All respirometric tests were performed by using the MARTINA respirometer (SPES s.c.p.a, Fabriano, AN, Italy). The maximum AOB activity was measured by applying the pH/DO-stat titration method (Artiga et al. 2005). The measuring principle of set-point titration is the following: controlled amounts of an appropriate titrant are added to a sludge sample to maintain constant the level of a chemical species which takes part in the bioreaction under study. The reaction rate is proportional to the measured titration rate via the reaction stoichiometry, while the amount of titrant dosed is proportional to the amount of substrate that has being converted by the bioreaction.
When dealing with nitritation, pH-stat titration is the most convenient option. The NaOH titration rate (rNaOH in mmol/h) is used to assess the ammonium oxidation rate (rNH in mgN/h) by using the ratio between ammonium removal and alkalinity consumption, that is, according to the two-step nitrification model:

$$r_{NH} = r_{NaOH} \cdot 14 \cdot \left(i_{XB} + 1/Y_{AOB}\right)/\left(i_{XB} + 2/Y_{AOB}\right) \qquad (1)$$

where, following the IWA-ASM usual notation (Henze et al., 2000):
i_{XB} = fraction of N in bacterial cells (0.086 gN/gCOD);
Y_{AOB} = growth yield coefficient for AOB (0.21 gCOD/gN).
The maximum specific ammonium oxidation rate of the sludge (rAOB,max, in mgN/gVSS/h), is calculated by taking into account the biomass content of the sludge sample in terms of volatile suspended solids (MLVSS, in gVSS):

$$r_{AOB,\max} = r_{NH} / MLVSS \qquad (2)$$

During the tests pH was fixed at 8.0±0.02 by sodium hydroxide controlled addition and DO was kept constant at 6.5±0.5 mg/L by controlled hydrogen peroxide addition, and temperature was maintained at 25±1°C by means of a thermostated bath.

2.5 Manometric batch test

The assessment of the dinitrogen gas production rate from the anammox reaction was performed by means of an OxiTop Control system according to the protocol described in Lotti et al. (2012). Each bottle was filled with granular anammox biomass coming from the full-scale plant in Dokhaven, Rotterdam (van der Star et al. 2007) and 200 ml of either mineral medium or wastewater or a blend of 50% wastewater and 50% mineral medium, depending on the test. Bottles were thermostated at 35±0.5°C in a shaker (160 rpm). Substrates were added by spike injections through the rubber septum. Then, the evolved N_2 was computed from overpressure data, according to the ideal gas law. For each test, the maximum N_2 production rate, the maximum specific anammox activity, SAAmax (mgN-N_2/gVSS/h), and the nitrogen mass balance was verified. Every 24h hours, substrates were spikes to achieve a final concentration of 50mgN-NO_2-/L and 50mgN-NH_4^+/L. Normally, 6 injections were performed in 7 days.

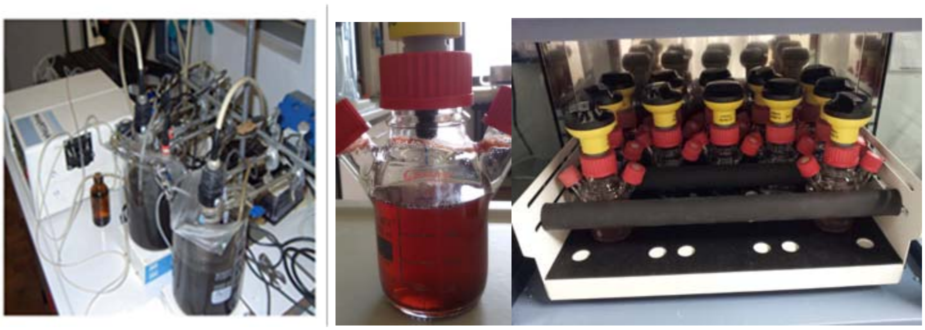

Figure 2 – AOB activity testing by a pH/DO-stat titrator (left). Manometric AAO activity testing (right)

2.6 Analytical methods

Commercial photochemical test kits (Hach Lange GmbH, Dusseldorf, Germany, Test LCK303, LCK304, LCK339, LCK340, LCK341, LCK342; LCK514; LCK314 spectrophotometer type LANGE Xion500) were used for ammonium, nitrite, nitrate and COD measurements on 0.45 µm filtered samples. Total Kjeldahl Nitrogen (TKN), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Biochemical Oxygen Demand (BOD), alkalinity (by the potentiometric method) were all measured according to the APHA Standard Methods for the Examination of Water and Wastewater. Metals were measured by Inductively Coupled Plasma –Mass

Spectrometry (ICP-MS) with a ICPMS model 7700X (Agilent Technologies, USA) according to the US-EPA method 200.8 EMMC version revision 5.4 (1994). Metals were measured by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) with a ICPMS model 7700X (Agilent Technologies, USA) according to the US-EPA method 200.8 EMMC version revision 5.4 (1994).

3. Results

3.1 Wastewater characteristics

Characteristics of wastewater samples are reported in Table 1.
On the raw wastewater sample from Industry 1, metals and ions content have been assessed with the following results: sulphate 58 mg/L; chloride 78 mg/L; Ca 38 mg/L; Al 1.6 mg/L; Va <10 µg/L, Zn 0.64 mg/L; Ag 0.69 µg/L; Cd:<0.5 µg/L; Co 1.39 µg/L; Cr 193 µg/L; Cu 0.066 mg/L; Fe 0.66 mg/L; Hg <2.5 µg/L; K 1.9 mg/L; Mg 9.2 mg/L; Mo <1 µg/L; Mn 2.6 mg/L; Na 116 mg/L; Ni 2.5 µg/L; Pb <2.5 µg/L; Se <0.5 µg/L; Sr 245 µg/L. As raw materials used in the three industries were similar, and concentrations are far from being toxic for the microorganism, previous analyses were not performed on samples from the other industries.

Table 1: Characteristics of the equalized wastewater used in the experimentation

Parameter	Raw wastewater			First wash discharges		
	Industry 1	Industry 2	Industry 3	Industry 1	Industry 2	Industry 3
pH	9.2	9	7.6	11	9.8	10.2
Alkalinity (mg$CaCO_3$/L)	1000	1320	360	860	770	471
CODtot (mg/L)	405	856	478	1940	1300	4010
CODsol (mg/L)	340	654	371	1750	1250	3400
BOD_5 (mg/L)	220	309	170	400	650	1150
BOD_{20} (mg/L)	330	415	230	540	840	2230
TKN (mg/L)	220	277	188	2780	1982	1784
NH_4-N (mg/L)	192	120	29	11	15	22

3.2 AOB activity tests

AOB activity has been measured through respirometric tests. Results showed a reduction of 20-40% for all the samples of equalized wastewater as well as after pre-aeration step (only industry 2 and 3). AOB activity showed similar values in both samples of concentrated wastewater and samples taken from the equalization tank (Figure 3). Equalized sample for industry 1 was not available. The dilution resulted after the mixing of the wastewater sample with nitrifying activated sludge.

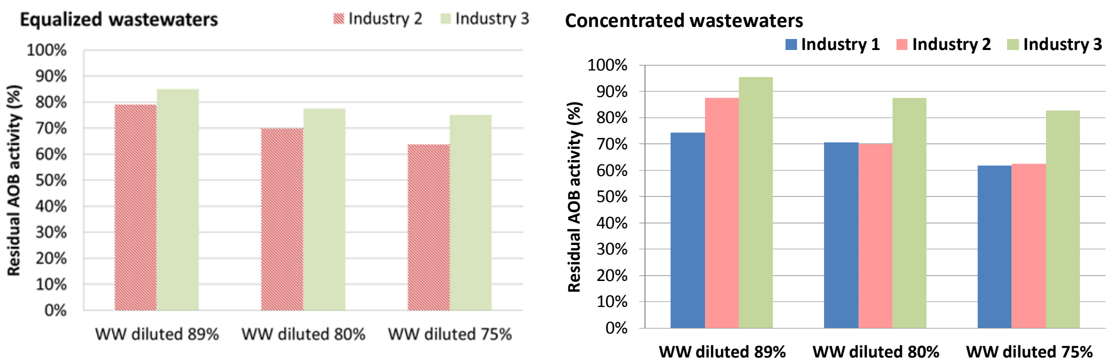

Figure 3: Residual AOB activity in equalized and concentrated wastewater samples at different dilution ratios; dilution ratio = 100 - % of wastewater in the test liquid; the test liquid is made of the wastewater sample mixed with nitrifying activated sludge (4 gTSS/L).

3.3 Anammox activity tests

Figure 4 shows the results of Anammox activity tests. Tests on equalized wastewaters confirmed the treatability with a residual specific maximum anammox activity (SAA) of 40-60% compared to the control with synthetic wastewater and in the range 0.1-0.4 gN_2-N/gVSS/d.
AAO activity in the concentrated wastewater was strongly inhibited (80 to 100%); this effect was due to accumulation of free ammonia, which in turn is caused by ammonification of urea during the test at high pH.

The feasibility of the process with concentrated wastewater may be possible, as actual ammonium concentration in a continuous-flow completely mixed reactor will be much lower.

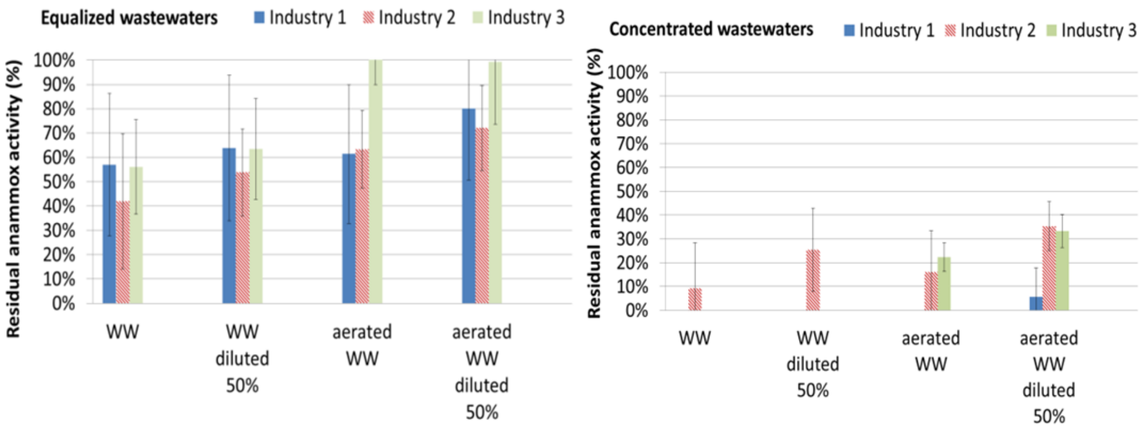

Figure 4: Residual anammox activity for test with equalized and concentrated wastewaters.

3.4 Membrane filtration tests and AAO activity tests

Pre-filtration of the first rinsing baths samples removed 35% to 65% COD. Nitrogen was not removed to a great extent, as a large portion of it was in the form of urea (Table 2). Permeate looked clear (Figure 5).

A second series of AAO activity tests was performed on raw and pre-filtered first rinsing wastewater. Figure 6 show higher residual activity values than those shown in Figure 5. Interestingly, the lower is the ammonification, the higher the residual activity. The cause has to be found in the accumulation of ammonium nitrogen at the end of the tests (1.2 to 3.1 g/L). In spite of the addition of HEPES, pH reached high values at the end of the tests (> 9). Therefore, it is assumed that inhibition by free ammonia was the main cause of the low activity.

Table 2: Results of filtration tests (12 kD cut-off membrane) on three different first-wash wastewater samples.

	Industry 1		Industry 2		Industry 3	
	wastewater	Permeate	wastewater	permeate	wastewater	permeate
pH	9.8		8.9		9.3	
COD (mg/L)	4580	2500	720	168	4200	1450
TKN (mg/L)	5650	5300	786	437	2550	2380
NH_4-N (mg/L)	38.0	39.6	8.0	6.5	22.9	23.3

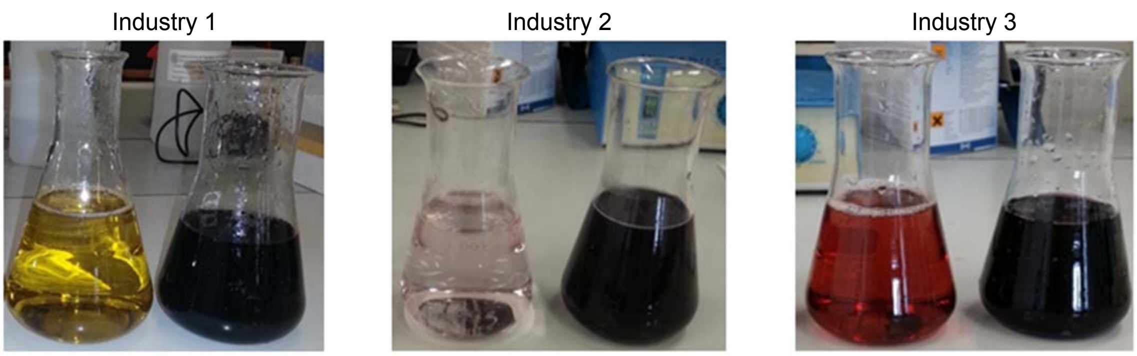

Figure 5: Results of filtration tests (12 kD cut-off membrane); permeate (left flask) and first-wash exhaust bath wastewater sample (right flask) from three ink-jet printing industries.

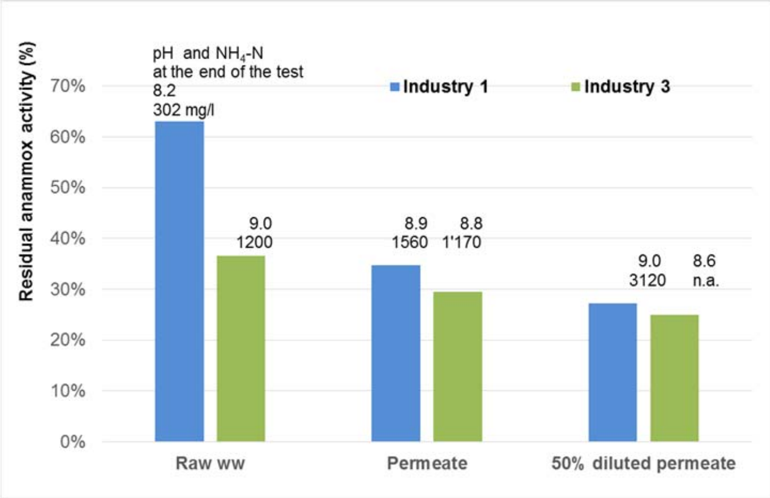

Figure 6: Residual anammox activity in raw first-wash wastewater, permeate and 50% diluted permeate of industry 1 and 3.

4. Conclusions

- Results obtained by lab-scale batch tests confirmed the feasibility of treating equalized mixed wastewaters from ink-jet printing factories by the partial nitritation/anammox process. Even though moderate specific activity reduction was observed, it should be considered that the biomass was not acclimated to the test conditions and acute inhibiting effects may be lowered after sufficient acclimation.
- More studies are needed to verify the feasibility of treatment of the first-rinsing bath more concentrated wastewater with PN/anammox process. As urea was hydrolysed to ammonium nitrogen in the batch tests, toxicity was due to the accumulation of free ammonia as high ammonium concentration (up to 3 g/L) and pH = 9 was reached at the end of the tests.
- The effect described above can probably be considerably reduced in a continuous-flow, completely mixed process. Long-term continuous-flow tests are currently performed in a lab-scale pilot plant to evaluate the efficiency and stability of the partial nitritation - anammox process on this kind of industrial wastewater.

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Reference

APHA, AWWA, WER, 2005. Standard Methods for the Examination of Water and Wastewater, 21th edition. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.

Artiga P., Gonzalez F., Mosquera-Corral A., Campos J.L., Garrido J.M., Ficara E., Mendez R., 2005, Multiple analysis reprogrammable titration analyser for the kinetic characterization of nitrifying and autotrophic denitrifying biomass, Journal of Biochemical Engineering, 26 176-183.

Global Industry Analyst Inc. (2014) Textile Printing - a Global Strategic Business Report http://www.strategyr.com/Textile_Printing_Market_Report.asp

Henze M., Gujer W., Mino T., van Loosdrecht M., 2000, Activated sludge models ASM1, ASM2, ASM2D and ASM3. IWA Scientific and Technical Report No. 9. IWA Publishing, London, UK, ISBN: 1900222248.

Hu Z, Lotti T, van Loosdrecht MCM and Kartal B., 2013, Nitrogen removal with the anaerobic ammonium oxidation process. Biotechnology Letters 35(8): 1145-1154.

Lackner S, Gilbert EM, Vlaeminck SE et al., 2014, Full-scale partial nitritation/anammox experiences - an application survey. Water Research, 55, 292-303.

Lotti T, van der Star WRL, Kleerebezem R et al. , 2012, The effect of nitrite inhibition on the anammox process. Water Research 46(8): 2559-2569.

van der Star WRL, Abma WR, Blommers D et al. , 2007, Startup of reactors for anoxic ammonium oxidation: Experiences from the first full-scale anammox reactor in Rotterdam. Water Research 41(18): 4149-4163.