Developement of an atmospheric plasma spraying process for the photocatalytic surface modification of glass spheres and subsequent examination

Isabell Herer
Deggendorf Institute of Technology
Deggendorf, Germany
Isabell.herer@stud.th-deg.de

***Abstract*— Due to the increasing consumption of water in Germany, caused by population, farming and industry, the purification of process water is becoming more necessary these days. Ingredients like dirt, lubricants or process residues must be filtered. Here especially microorganisms play a major role because of their noxious effects on men and animals. For this reason, there are already several filter systems in use. Sand filters for example are a cost – efficient method to ensure a mechanical particle filtration. Nevertheless based on an irregular grain structure, microorganisms adhere to the grain surface the longer the filtration period takes. The consequence is a reduction of the filtration performance. For an application of glass spheres as a filter material, this is not an issue, since the sleek surface and homogeneous form prevent an adhesion of contamination (Figure 1). So the main intention is to combine a mechanical filtration with an antimicrobial degradation by modifying the glass sphere surface with a photocatalytic and therefore antimicrobial titanium dioxide coating, in conjunction with plasma technology. For this process, an experimental setup was developed and deposition tests on plane glass substrates and glass beads where examined via SEM-analysis, UV/VIS and Raman– spectroscopy afterwards, using the ISO 10678:2010-09 standard for the determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue.**

Keywords—water filtration; antimicrobial coating; titanium dioxide; atmospheric plasma deposition; plasma spraying; glass beads; methylene blue

I. Introduction

In the course of human history, various cultures have been dependent on converting contaminated water into water of drinking quality. Irrelevant whether it is salt water or contaminated by germs from still waters, the basic idea of water purification consists of filtering out unwanted substances or organisms. The present day is mainly characterized by filter systems that ensure mechanical particle removal. The filter cartridges filled with sand, or membrane layers, force impurities to adhere to these layers or get stuck in between. Chemical substances like chlorine, or gases such as ozone are then usually used for disinfection. However, since this is a high burden on the environment, some manufacturers of filter systems rely on the use of activated carbon filters and the application of reverse osmosis [1].

The future of water treatment now is in combining the filtration and purification process. Both process steps need to be implemented within one system, which should save maintenance costs on the one hand and time on the other. In addition, a reduction in environmental pollution should not be neglected, as the final storage or disposal of chemicals is a disturbing factor. The filtration of dirt as well as the killing of microorganisms is to be realized by means of a filter system filled with glass beads. The glass beads, modified by atmospheric plasma spraying, not only serve the purpose of mechanical particle separation, but also the photocatalytic decomposition of germs. This decomposition, which is based on reduction and oxidation mechanisms, is initialized by UV irradiation of the glass beads in the filter, which is why the titanium dioxide layer on the surface of the beads, is an important influencing factor. Figure 2 illustrates the desired modified surface structure of the glass beads after the plasma spraying process.

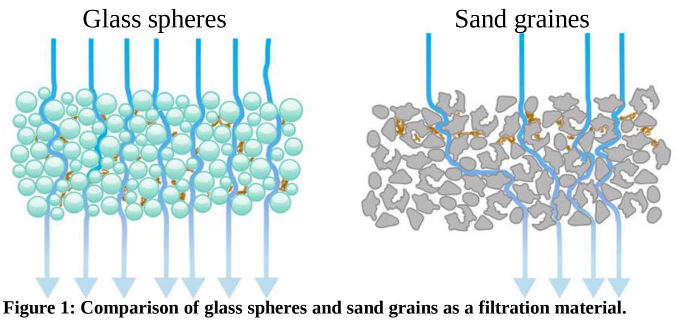

Figure 1: Comparison of glass spheres and sand grains as a filtration material.

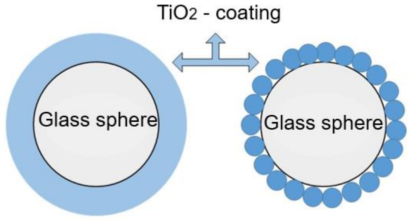

Figure 2: Schematic depiction of the desired Coating outcome.

II. Basics

A. Atmospheric plasma spraying

Plasma spraying among atmospheric conditions is a process for multiple purposes, as coatings can be deposited with many materials like metal, ceramics and composites. Generally the process is executed with a plasma spray gun, in which the coating- fluid, -solid or -powder is introduced into the plasma beam. The coating particles then get accelerated onto a substrate where they cool down and solidify [2]. Figure 3 shows a schematic depiction of the spray gun that is used for this specific process.

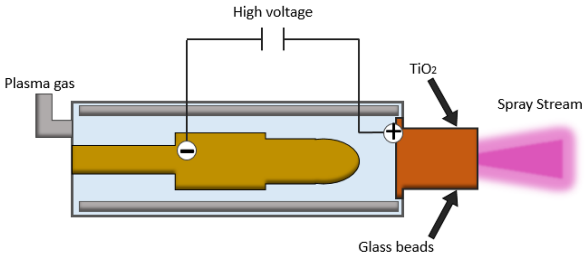

Figure 3: Schematic depiction of the plasma gun that is used for this process.

B. Titanium dioxide

Titanium dioxide appears in three modifications: Rutile, anatase and brookite. They differ in physical and optical properties, such as crystal structure or refractive index. Due to its versatile properties, titanium dioxide offers a wide range of applications. On the one hand, due to its high refractive index (rutile modification 2.55; anatase modification 2.80), it is added as a brightening agent to paints, papers, ceramics and ointments. On the other hand, it is added as a non-toxic additive E171 to foodstuffs. It is also used in the microelectronics and semiconductor industry thanks to its semiconductor properties. However, the most important property of titanium dioxide, especially for this work, is its ability to break down organic compounds into water and carbon dioxide by photocatalysis. Here it applies that the energy of the light radiation corresponds to the energy of the band gap of titanium dioxide in the anatase modification (3.2 eV; 365nm = UV/A). This is the only way to ensure that electron hole pairs are formed within the TiO_2 layer. Those diffuse to the surface where they stimulate reduction and oxidation mechanisms [3]. Figure 4 shows the photocatalysis of titanium dioxide.

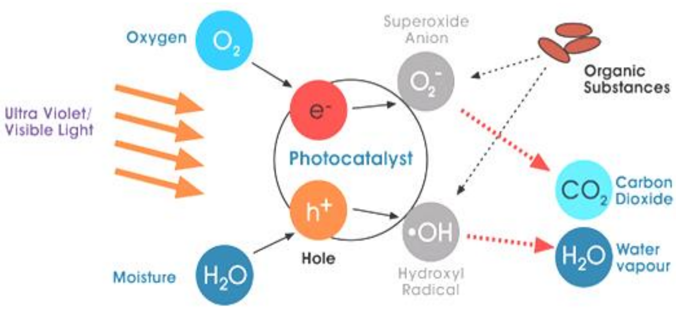

Figure 4: Reaction scheme of the photocatalysis of titanium dioxide.

III. Related work

There have been several approaches in the past, to deposit titanium dioxide. H. Gutzmann objected to produce TiO_2 layers of agglomerated and sintered ceramic titanium dioxide powders by cold spraying. The principle of cold gas spraying is based on a spray gun, which is supplied with a preheated carrier gas (MPa). Powder particles are then injected into the front chamber of the nozzle and accelerated out of the nozzle by the gas pressure. When these powder particles hit the substrate, they solidify or transfer their thermal energy to the substrate and layer formation occurs [4]. D.L. Cunha and a group of other researchers, worked on the coating of glass spheres with immobilized titanium dioxide. The aim of this process was to remove impurities in the environment. Pretreated borosilicate glass spheres (Ø 5mm) were dipped into a solution of titanium dioxide, isopropanol and nitric acid for 60 seconds by dip coating. The process was repeated twice. After subsequent drying at 80 °C (for 90 minutes) and calcination at 400 °C (for 120 minutes), tests on photocatalytic activity and SEM analysis showed that an efficient and stable TiO_2 layer was produced on the glass beads [5]. T. Tölke completed her doctorate at the Friedrich Schiller University in Jena on the subject of "Photocatalytic coating systems for highly transparent self-cleaning glass". She mentions various types of coating application, but has herself exclusively dealt with reactive DC sputtering. This process takes place in a closed chamber. A solid state target serves as cathode and by applying a DC voltage a low pressure plasma is initialized between the substrate to be coated (precondition: conductive). Sputtering releases material from the target and transports it to the substrate surface [6].

IV. Setup

The experimental setup essentially consists of a pneumatic process gas supply and the plasma gun shown in figure 3. The whole system is operated with nitrogen. The plasma ignition as well as the monitoring of current, voltage and power are controlled by a software, compatible to the plasma gun. The injection of the glass beads in powder form (borosilicate beads with a diameter of 20 µm) and the titanium containing precursor, is carried out laterally into the plasma nozzle. The supply of carrier gas, glass powder and precursor is manually controlled by magnetic valves. By applying a DC voltage of 20 kV to the cathode and anode, the carrier gas is strongly ionized, so that the plasma flame is ignited. The precursor tetraethylorthotitanate ($(C_2H_5O)_4Ti$) is finely atomized by a stainless steel bubbler and fed to the plasma flame. Due to the temperature in the hot spot (up to 10000 K) the ethyl radicals (C_2H_5) are split off, so that the TiO - groups form a bond, resulting in TiO_2 - molecules. These TiO_2 - molecules should then form a coating layer around the glass beads which are also fed into the plasma flame. The coating tube in figure 5 was used as the first prototype. The plasma gun was placed inside the tube. The glass beads fed into it could be collected in a container at the end of the tube. Due to the high temperatures inside the tube, a jacket cooling system was installed to prevent the glass beads from sticking to the inner wall of the tube.

After adaptation of the prototype, the coating process now takes place in a sealed chamber, which is connected to a suction system with an intermediate cyclone separator. This catches the glass beads and keeps the evolving ozone vapours away from the environment.

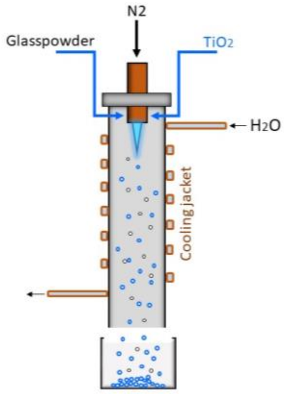

Figure 5: Schematic depiction of the coating tube.

V. Examination and Results

In order to be able to make statements about the liquid phase deposition of titanium dioxide by atmospheric plasma spraying, flat glass substrates and beads were coated. The following methods were used to analyze the chemical composition of the coating, the surface properties of the beads and the photocatalytic activity of the deposited TiO_2 layer.

A. Raman spectroscopy

Using Raman spectroscopy, the chemical components of TiO_2 (rutile and anatase), which are important for photocatalysis, could be detected in the collected glass powder. In Figure 6 the peaks characteristic for the two modification forms are illustrated in the spectrum. This proves that the deposition of TiO_2 from the liquid phase by atmospheric plasma spraying was successful.

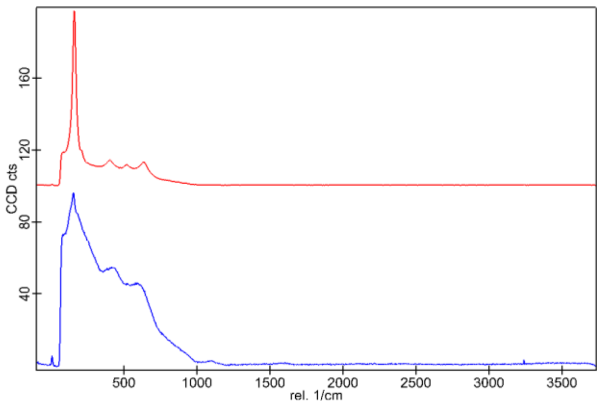

Figure 6: Raman spectra of glass beads, coated with TiO_2 (red is for anatase, blue is for rutile).

B. SEM analysis

Since Raman analysis only allows statements about the chemical composition of samples, the coated glass powder was additionally examined with a scanning electron microscope. This allowed the composition of the beads and their surface to be analysed.

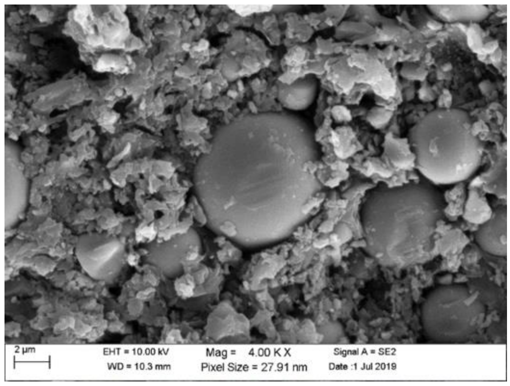

Figure 7: 2 µm image section of coated glass beads via SEM-analysis.

In addition, EDX detection (energy dispersive x-rays) was used to determine where the TiO_2 is located in the glass powder.

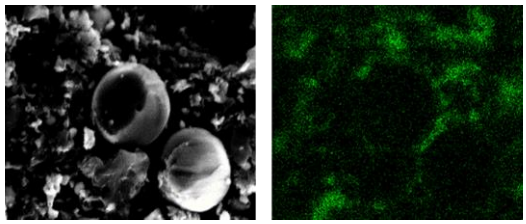

Figure 8: EDX-image of coated glass beads (the green areas correspond to titanium dioxide).

C. UV/VIS spectroscopy

To investigate the photocatalytic activity, ISO Standard 10678:2010-09 for the investigation of the photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue, was utilized. Figure 9 illustrates the experimental setup

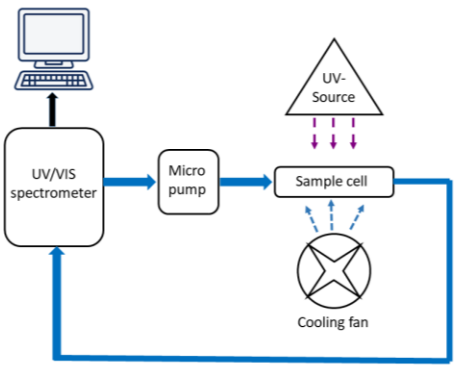

Figure 9: Experimental Setup for the analysis of the degradation of methylene blue via UV/VIS-spectroscopy.

The sample cell contains a glass carrier coated with TiO_2. The micro pump ensures a continuous flow of liquid through the assembly.The time for one cycle is 45 seconds, 100 cycles were measured each time. Due to an irradiation of the sample cell with UV/A – light (365nm) and a radiation power of at least $1mW/cm^2$, the titanium dioxide layer got activated and a photocatalysis was initialized. This was proven by the falling absorption curve in the spectrum, since the methylene blue concentration, initially 10^{-5} mol/l, decreases over time.
This simulates the decomposition of organic substances in water by photocatalysis. Figure 10 shows the decrease of the methylene blue concentration of a sample, that was irradiated with different powers, in comparison to a reference sample without a photocatalytic layer. The sample was irradiated with 1 mW/cm^2 (yellow graph), 1.5 mW/cm^2 (pink graph) and 2 mW/cm^2 (green graph). The result, when irradiated with 1 mW/cm^2 power, displays the fastest reduction of the methylene blue concentration within 630 seconds.

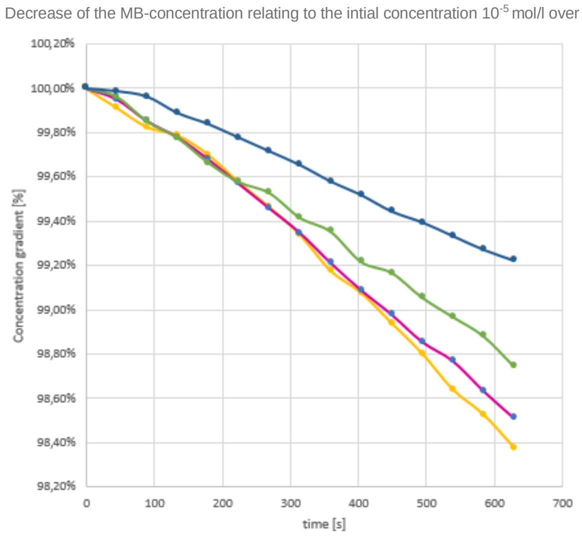

Figure 10: Decrease of the methylene blue concentration relating to the initial concentration over time; the blue graph corresponds to the reference sample.

VI. Discussion

The coating experiments thus far show, that the liquid phase deposition of titanium dioxide from a precursor is possible using atmospheric plasma spraying. However, if one looks at the results of the SEM analysis, the TiO_2 particles are located between the glass beads. A covering layer could not be generated yet. This is due to the very short contact time of the two media within the plasma jet and can possibly be improved by coating the same spheres several times. The analysis of the degradation process of methylene blue proves a faster decomposition in virtue of the photocatalytic coating, which in turn strengthens the developed process.

References

[1] BestWater,[Online],Available:https://www.bestwater.de/ratgeber/wasserfiltration-und-wasserfilter/101-warum-die-menschheit-seit-jahrtausenden-wasser-filtert, [Access on 25 05 2020].

[2] G.Yang, X. Suo, "Advanced Nanomaterials and Coatings by Thermal Spray – Multi-Dimensional Design of Micro-Nano Thermal Spray Coatings," Elsevier, p. 6, 2019.

[3] A. Markowska-Szczupak, K. Ulfig, A.W. Morawski, "The application of titanium dioxide for deactivation of bioparticulates: An overview," Science Direct, Catalysis Today 169, pp. 249 – 257, 2011.

[4] H. Gutzmann, „Kaltgasspritzen von Titandioxid - Bindungsverhalten und photokatalytische Eigenschaften,Diss.," Helmut - Schmidt - Universität / Universität der Bundeswehr, Hamburg, p. 11, 2014.

[5] D. Lopes Cunha, A. Kuznetsov, C. A. Achete, A. da Hora Machado und M. Marques, „Immobilized TiO2 on glass spheres applied to heterogeneous photocatalysis: photoactivity, leaching and regeneration process," PeerJ, p.4-7, 6 3 2018.

[6] Dipl.-Chem. Tölke, Photokatalytische Schichtsysteme für hochtransparente selbstreinigende Gläser, Diss., Jena: Friedrich-Schiller-Universität, p.27, 2009.