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TENSILE STRENGTH OF NYLON NETTING SUBJECTED TO VARIOUS CONCENTRATIONS OF DISINFECTING CHEMICALS

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ABSTRACT

This paper presents a study of traditional netting materials subjected to disinfecting chemicals during fish farming and treatment of net cages. A series of tests were performed in order to study the effect of various concentrations of disinfecting chemicals on the tensile strength of Raschel knitted Nylon netting materials.

Simulated spill of diluted hydrogen peroxide to the jump fence during de-lousing did not affect the strength of the applied new and used knotless nylon netting samples. Hydrogen peroxide reacted with biofouling forming gas bubbles, but this did not result in reduced netting strength.

The performed tests did not indicate any effect on netting strength from a simulated single, traditional bath disinfection as performed at service stations applying the disinfectant Aqua Des containing peracetic acid. However, increasing the Aqua Des concentration from 1 to 10 % resulted in a strength reduction of 3-6 %. Simulated spill of concentrated Aqua Des on the jump fence of a net with copper coating residuals resulted in a severe reduction in strength of 45 %. This strength loss was probably a consequence of chemical reaction between copper and Aqua Des, and uncoated netting did not experience any loss in strength subjected to the same chemical exposure. These findings from application of Aqua Des should also apply to other peracetic acid disinfection chemicals with trade names as for example Perfectoxid and Addi Aqua.

NOMENCLATURE

AA	Acetic acid
AD	Aqua Des (liquid disinfectant)
H_2O_2	Hydrogen peroxide
HP	Hydrogen Peroxide
PA	Peracetic acid
SEM	Scanning Electron Microscope

INTRODUCTION

Control of parasites and diseases is one of the greatest, if not the greatest, challenge in industrialized fish farming worldwide. Consequently, disinfecting chemicals are applied regularly to remove parasites from fish and to prevent spreading of virus and bacteria between farms.

Net cages for aquaculture are subjected to chemicals for disinfection both indirectly during parasite control, typically de-lousing of fish and removal of amoeba causing AGD (Amoebic gill disease), and through disinfection of net cages at service stations before repairs and recertification. These chemicals contain substances such as hydrogen peroxide and peracetic acid, which may degrade polyamide resulting in reduced strength and elasticity [1][2]. Polyamide 6 (PA6) is a common material in net cages for aquaculture, and in Norway most nets are made of this. There has been a couple of reported incidents with net damage due to spills of disinfecting chemicals in the jump fence [3], i.e. above the water surface. The industry seek more knowledge about the possibility that disinfecting chemicals may damage or degrade the nets.

The use of hydrogen peroxide in the aquaculture industry has increased in previous years. According to the Norwegian trade magazine Intrafish, 30.000 tons active substance was applied in de-lousing of cultured fish during 2014, four times as much as in 2013 [4]. During in-cage de-lousing, the net cage volume is reduced and a tarpaulin is applied enclosing the net volume. Hydrogen peroxide is supplied to the net volume through perforated hoses until a concentration of approximately 0.2 % (2000 ppm) is achieved. The recommended treatment duration is approximately 20 minutes after ended application of hydrogen peroxide, but may in practice be longer [5]. Hydrogen peroxide for use in fish farming is supplied at a concentration of 49,5 %. For HSE reasons, it is often diluted with seawater down to a concentration of 15 % in a closed tank before it is applied to the fish cage.

Disinfection of nets at service stations involves submerging the nets in a bath consisting of disinfecting chemicals diluted by seawater. Either the net is submerged in a disinfecting bath, or chemicals are added to the washing machine. Peracetic acid is a commonly applied disinfecting chemical, with trade names as Aqua Des, Perfectoxid and Addi Aqua. Aqua Des is normally applied in a concentration of 0.5 % (dilution rate of 1:200, [7]), sometimes slightly higher to account for negative disinfection effects due to bio-fouling remains (dilution rate of 1:125, [7]). The treatment duration is from 30-40 minutes for a standard net to 60 minutes for nets previously containing fish with viral disease. After the disinfection, some service stations will rinse the net with seawater, while others do not.

Peracetic acid (PAA) is the peroxide of acetic acid (AA) and is a strong oxidant and disinfectant. Aqua Des and other commercial PAA products contains a quaternary equilibrium mixture containing AA, hydrogen peroxide (HP), PAA and water. HP will contribute to the disinfection properties of the PAA mixture, however PAA is a more potent antimicrobial agent than HP, and HP require much larger doses than PAA for the same level of disinfection. When peracetic acid dissolves in water, it disintegrates to hydrogen peroxide and acetic acid, which finally will result in the formation of water, oxygen and carbon dioxide [6]. PAA has a half-life in seawater of 4-6 hours at concentrations of 100 – 300 mg/l, corresponding to Aqua Des dilution rate between 1:500 and 1:167, and less for lower concentrations. In concentrated form, Aqua Des has a pH less than 1 [7].

PAA may be consumed in an aqueous solution through three reactions: spontaneous decomposition, hydrolysis and transition-metal-catalyzed decomposition [6]. Copper is regarded a transition-metal and may accelerate decomposition of PAA.

Both hydrogen peroxide and Aqua Des disinfect through release of active oxygen, which will oxidize and damage organic materials and metals. Peroxides are in general thermodynamic instable, and the chemical reaction may be instable, involving a risk of ignition and fire [6].

There is not much available literature concerning chemical damage or degradation of polyamides exposed to hydrogen peroxide and peracetic acid. It is established that sterilization of polyamides using hydrogen peroxide plasma may have noticeable effect on long-term stability of conventional PA 6 [8]. A study of possible effects of diluted hydrogen peroxide vapor disinfection of transportation systems, resulted in less than 10 % loss of strength of a Nylon textile subjected to 35 % hydrogen peroxide [9]. According to technical data, Nylon has a limited resistance towards diluted hydrogen peroxide and acetic acid [1][2]. In addition, acetic acid and PAA may cause metal corrosion (including copper) at very low concentrations [6][11], indicating that copper particles from anti-fouling coating residuals may be involved in chemical reactions with disinfecting chemicals. Both organic materials and heavy metal ions, for instance of copper, will accelerate decomposition of PAA and HP.

As previously described, disinfecting chemicals are applied in closed volumes with seawater until the requested treatment concentration is achieved, which is typically below 1 %. However, the chemicals are delivered at significantly higher concentrations, and it is important to investigate whether higher concentrations, spills and application of concentrated chemicals may damage the net. Possible effects of biofouling and copper particles are also of interest: Fish farmers report that hydrogen peroxide will react with biofouling during de-lousing, resulting in the formation of gas-bubbles, and are concerned that this may affect the strength of netting. Copper is often present at nets through application of anti-fouling coatings, and it is important to investigate whether copper may accelerate chemical reactions involving hydrogen peroxide and/or peracetic acid.

This paper presents a study of traditional netting materials subjected to disinfecting chemicals during fish farming and treatment of net cages. A series of tests were performed in order to study the effect of various concentrations of disinfecting chemicals on the tensile strength of Nylon netting materials. The study included traditional Raschel knitted Nylon netting, with and without bio-fouling and copper coating residuals, and disinfecting chemicals containing hydrogen peroxide and peracetic acid.

MATERIALS AND METHODS

The disinfecting chemicals hydrogen peroxide (from Akso Nobel, Sweden) and Aqua Des (from Aqua Pharma, Norway) were applied to netting samples with different concentrations and exposure time. Three different netting materials were applied in these tests as described by mesh size and strength in Table 1. All netting materials were traditional Raschel knitted PA6 multifilament netting, so-called knotless netting. Pictures are given in annex A (Figure A-1). Netting N1 was unused and without coating. N1_bf was samples of netting N1 submerged at a Norwegian fish farm for 6 months (April-Sep), accumulating bio-fouling consisting of mainly Hydroids in addition to smaller amounts of moss animals, mussels, snails and barnacles. During the 6 month field trial the mesh size of the netting was reduced by approximately 10 %. Netting sample N2 had been applied in fish production two times, each time for a period of approximately 10 months. The net was treated with anti-fouling coating containing copper prior to each production period, in total two times. It had been at a service station after each of the production periods. At service, the net was washed in a net washing machine and treated with disinfecting chemicals.

Table 1: Netting materials applied in chemical exposure tests.

Netting material	Mesh size (used/original) [mm]	Mesh strength (used/original) [kg]	History
N1	- / 30	- / 82	New, unused netting
N1_bf	27 / 30	70 / 82	N1 with fouling. Un-coated netting immersed at a fish farm for 6 months.
N2	38*/ 42	88, 97**/ 136	Used two times for approx. 10 months. Residuals of anti-fouling coating.

* Estimated as two times mesh side

** Two different net samples were applied

The applied hydrogen peroxide (H_2O_2) was of the same type as used during de-lousing at fish farms, and was supplied at a concentration of 49.5 %. Aqua Des in concentrated form consists of 20-25 % hydrogen peroxide, 5-10 % peracetic acid and 10-15 % acetic acid. Both chemicals contained stabilizers to prevent unwanted reactions during storing and transport.

Each chemical exposure test included five dry net panels (room conditioned) of 7x7 meshes that were put into a 500 ml mix of filtrated seawater and chemicals. All tests were performed in room temperature varying from 18-21 degrees Celsius. After the chemical exposure, the net samples were dried for 24 hours before being rinsed in fresh water by letting them soak for 24 hours. For the experiments with high concentrations of chemicals, the water was chanced at least once during the first hour.

The weight of five panels was approximately 27 and 60 grams in room atmosphere for netting N1 and N2 respectively, i.e. the chemical exposure tests involved 54-120 g netting per liter chemicals. In practice, the relationship between amount of netting and disinfection fluid will vary significantly depending on the size of the net and tank. Assuming a 4-ton net and a tank with 20 m^3 fluid, involves 200 g netting per liter, however this number may be both higher and lower. The applied relationships between amount of netting and fluid are considered to be within the lower parts of normal conditions, and thus a conservative condition.

A series of tests were performed, involving several combinations of the tree netting materials and different concentrations of the two applied chemicals. The different tests are presented in Table 2, where X marks a tested combination, and the following note indicates the period of time for which the netting samples were immersed in the given chemical concentration. The various concentrations were achieved by diluting with filtrated seawater.

First, uncoated netting with and without fouling (N1 and N1_bf) were immersed in a fluid of 15 % H_2O_2, which is equal to the concentration of applied de-lousing chemical. The samples were left in the fluid for two hours to study the reaction. Next, spilling of high concentration chemicals to parts of the net above water was simulating by submerging netting samples for 5-10 seconds and letting them dry in air. This would allow for air (oxygen and carbon dioxide) to participate in chemical reactions, and resulting development of e.g. heat, oxidants and acids may be concentrated on the netting surface. Finally, disinfection of nets at service stations were simulated, both as a "worst case" normal disinfection and by applying high concentration of Aqua Des (peracetic acid). For the normal disinfection, netting was submerged in a solution of 1 % Aqua Des for 1 hour. In order to study the possible effect of higher concentrations of Aqua Des during disinfection, the same test was performed with a concentration of 10 % Aqua Des. The acidity of the fluid was measured during these tests using a digital pH-meter with an accuracy of +/- 0.2, calibrated at pH 4.0. The tests with 1 % and 10 % Aqua Des was repeated using samples from another part of N2 and 25 replicates.

The results from the chemical exposure tests were compared with reference samples not subjected to any chemical exposure tests.

Table 2: Chemical exposure tests performed for the different netting materials (N1, N1_bf and N2).

	H_2O_2		Aqua Des			
	15 %	30 %	1 %	10 %	50 %	100 %
N1	X1)	X2)			X2)	X2)
N1_bf	X1)	X2)				
N2	X2)		X3)	X3)		X2)

1) 2 hours immersion, 2) 5-10 seconds immersion, 3) 1 hour immersion

The effect of chemical exposure was evaluated through tensile testing. The netting samples were wetted in tap water for 16-48 hours. Traditional mesh strength tests were performed [10], and changes in strength, dimensions and stiffness were assessed. All strength tests were performed with at least 20 replicates, and average values, standard deviation and 95% confidence interval were calculated for each test and reference samples. Statistical differences were investigated using

ANOVA, assuming normal distribution, and applying a t-test and a significance level of 0.05.

SEM (Scanning Electron Microscope) was applied to study the surface of netting N2, including the reference sample and samples subjected to 15 % hydrogen peroxide or concentrated Aqua Des. Each SEM-sample consisted of a piece of a netting twine, which was coated in gold for improved conductivity.

RESULTS

Mesh strength

Figure 1 shows the strength of netting materials subjected to hydrogen peroxide relative to the average strength of the reference test. Assessing the confidence intervals of the different tests, indicate that there are no significant differences between the calculated average strength values. Thus, the tests performed in this work do not identify any effect on netting strength due to spill of 15-30% hydrogen peroxide.

Figure 2 shows the relative strength of netting materials subjected to Aqua Des. Assessing the confidence intervals of the different tests of unused netting, N1, indicate that there are no significant differences between the calculated average strength values. Thus, the tests performed in this work do not identify any effect on netting strength due to spill of 50-100% Aqua Des on unused netting without coating.

The "worst case" disinfection test involving 1 % AD had no effect on the strength, stiffness or color of used netting (N2). The panels subjected to the high concentration disinfection involving a fluid of 10 % Aqua Des, had an average strength 3 % lower than the reference tests, and the ANOVA test indicate that the reduction in strength was significant. The tests with 1 % and 10 % Aqua Des was repeated using samples from another part of N2 and 25 replicates. Mesh strength test resulted in a significant average strength reduction of 6 % after treatment with 10 % Aqua Des compared to treatment with 1 % Aqua Des. It is thus probable that a disinfection applying a relatively high concentration of 10 % Aqua Des will reduce the strength of netting with copper residuals by a few percentage. Used netting subjected to concentrated Aqua Des had a reduction in strength of 45 %.

Dimensions and stiffness

Figure 3 shows force-elongation curves for single tests, which represent the average of the full test series. The used netting experienced several drops in tensile force during the final stages of stretching before the ultimate force was reached. This is common in used netting, and is due to local fractures in individual bundles of filaments prior to global fracture of the twine. Unused netting, N1, exposed to 100 % Aqua Des showed a reduction in mesh size of 2 mm and correspondingly increased elongation at break. Apart from this, no changes in dimensions of stiffness were observed for any of the netting samples after exposure to chemicals. This includes netting N2 subjected to concentrated Aqua Des, which in spite of the 45 % reduction in mesh strength showed no changes in dimensions or stiffness: The force-elongation curves from the mesh strength tests were similar to the reference sample up to the point where local fractures stared to occur.

Netting with biofouling, N1_bf, had an initial mesh size that was 10 % smaller than the unused N1, and its stiffness (slope of force-elongation curve) was increased by approximately 50 %.

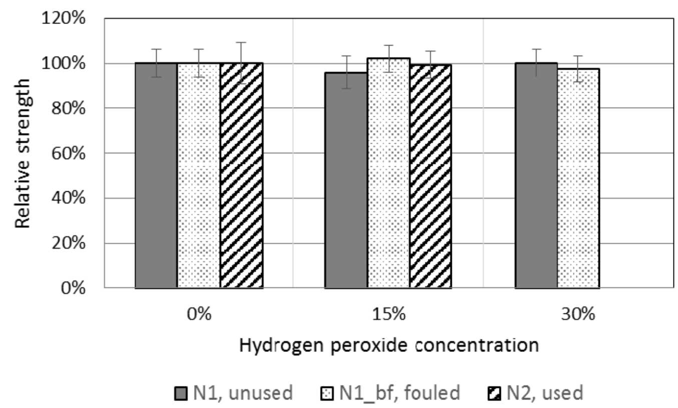

Figure 1: Strength of netting subjected to diluted hydrogen peroxide relative to strength of reference test (0% hydrogen peroxide). Given in percentage as average value with standard deviation.

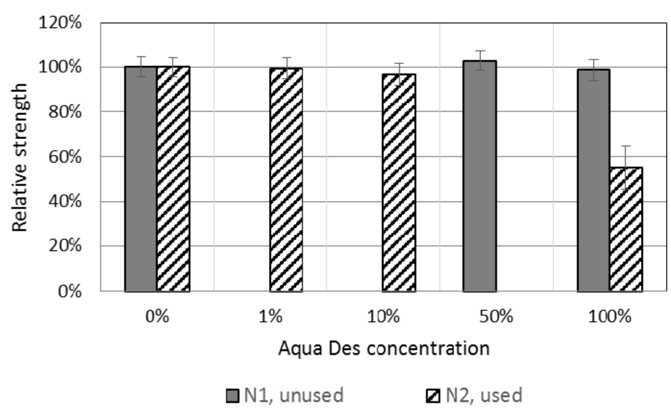

Figure 2: Strength of netting subjected to diluted and concentrated Aqua Des relative to strength of reference test (0% Aqua Des). Given in percentage as average value with standard deviation.

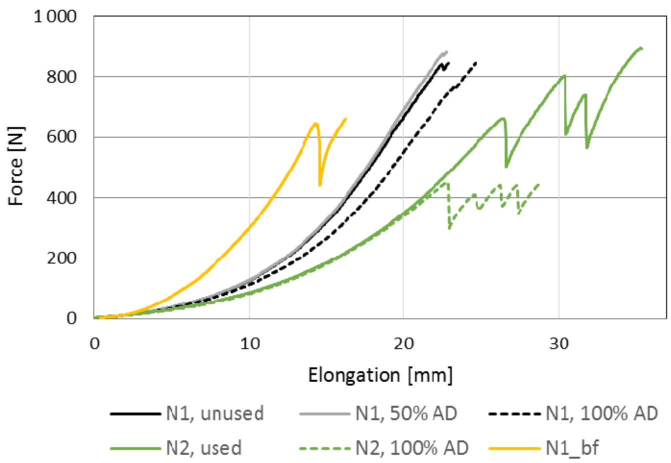

Figure 3: Representative force-elongation curves from mesh strength tests of unused (N1) and used (N2) netting. Results from reference tests, netting with biofouling (N1_bf) and netting subjected to concentrated Aqua Des (AD) and fluid with 50% AD are given.

Observations

For all chemical exposure tests with 1 or 2 hours immersion, development of gas bubbles was observed. The formation of gas was most prominent for netting with biofouling and used netting in 10 % Aqua Des.

N1 had no effects of chemical exposure visible to the eye, i.e. no changes in color or shine. Hydrogen peroxide exposure had some visual effects on fouled netting; the panels with biofouling (N1_bf) were bleached and a lot of the biofouling was removed (Figure A-2). Microscopy showed that parts of hydroids growing into the netting were still present (Figure A-3). The used netting, N2, obtained a brownish tint after the hydrogen peroxide exposure, while exposure to 100 % Aqua Des gave the netting a blue-green tint.

Temperature was measured during chemical exposure, and apart from N2 in 10 % Aqua Des (AD), the fluid temperature was constant. A gradual increase in temperature from 20.5 to 22.5 °C was observed for N2 in 10 % Aqua Des. Simultaneously, an increase in pH from 2.7 to 3.1 was measured. However, this is on level with the accuracy of the pH gauge, so no firm conclusions can be made. For the 1 % AD test, the temperature was 21 °C throughout the exposure time, and pH was measured to be 4.0 at the beginning and 4.1 at the end of the test. After the simulated bath disinfections (1 % and 10% Aqua Des), the fluid had a turquoise color.

For the high concentration chemical spill tests, i.e. test with 5-10 sec immersion duration (Table 2), temperature was not measured during immersion, but during drying in air. Except for used netting in 100 % AD, no change in temperature was observed. For N2 in 100 % AD, fume emission was observed during drying after chemical exposure. After a few seconds, the fuming ended and the temperature was measured as 60 °C. During the drying, the color of the netting changed from grey to a mixture of brown and turquoise spots. After 24 hours, the netting had regained its grey color with distinct turquoise areas (Figure A-4).

DISCUSSION

The results from this work show no indications of reduced netting strength due to de-lousing operations with hydrogen peroxide (HP). No damage was observed after simulated spills of relatively highly concentrated HP, and bath disinfection at much lower concentrations should not have any immediate effect on netting quality. However, it cannot be disregarded that other net materials and coatings, and even higher concentrations of HP may lead to damages to the net cage. In particular due to spills from accidental or incorrect application of chemicals to parts of the net above the water surface.

It has been shown that hydrogen peroxide may oxidize fouling organisms on the net during de-lousing, resulting in formation of gas bubbles as observed by fish farmers. Effects of repeated exposure to H_2O_2 has not been studied, however the results from this study and other studies of used netting does not indicate that de-lousing with low concentrations (approximately 0.2 %) of hydrogen peroxide may damage the net. Further, test involving repeated and long-term exposure is required to make firm conclusions in this matter. The possible effect of amount of copper residuals in the net should also be investigated, as increased copper content may increase chemical damage.

These tests did not indicate any effect on netting strength from a simulated single, traditional net disinfection as performed at service stations. However, the application of disinfecting chemicals with peracetic acid, such as Aqua Des, Perfectoxid and Addi Aqua, should be performed with care. Concentrated Aqua Des may severely damage netting, and also diluted peracetic acid at relatively high concentrations may affect the strength of netting.

Based on the observed residual products of blue-green color and published investigations of copper corrosion by acetic acid [11], it is probable that Acetic acid in Aqua Des reacts with copper forming copper acetate. Copper acetate are crystalline solids that are soluble in water. Other, insoluble crystals containing copper, like cuprite, may also have been formed [11]. Using a light microscope, it was observed that parts of the netting fibers had acquired a turquoise color (Figure A-5). Nylon is known to absorb water and may absorb solved Copper acetate, which in practice may dye Nylon fibers though chemical bounds with the Polyamide polymers. This process may be facilitated by acetic acid.

The cause of the severe loss in strength of used netting subjected to peracetic acid was sought through application of SEM. This work involved a limited study applying SEM to single samples of netting twine (Figure A-6). The results indicate that surface damage can be found in some areas, while other areas appeared undamaged. In the same area as possible surface damage was observed, small particles were present, but the chemical composition of these particles was not identified.

It is considered probable that strength reduction was caused by damage to the fiber surface and/or crystalline reaction products. It is possible that both surface damage and crystalline particles will occur locally in areas with copper coating residuals. By visual inspection, most coating residuals seemed to be located in the knots. Local development of high temperatures due to an exothermic reaction between copper and Aqua Des may result in damage of the fiber surface, making it brittle. Further, the brittle surface would form surface cracks, which may develop and propagate through the fiber during stretching, leading to premature failure and reduced mesh strength. Peracetic acid has the ability to degrade Nylon, affecting the bulk properties of the fibers. Since the stiffness of the netting has not been changed, global degradation of Nylon is probably not a major cause of reduction in strength for these short-term chemical exposure tests. Hard, sharp crystals within the netting structure may cut the fibers during stretching; forming notches that may facilitate crack propagation and premature tensile failure.

The tests were performed in room temperature. Lower ambient temperatures will be expected to reduce chemical reactions, while increased temperatures will typically accelerate decomposition of disinfectants. Room temperature will thus probably represent a high reaction condition, within normal conditions for the simulated bath disinfections. For simulated spills, the temperatures may in worst case be even higher, as sunlight may increase the temperature in the jump fence.

CONCLUSIONS

This work did not identify any reduced strength in traditional Raschel knitted nylon netting due to simulated spill of diluted hydrogen peroxide to the jump fence during de-lousing. Hydrogen peroxide may react with biofouling, but this did not result in reduced netting strength.

The performed tests did not indicate any effect on netting strength from a simulated single, traditional bath disinfection as performed at service stations applying the disinfectant Aqua Des containing peracetic acid. However, increasing the Aqua Des concentration from 1 to 10 % resulted in a strength reduction of 3-6 %. Simulated spill of concentrated Aqua Des on the jump fence of a net with copper coating residuals resulted in a severe reduction in strength of 45 %. This strength loss was probably a consequence of an exothermic reaction between copper and Aqua Des, and uncoated netting did not experience any loss in strength subjected to the same chemical exposure. These findings from application of Aqua Des should also apply to other peracetic acid disinfection chemicals with trade names as for example Perfectoxid and Addi Aqua.

Applying Aqua Des, in accordance with guidelines for bath disinfection of nets [7] will probably not affect the strength of netting. However, it is important to avoid fluids with high concentrations of peracetic acid to get into contact with nets with copper coatings or copper coating residuals. It is of particular importance to avoid spilling of disinfecting chemicals, especially with high concentrations, at parts of the net in direct contact with air. In air, chemical spills may lead to development of concentrated heat, acids, oxidants and other products that may damage the net.

ACKNOWLEDGMENTS

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ANNEX A

PICTURES OF NETTING SAMPLES

Figure A-1: Netting materials subjected to chemical exposure tests. From left: N1, N1_bf and N2.

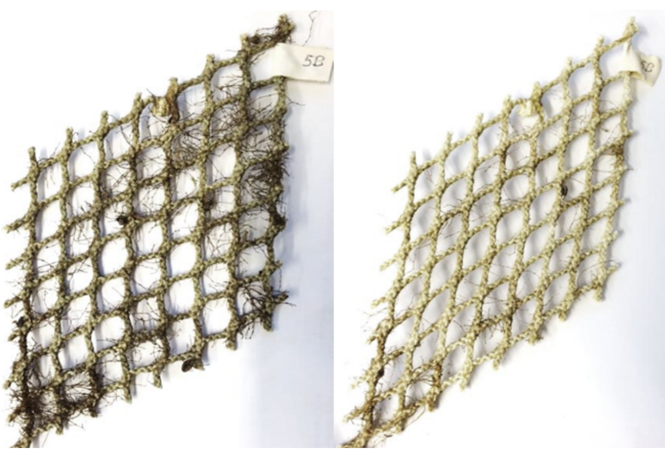

Figure A-2: Netting with biofouling (N1_bf) before (left) and after (right) exposure to hydrogen peroxide.

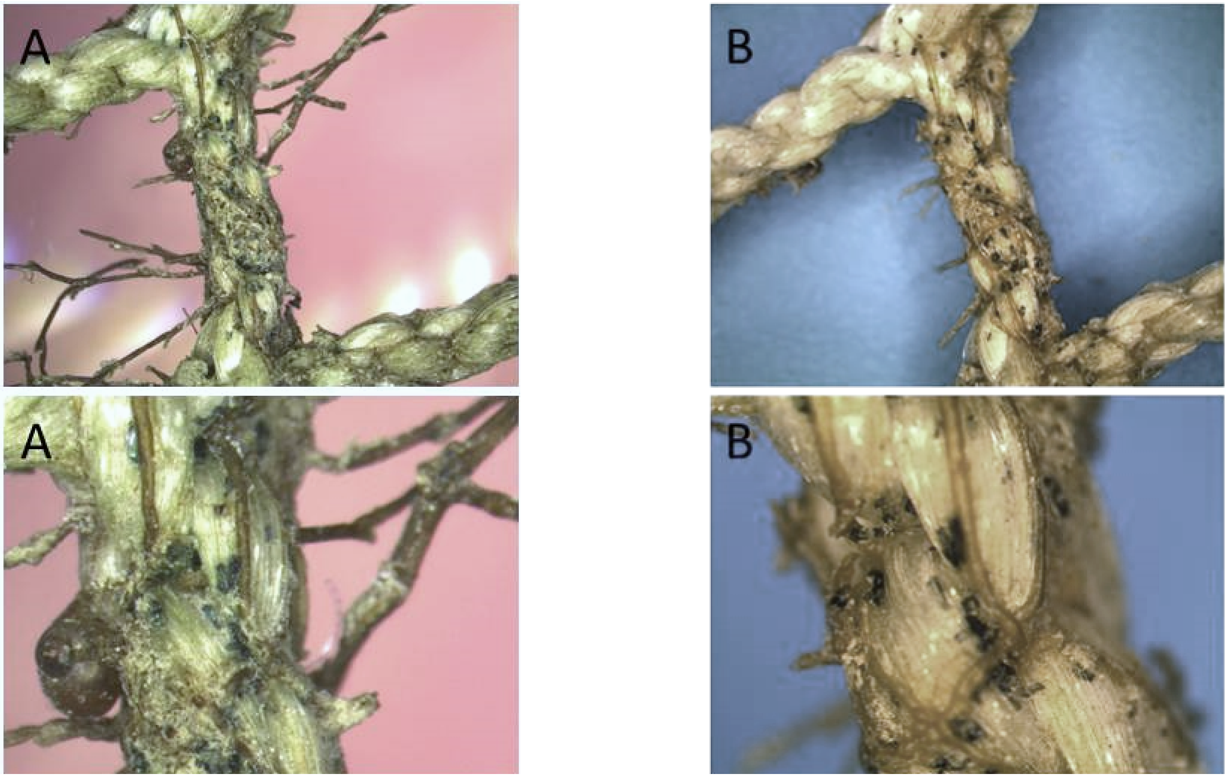

Figure A-3: Detailed view of a selected area of netting before (A) and after (B) exposure to hydrogen peroxide, seen through a light microscope.

Figure A-4: Used netting with copper residuals, N2, subjected to 10 % Aqua Des (left) and concentrated Aqua Des (right).

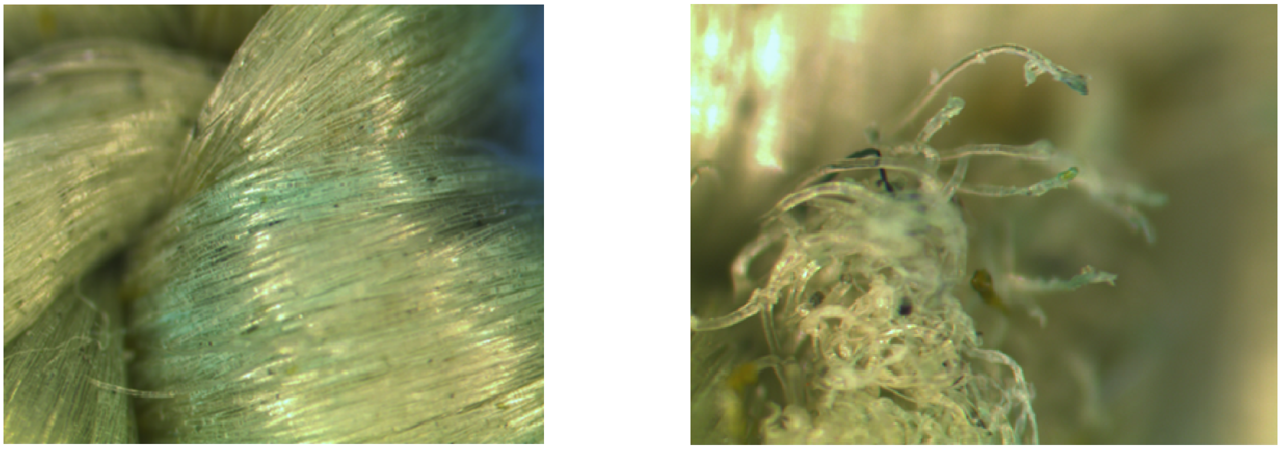

Figure A-5: Dying of Nylon fibres by reaction products containing copper.

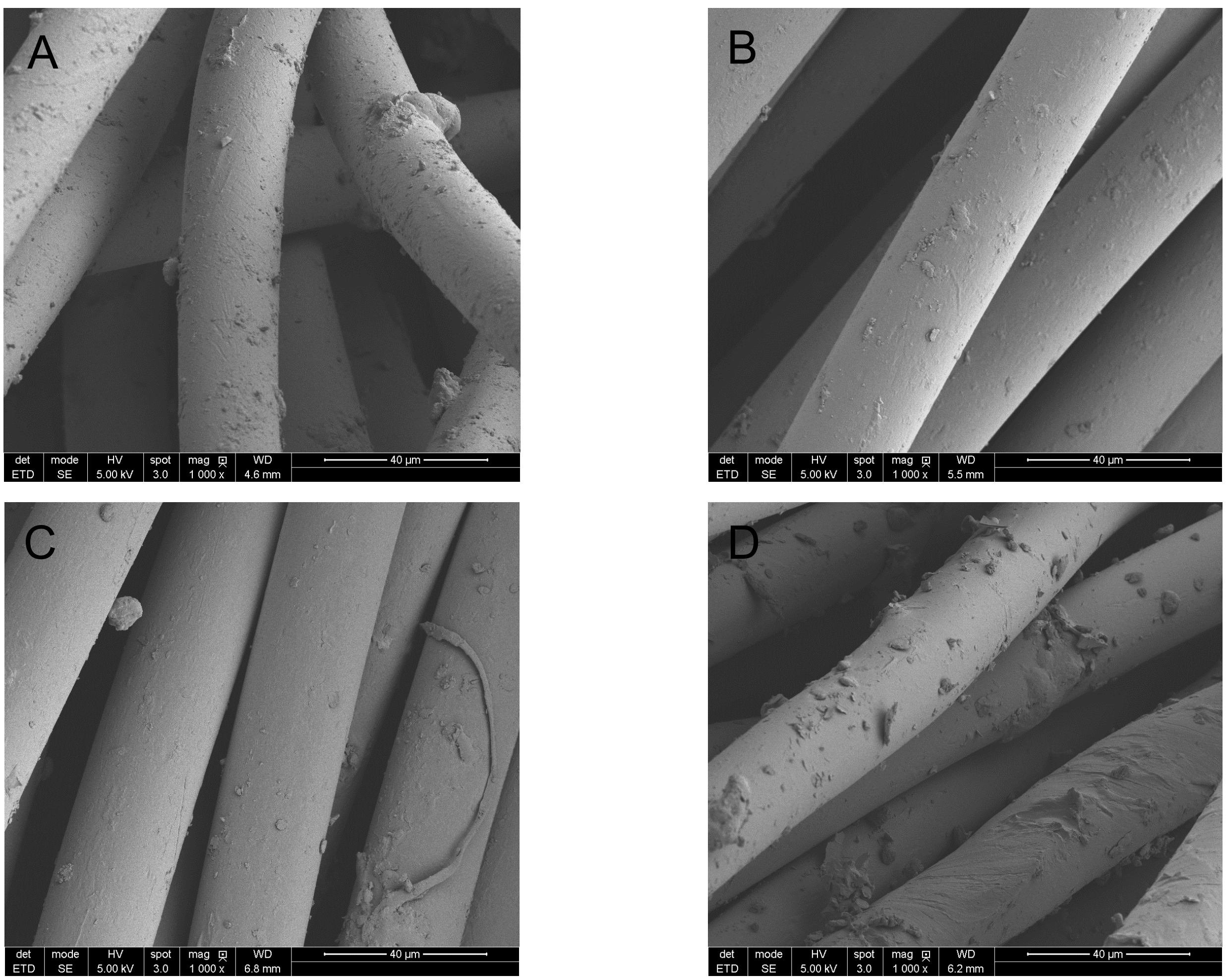

Figure A-6: SEM of used netting, N2, A) before chemical exposure test, B) after 15 % hydrogen peroxide test, C and D) after 100 % Aqua Des test