

## SEPARATION OF THE ENGINEERED NANOPARTICLES FROM INDUSTRIAL WASTEWATER IN THE COATING INDUSTRY

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### Abstract

Functional engineered nanoparticles (ENPs) are produced and used in various branches of the industry. Because of their small size, nanoparticles have many specific properties. They are used as pigments in dyes and paints of various industrial applications, catalysts and ceramics, in pharmaceutical agents as well as in specialty chemicals. Nanoparticles are very often applied in wet processes, enter the process waters and subsequently release to the environment. ENPs have several advantages and their use is rapidly growing. However, there are serious potential health & safety hazards linked to these substances as well as potential adverse environmental impacts. Therefore there is a need for innovative technologies which can remove ENPs efficiently from wastewater.

Our research is focused on removal of nanoparticles from wastewater in the coating industry. The “NanoFloc” project is developing a novel and cost effective system for removal of engineered nano-particles from water used in surface coating. The NanoFloc treatment technology is based on electrocoagulation process. It is based on destabilisation of nano suspensions and agglomeration of charged nanoparticles in suspensions using electric field and flocculation in one step.

The task is solved by a consortium of industrial partners and RTDs with a high level of experiences in design and optimization of wastewater treatment technologies, esp. electrochemical processes. Participants include Fraunhofer IGB (DE), Technologisk Institutt AS (NO), BAMO Mesures (FR), Melotec GmbH (DE), Westmatic AB (SE) and ASIO, spol. s r.o. (CZE).

**Keywords:** Functional engineered nanoparticles, electrocoagulation, nanoparticle removal

### 1. INTRODUCTION

Today nanotechnology is an industrial sector with a great potential. Materials with dimensions 1-100 nm offer wide range of applications. Effect of ENPs on environment and organisms has not been properly described yet. There are many concerns about adverse effects of ENPs connected with its special physical properties. This article deals with removal of ENPs, which are used in painting and coating industry from wastewaters produced during wet operations.

ENPs have very unique properties. While above 100 nm classical physics is applied, for smaller sizes the principles of quantum physics are valid. An alteration of particle size changes properties like solubility, transparency, colour, conductivity and melting point. Moreover the fraction of surface atoms is quite high for nanoparticles. A spherical iron particle with a diameter of 5 nm e.g. consists of approximately 27% surface atoms. In contrast the percentage of surface atoms in a particle with a diameter in the micrometer range is only 0.15%. Surface atoms are not completely surrounded by other atoms and therefore have very reactive free bonds [1].

A large number of reactive, catalytically active surface atoms can also have undesirable effects and might cause toxicity. Some researchers even assume that the potential toxicity of nanoparticles is increasing with decreasing of particle sizes. Nanoparticles can invade through the respiratory and digestive system [2]. From this point of view, nanoparticles in water can cause a health and safety risk [3].

With the use of nanoparticles, totally new surface effects are available which are successfully used in several applications today. Especially in modern coatings, nanoparticles are used to have easy-clean-properties, dirt-repellent or hydrophobic qualities as well as very good mechanical properties like abrasion-resistance and scratch-resistance. The nanoparticles are available in lacquers; they are not fixed to other substances or components of the lacquer. The efficiency of the spray booth technique is quite low because the overspray rate varies from 20% to 90%. This means that 10% to 80% of the total lacquer does not meet the work piece but the wet scrubber systems instead. The wet scrubber systems collect the overspray with water baths. This water has to be cleaned for reuse.

With the current state of the art technique it is quite complicated and expensive to remove the nanoparticles from this effluent to ensure that it does not harm humans and pollute the environment. The nanoparticles have very high surface area. The higher the surface area and the contact to the surrounding media the higher is the surface potential and interaction forces. This means that particles in the nano-size range stay stable in the water because of their size compared to particles with bigger diameters from the same material [1].

The NanoFloc project is developing a new technology combining two techniques, namely agglomeration of ENPs with electric field and stabilization of ENP-agglomerates with very fine hydroxide flocs generated electrochemically. Flocs with nanoparticles will then be separated from the wastewater. The reactor is equipped with the sacrificial and inert electrodes. Electrochemically assisted coagulation consists of the *in situ* generation of coagulants by the electrodisolution of a sacrificial anode, usually of iron or aluminium. The inert electrodes are made of stainless steel or noble metals which do not release ions but build up an electric field.

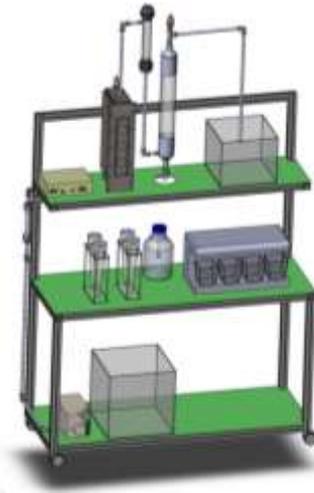
The advantages of the electrocoagulation process over the conventional dosing of coagulants are mainly the simple equipment required and the easy automation of the process. The process requires no addition of chemicals, and the amount of coagulant dosed can easily be controlled by varying the electrical current applied. In this context, the low current density requirement allows electrocoagulation to be powered by green energy processes such as solar panels, windmills and fuel cells [4]. Other advantages of the electrochemical technology related to the generation of gas bubbles (primarily of H<sub>2</sub>) are the production of a soft turbulence that promotes the flocculation process (electroflocculation) [5] and separation of the particulate pollutants, which are carried to the top of the solution where they can easily be collected and removed (electroflotation process) [6].

The aim of this article is to introduce the NanoFloc laboratory technology and to show the efficiency of TiO<sub>2</sub> nanoparticles removal from synthetic wastewater. NanoFloc is an SME managed project. The protection of foreground is planned. Therefore, details of the methodology and innovations are deliberately withheld from the public until the results are protected.

## **2 MATERIALS AND METHOD**

### **2.1 Laboratory electrocoagulation system**

The laboratory unit is based on electrocoagulation and flocculation. The scheme of the laboratory system is shown in Fig. 1. Main parts of the system are the electrocoagulation reactor, flocculation column and clear phase container. A separation unit to remove loaded flocs from the clear phase will be designed and tested in parallel with the pilot plant to be developed.



**Fig. 1** Laboratory electrocoagulation system

The electrocoagulation unit is equipped with sacrificial electrodes. Aluminium and iron plates containing between 97 – 98% Al/Fe were used as sacrificial anodes. Both metals produce low solubility hydroxides in a specific pH range. The produced hydroxides produce flocs that will grow while entrapping suspended nanoparticles from the lacquer.

### 2.1 Model wastewater

The task was to produce synthetic wastewater containing Ti nanoparticles that resembles the effluent from a wet scrubber booth as close as possible. Two dilutions were prepared (1:5000 and 1:250). A dilution factor of 1:5000 is a typical lacquer concentration after the overspray of a spraying booth is washed with a wet scrubber. A second dilution factor was tested (1:250) because the stream after electrocoagulation presented a metal concentration (Ti) under the measurement limit of the selected analytical method.

### 2.2 Analytical methods

Inductively coupled plasma mass spectrometry (ICP-MS) was the analytic method to measure the metal concentration (Ti or Al) in the clear phase. 10 mL from the 5 L sample was taken to be firstly digested using hydrofluoric acid 40% at 210 °C for 20 min in a microwave Mars CEM to dissolve all the nanoparticles still present in the clear phase. The sample was then measured using a Perkin Elmer Elan DRC (ICP-MS) to obtain the metal concentration.

### 2.3 Process description

Treated water is pumped to the electrolysis cell, where the ions (aluminium or iron) are dosed via electrolysis. The mixture of ions, metal hydroxide, electrolysis gases and treated water is degassed. The degassed mixture is led to the flocculation column in which neutralized particles and flocs will be forced to collide to increase floc size and adsorption of particles.

The suspension is pumped across the reactor at different electric currents values up to 4 A. Two different electrode materials were used (aluminium and iron). The pumping flow is 20 L/h. 30 L from each suspension is prepared as feed. 4 L of wastewater were passed through the unit to reach steady-state and afterwards a 5 L sample was taken. The sample is left for 24 h to settle in order to remove the particle loaded flocs from the clear phase that is analysed.

### 3 RESULTS AND DISCUSSIONS

Ti nanoparticles reduction of 94.5% - 98% was achieved while using aluminium electrode (dilution factor 1:5000). The detection limit of the analytic method was higher than the concentration obtained after electrocoagulation.

A new series of experiments were performed in order to avoid being lower than the detection limit of the ICP-MS method. A higher initial concentration was set with a dilution factor of 1:250. Ti reduction of 37.4% – 99.8% was achieved with this dilution factor and aluminium as sacrificial anode.

Experiments using iron electrodes as sacrificial anodes and dilution factor 1:250 showed the efficiency of TiO<sub>2</sub> nanoparticles removal of 27.8 – 99.7% (Fig. 2 – right).

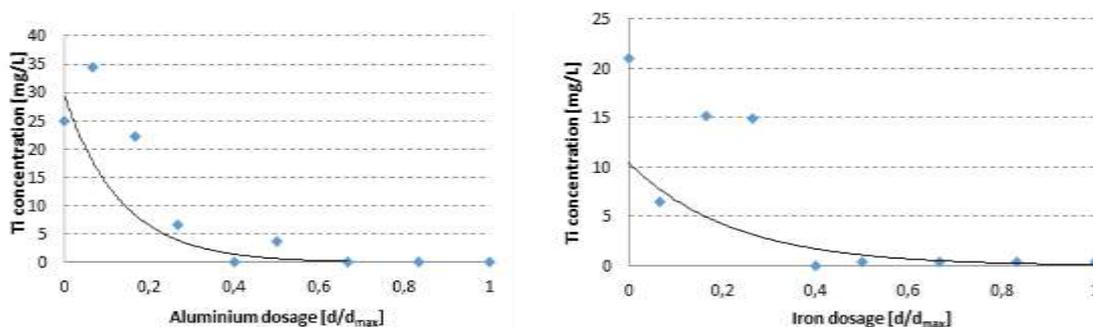


Fig. 2 Ti concentration versus aluminium dosage (left); TiO<sub>2</sub> NP concentration versus iron dosage (right). Aluminium/iron dosages are given as a ratio of applied dose to maximum dose. Maximum dose is a crucial and confidential information

Removal of TiO<sub>2</sub> nanoparticles with aluminium electrodes (99.8%) was slightly better than with iron electrodes (98.3%) at the same conditions.

Electric current needed for corresponding efficiency is not publishable at this moment. It is necessary to increase the residence time in which the nanoparticles are in contact with the metal hydroxide flocs when the electric current is lower. Lower energy input can be achieved by increasing the residence time of the wastewater with the hydroxide flocs.

### CONCLUSIONS

The NanoFloc laboratory electrocoagulation system was designed, modelled, constructed and tested. Tests using synthetic wastewater were done to investigate the extent of nanoparticle agglomeration and removal (titanium dioxide). Two different dilution factors, 1:5000 and 1:250, were used for synthetic wastewater preparation. Removal due to a continuous agglomeration and coagulation process in the reactor using aluminium electrodes resulted to 99.8% reduction of TiO<sub>2</sub> nanoparticles. Around 98.3% TiO<sub>2</sub> nanoparticles removal was achieved using iron electrodes. With a more efficient separation process the removal will be higher.

The electrocoagulation of concentrated lacquer results in flocs that float and hardly settle. The latter makes sedimentation economically and technically not feasible as separation process. A feasible separation unit has to be designed and tested to remove the agglomerated nanoparticles in flocs from the clear phase.

Technology based on electrocoagulation showed good results. Limit concentrations of the engineered nanoparticles in the industrial effluent have not been defined yet. There is a lot of controversial discussion about the health and environmental risk of nanomaterials. Setting of strict effluent limits can be expected in the near future. Health and safety risks together with possible new directives will be a strong driver and motivator for industry to adopt NanoFloc technology.

## ACKNOWLEDGEMENT

***NanoFloc has received financial support from EU's FP7 administered by the Research Executive Agency (REA) under grant agreement No 315195.***

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