



The project for sustainable water use in chemical, paper, textile and food industries

Report on impact of nanoscale silver

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Executive summary

This report is a result of the project AquaFit4Use, a large-scale European research project co-financed by the 7th framework programme of the European Union on water treatment technologies and processes.

This report describes investigations devoted to studying the impact of Ag nanoparticles on biological processes in effluent treatment. The action of silver nanoparticles has been analysed using model systems for anaerobic and aerobic treatment processes. The impact of nanoscale silver on the respiratory activity of aerobic activated sludge was traced continuously by means of respirometric measurement. Industrial process media (effluents, activated sludge, pellet sludge) from a paper mill were used for the analyses.

Furthermore, trials were conducted in lab-scale and on mile-site to study the action that surface-bonded Ag nanoparticles had on preventing slime formation. For this purpose, especially prepared steel plates were positioned in the splash zone of a paper machine and the coating of the surface compared once the exposure time has expired.

The methods used are explained, the testing equipment is described. The results of the individual test series are presented both in tabular and graphical form.

The results demonstrate that no impairment of effluent treatment processes is to be expected when Ag nanoparticles are used in the concentrations recommended by the manufacturer.



AquaFit4Use is co-financed by the European Union's 7th Framework Programme





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1 Introduction

This report is a result of the project AquaFit4Use, a large-scale European research project co-financed by the 7th framework programme of the European Union on water treatment technologies and processes.

The research objectives of AquaFit4Use are the development of new, reliable cost-effective technologies, tools and methods for sustainable water supply use and discharge in the main water using industries in Europe in order to reduce fresh water needs, mitigate environmental impact, produce and use water of a quality in accordance with the industries specifications (fit-for-use), leading to a further closure of water cycle.

For more information on AquaFit4Use, please visit the project website: www.aquafit4use.eu.

1.1 State of the art

1.1.1 Application of (nano-)silver in paper production and paper use

Silver as an antimicrobial agent has been known for a long time. The concept of “active packaging” deals with the use of several natural and chemical substances, among them silver, to produce packaging materials with antimicrobial or bacteriostatic characteristics for food and non-food packaging /1, 2, 3/. It is expected that nanosilver products will see increasing use in future.

The amounts of nanoscale silver used for this purpose are not yet well known either. Specifications by the manufacturer recommend concentrations of 1 – 25 ppm nanosilver. Depending on the type of use (e.g. use in coating colours) nanoscale silver concentration appears to be low in the paper product.

The entry of these particles in the water circuits and the wastewater is possible because of the intensive use of recycled paper in the case of intensive use of nanosilver products. Even the risk of nanoscale silver affecting human health, when correctly used, is assumed to be negligible /4/. Nanosilver may cause a disturbance of biological effluent treatment processes due to their antimicrobial properties.

Nanosilver products are currently not yet being used on an industrial scale in papermaking (at least not in Germany). At present, they are still being used in the development stage on laboratory and pilot scales.

1.1.2 Effluent treatment in paper mills

• The role of effluent treatment in paper mills

The production of paper goes hand in hand with the intensive use of water. The effluents of papermaking are contaminated with organic substances which are to a large extent biologically degradable. So the effluents of nearly all paper mills will be treated by mechanical and biological processes to remove the organic load from these effluents. The established processes use different types of anaerobic (e.g. UASB, EGSB) and aerobic biological processes (activated sludge, MBBR, biofilters).

When nanosilver products are used in papermaking, these particles may also be transferred to the process and wastewater streams and eventually reach the effluent treatment plants. Because of the antimicrobial properties of nanoscale silver, disturbances of the biological processes may occur depending on their concentration.



- **Behaviour of nanoparticles in biological processes**

The behaviour of nanoparticles in biological treatment processes and their impact on biomass is currently not well known. On the one hand, adsorption of nanoparticles onto biomass, especially at extracellular substances, on the other hand inhibition of the activity of biomass may be expected /5/.

Investigations concerning the behaviour of Cerioxide nanoparticles in biological treatment processes showed adsorption onto activated sludge to be the main reason for elimination but also the outwash of nanoparticles to the effluent (6%), obviously dispersed by surface active substances from bacteria /6/.

1.2 Objectives

Nanoscale silver is used in various products/processes, for example in sport clothes, wall colours, water treatment, medicine technology and marine engineering aiming on reducing biological growth. Newer R&D activities deal with implementation of nanosilver in packaging. So, there is a clear demand to ensure stable production, protection of health and environment to provide possible negative developments.

There are four main objectives:

- Measuring methods for nanoscale silver (NSilver) will be used in the processes and water circuits of the paper sector. In a first monitoring the actual concentration level of NSilver will be studied in at least one paper mill.
- Learning from established applications in different sectors: the overall goal is to generate knowledge in terms of using tailor-made nanosilver structures in high loaded microbiological process water and effluent streams. Consequently the need of biocides can be significantly reduced
- Application of effective surfaces in pilot or laboratory trials. This will focus on the differentiation of the effectiveness of dissolved or surface-bounded NSilver and the economic impact.
- Laboratory trials will be carried out to test the impact of NSilver in biological wastewater treatment plant. Objective is the investigation of the impact of different NSilver levels to the degradation level of aerobic and anaerobic water treatment. This will focus on the definition of first critical concentration levels to provide malfunctions of wastewater treatment plants.

2 Results and achievements

2.1 Major results and achievements

The work was divided in two study topics. The first focused on the effect of nanoscale silver on the processes of aerobic and anaerobic wastewater treatment. The second dealt with the prevention of biofilm growth on plates which were prepared with an antimicrobial coating colour, based on nanoscale silver.

The nanoscale silver product was expected to show inhibitory effects on biological degradation processes. Nevertheless, the results show this effect to be limited. Properly used product (concentrations in the range up to 300 mg/l) showed no significant impact on the efficiency of COD elimination in the anaerobic and aerobic tests. Only concentrations of greater than 500 mg/l showed a slightly drop in the degradation rate and COD elimination.



The more sensitive respiration test was the only test in which total inhibition of the activated sludge activity at 1000 mg/l nanoparticle (100 mg/l nanoscale silver) was observed. Because soluble silver in this concentration also shows inhibition effects, this impact is not specific for nanoscale silver. At lower product concentrations, only a concentration-dependent extension of the lag period was established.

Summarizing these results, nanoscale silver products in concentrations below 300 mg/l of product (30 mg/l Ag) show no evident influence on the processes of biological effluent treatment. Assuming only a fraction of the product used enters the wastewater, there is no danger to be expected by the use of nanoscale silver products.

The use of surface-bonded silver to prevent slime growth under the rough conditions of a paper machine was tested with painted steel panels. The results showed only a small effect. The antimicrobial effect of surface-bonded nanoscale silver seems to be too weak to keep the surface free of slime coating build-up.

2.2 Effect of nanoscale silver on biological processes of waste water treatment

2.2.1 Detection of nanoscale silver in process water

The detection of Ag nanoparticles generally encounters a problem, viz. the methods for determining nanoparticles that are conducted with light scattering methods only describe the particle size, but not the chemical character of the particles. Another difficulty in determining nanoparticles in industrial process or effluent matrices arises from the fact that other particles with dimensions less than 1 micron are present in the matrix in addition to the particles to be measured, and the measured size distribution is multimodal. Since there is an exponential relationship between particle size and the measured intensity of the backscattered light to the power of 6, one must be careful to calculate the number weighted particle diameters when evaluating the measurements in order to suppress this effect to a large extent.

Model experiments with nanoscale silver in effluents have demonstrated that Ag nanoparticles in the effluent treatment process are adsorbed on the activated sludge in the biological stage. Similarly, Ag nanoparticles can be eliminated almost completely by chemical precipitation. Although the DLS method is capable of detecting particles in the size of the particles used, the corresponding Ag concentrations, however, are below the detection limit of the chemical method.

No silver could be detected using ICP-MS in measurements of the silver content in process water from two paper mills. This confirms the fact that nanoscale silver is not being used on a large industrial scale at present.

2.2.2 General remarks concerning degradation tests

All degradation tests were performed using different dosages of nanosilver product ranging from 100 mg/l to 1000 mg/l product. The recommended dosage of nanoparticle was 100 – 250 mg/l product. The trials at higher dosages (>500 mg/l) were intended to show if any overdosage of the product (e.g. in case of an accidental release) would lead to major disturbances of the degradation processes. One test series was carried out without application of nanoscale silver and was used as reference series.

In anaerobic and aerobic degradation tests, effluents from a paper mill is used as the substrate and anaerobic pellet sludge from an UASB reactor or activated sludge from the aerobic stage are used as inoculums. The respiration test uses activated sludge as the inoculum and a BOD standard (D-glucose, L-glutamic acid) as the substrate.

2.2.3 Anaerobic test

The results of the anaerobic tests (see Figure 1) show no drastic reduction in COD elimination rates depending on the concentration of nanoscale silver. A slight lag in degradation rate and a lower degree of COD elimination (approx. 5%) were observed for the highest product concentration of 1000 mg/l. At concentrations below 500 mg/l nanosilver product, COD elimination is marginally smaller and seems to be in the range of experimental error.

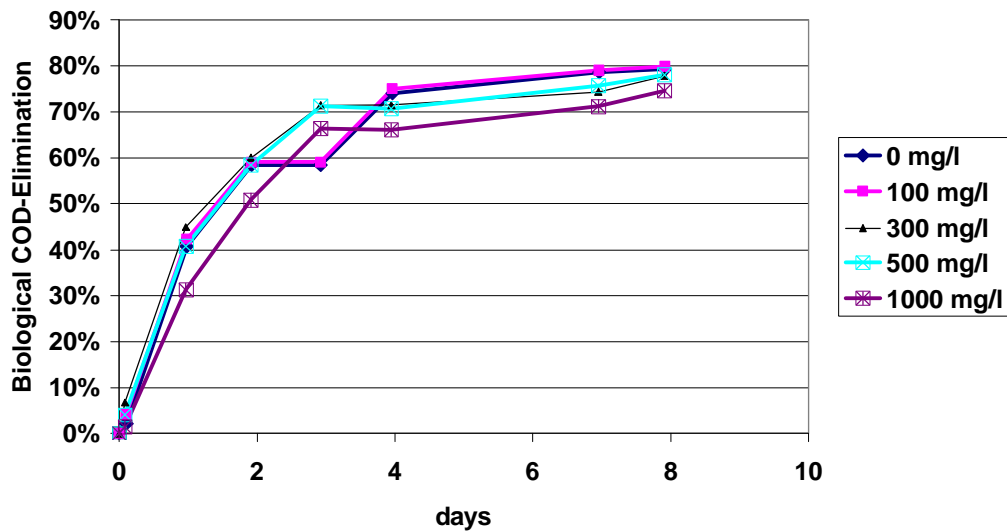


Figure 1: Anaerobic degradation test

Table 1 COD values of anaerobic test samples depending on time and Nano-Ag-conc.

Time [days]	Concentration of Nano-silver-product				
	0 mg/l	100 mg/l	300 mg/l	500 mg/l	1000 mg/l
	COD mg/l				
0	1820	1893	1897	1963	1926
0.10	1780	1813	1769	1883	1897
0.98	1078	1092	1045	1162	1323
1.92	758	775	758	815	947
2.92	758	775	543	564	647
3.96	472	472	541	574	653
6.96	388	397	486	476	555
7.92	377	381	421	430	489

2.2.4 Zahn-Wellens test

The results from aerobic Zahn-Wellens tests (Figure 2) are similar to the results from the anaerobic test. Only at the higher dosages was there a slight decrease in elimination rates but at the end of the test after 21 days they both showed nearly the same COD elimination of 90%.

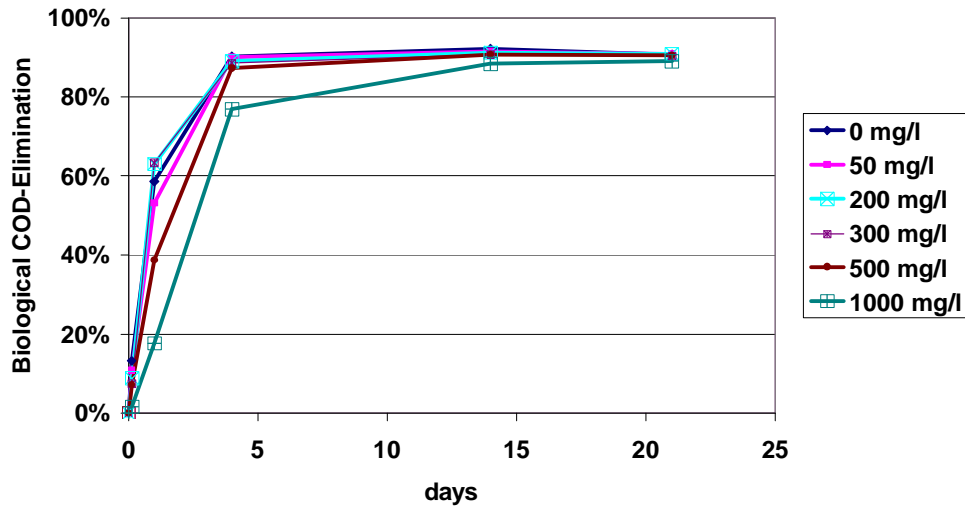


Figure 2: Aerobic degradation test (Zahn-Wellens test)

Table 2 COD values of aerobic test samples depending on time and Nano-Ag-conc.

Time [days]	Concentration of Nano-silver-product						
	0 mg/l	50 mg/l	100 mg/l	200 mg/l	300 mg/l	500 mg/l	1000 mg/l
0	1930	1930	1930	1930	1930	1930	1930
0.125	1674	1722	1729	1761	1786	1792	1898
1	798	904	793	713	706	1183	1589
4	187	190	192	209	221	244	445
14	152	163	161	168	177	177	223
21	177	177	179	174	186	183	211

Figure 3 below shows selected batch tests at the beginning and at the end of the degradation test. From left to right, the vessels shown are the “reference” (0 mg/l silver), 200 mg/l and 1000 mg/l.



Figure 3: Batches at the beginning (left) and at the end (right) of the Zahn-Wellens test

The obvious effect of Ag dosage can be seen clearly as the coating colour changes to black.

2.2.5 Respirometric test

Respirometric tests were performed in addition to the aerobic degradation test. The test conditions of the respirometric test (Table 3) were nearly the same as the Zahn-Wellens test. Especially the relation between nanoscale silver and the dry substance of the biomass was adjusted to the same value. The main difference was the initial sludge load which was 4½ times higher then in the Zahn-Wellens test.

Table 3 Test conditions

parameter		dimension
COD wastewater (BOD-Standard)	~360	mg/l
concentration inoculum	0.08	g/l
initial sludge load	4.5	g COD/g MLSS
N-dosage	1.3	mg/l NH ₄ -N
P-dosage	97	mg/l PO ₄ -P
Nano-Ag-product dosage	0 - 1000	mg product / g MLSS

The test shows the oxygen uptake during the elimination of organic substance (BOD standard). The target value was about 200 mg/l and was almost reached in most test runs. The results indicated only a very low influence of nanoscale silver addition at low doses (< 200 mg/g MLSS). Referring to the reference test, only a small extension of the lag phase was observed before the start of the degradation phase. The higher the dose, the longer this lag phase was. At the concentration of 1000 mg product per gram of biomass, total inhibition of respiration was observed during the test time of 100 hours.

These results are in accordance with the results of the aerobic degradation test, which pointed out that nanoscale silver in concentrations resulting from conventional use does not cause a disturbance of the biological treatment processes.

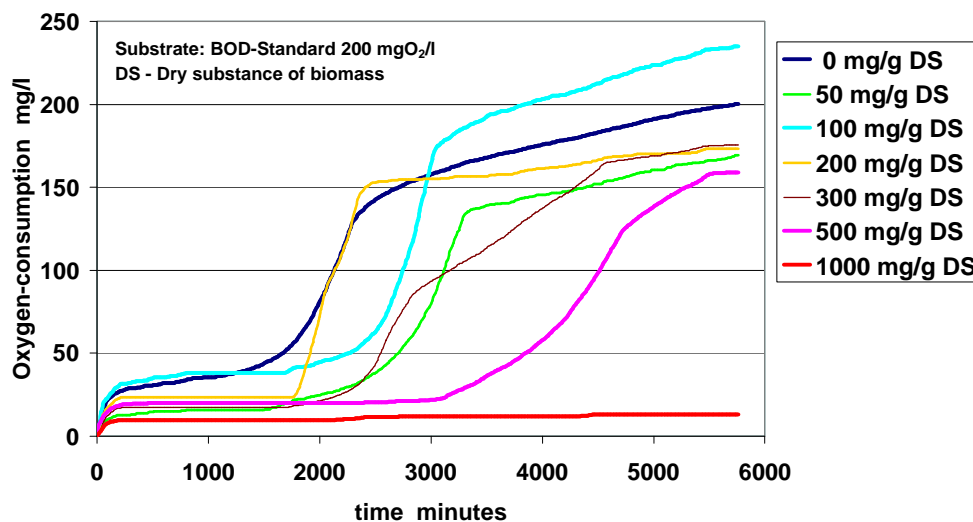


Figure 4: Respiration test run

2.2.6 Testing the effectiveness of surface-bounded nanoscale silver on surfaces

One of the most frequent problems in paper mills is the growth of biofilms in technical equipment. Therefore surfaces with antimicrobial properties to prevent biofilm growth could avoid many

resulting problems. The use of surface-bonded nanoscale silver was tested with steel panels which were painted half with normal coating colour and half with nanoscale silver containing coating colour. During the exposure time, the panel in the circuit water showed no growth of slime on either coating colours, with and without nanoscale silver.

The following images demonstrate the growth of biofilm and a mixture of fibre and slime on the panels, which were located at different places near the paper machine (wet, warm and misty) for 47 days.



Figure 5



Figure 6



Figure 7



Figure 8

Obviously the intensity of the growth of biofilm or slimes is very high and the effectiveness of surface-bonded nanosilver is too weak to prevent a build-up of slime. Furthermore, other principles beside biological growth may contribute to the development of slime and shield the surface-bonded silver.



3 Conclusions

3.1 Major achievements

- Nanoscale silver in the production of special paper with antimicrobial properties is currently still being used only on the laboratory and pilot scale. For this reason, there is no experience regarding the amounts required on an industrial scale.
- Proceeding from the principal intended use of nanoscale silver in coating colours as an antimicrobial finish for paper surfaces, the only feasible way of incorporating nanoscale silver into the process water and effluents of the papermaking process is by slushing the broke or by using an appropriately finished recovered paper. Hence, the load of nanoscale silver in the effluent should be low assuming that the recommended amounts of 1 – 25 ppm are used.
- It was found in model experiments on anaerobic and aerobic biodegradability that concentrations of nanoscale silver <30 mg/l did not cause any impairment of these processes. Contents above this value, however, reduced process efficiency. Hence, when nanoscale silver is used properly, no disruptions of the effluent treatment processes are to be expected.
- Initial studies on the reduction of biofilm growth on surfaces with fixed Ag nanoparticles (nanosilver coating colour) had only a small effect. The test plates that were tested in the splash zone of a paper machine showed considerable microbial growth with a fibre/slime layer irrespective of the foundation. The microbicidal effect of the Ag-doped colour was too weak or it was shielded by the large amounts of fibre/slime mixture that were applied to the surface. Future studies should aim at clarifying the causes of the observed phenomena.

3.2 General recommendations

The studies have shown that, when the products were properly used, no environmental impacts were discovered under the conditions described here (use of Ag nanoparticles in coating colours and discharge into the water systems of a paper mill via the broke and recovered paper).

The studies on the use of surface-bonded nanoscale silver have demonstrated that, in view of the high exposure of the surfaces to shower water containing fibres and solids, no effect that might prevent the deposits from forming was detected. The tests were intended to be repeated under other conditions, also using other nanosilver-doped coating colours.



4 Literature

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