

# Titanium Coagulants in Water Purification and Water Treatment Processes in Additive Manufacturing

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**Abstract:** Considerable attention is paid to improving the environmental safety of additive manufacturing. Manufacturing of articles from titanium using additive technologies (powder metallurgy) is characterized by a high water consumption, and, thus, a large amount of wastewater generated. The paper presents the main trends of using titanium compounds as coagulants for the treatment of natural water (treatment to industrial water grade) and wastewater from additive manufacturing of articles from titanium. It was ascertained that in the processes of wastewater and recycled water treatment, titanium-containing coagulants are much better than the traditional coagulants based on aluminium and iron salts. Treatment of water from surface sources to industrial water grade using titanium coagulants is also highly efficient, and the residual concentrations of pollutants are on average 2.0 - 3.0 times lower than when using the traditional reagents. The use of titanium salts as coagulants allows an average 2-fold reduction of reagent consumption. Coagulation sludge (sediment) forming in the course of water treatment is titanium dioxide and can be used in future as a raw material in different industries.

**Keywords:** Water Purification, Titanium Coagulants, powder metallurgy.

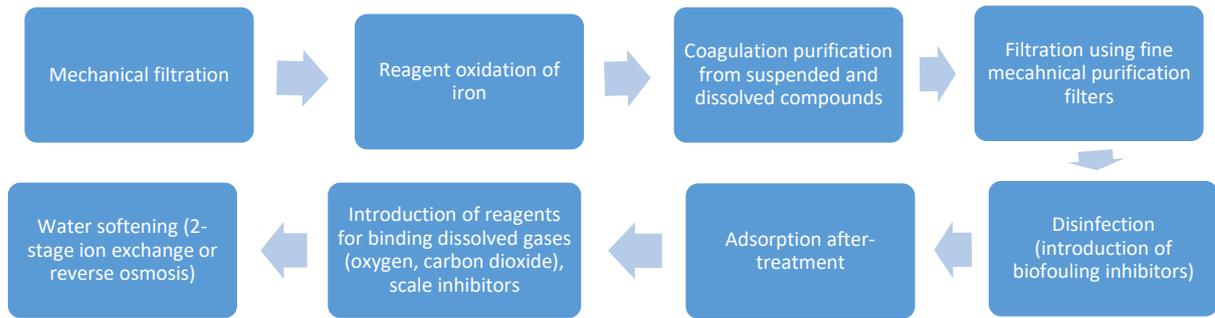
## 1. Introduction

The growing level of industrial development brings about a demand for materials with innovative properties. Currently, powder metallurgy (additive technologies) is considered as one of the most potential trends in metallurgy, which allows manufacturing the articles of complex shapes having specific properties. The demand for additive manufacturing, technologies and materials is growing each year [1, 2].

Regardless of the coating production method applied: electron beam melting of material, laser melting, etc., additive manufacturing uses clean fresh water for cooling the heating equipment and contact surfaces as well as for hydrotreating or gas purification of the surfaces of articles. In some cases, deep treated water is used when operating the units with water atomization (gas atomizer/sprayer) [3-5].

Requirements to the quality of water used in additive and metallurgical production processes are quite stringent, and treated water should have the minimum content of hardness salts, iron, chlorides and aggressive gases (oxygen, carbon dioxide) [6-8].

The general water treatment scheme for additive industry is presented in Figure 1.



**Figure 1.** Typical cooling water treatment flowchart

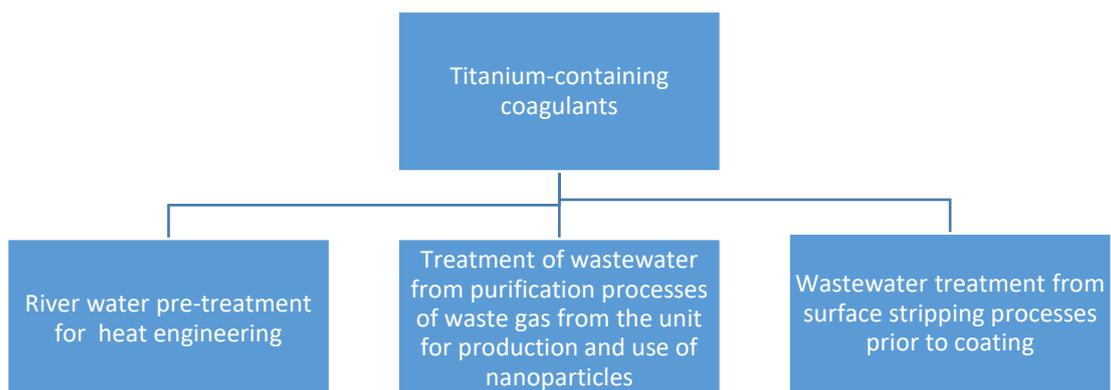
From the data in Figure 1 it is clear that water treatment is a multistage process, and it becomes possible to optimize the individual processes for increasing their efficiency and the economic efficiency of production.

Water treatment processes are, as a rule, limited to reactant treatment for reducing the content of suspended matter. That is why, increasing the efficiency of suspended matter removal is an extremely urgent task.

Commonly salts of iron (chloride) or aluminium (sulfate/oxychloride) are used for coagulation water treatment. Despite their high efficiency, these reagents have a number of significant disadvantages [9, 10].

This situation can be overcome using titanium-containing coagulants which demonstrated an extremely high efficiency (at dosages 50 – 60% lower compared to traditional coagulants) in wastewater treatment in different industries [11, 12], surface water treatment processes [13, 14], water treatment before the reverse osmosis desalination system and other water treatment processes [11, 12, 15]. Among the main advantages of titanium-containing reagents are their lower dosage, and, therefore, the minimal secondary contamination of water with coagulant ions, and a wide range of operating water pH and temperature values [11, 12].

Potential areas of using titanium-containing reagents in additive manufacturing conditions are presented in Figure 2.



**Figure 2.** Use of coagulants in processes involving additive technologies

An equally important aspect of the use of titanium-containing coagulants in wastewater treatment in additive manufacturing when working with titanium compounds is a possibility of recovering the sludge of the treatment process [16-18].

## 2. Experimental procedure

The main goal of the work is to assess the possibility of using titanium-containing reagents in water purification and water treatment processes for the needs of additive manufacturing working with titanium compounds. The choice of production is determined primarily by the similarity of the reagent for water purification/water treatment and the material used (the forming pollutants consist of 99% titanium compounds).

Coagulation efficiency was assessed on a laboratory flocculator JLT 4 (VELP) following the standard Jar-Test procedure [19, 20]. As part of the study, the effective dosage of various coagulants was selected, and residual content of pollutants in treated water was assessed.

Samples of treated water were analysed for the content of dispersed particles using a portable turbidimeter HANNA (HI 98703-02). Color index was determined using a chromium-cobalt scale on DR 2800 HACH USA spectrophotometer.

The study of elemental composition of coagulation sludge was performed on JEOL 1610LV scanning electron microscope with an energy dispersive spectrometer (point-probe analysis) SSD X-Max Inca Energy (JEOL, Japan; Oxford Instruments, UK). The phase composition was determined using DRON-3 M X-ray diffractometer.

The following coagulants were used:

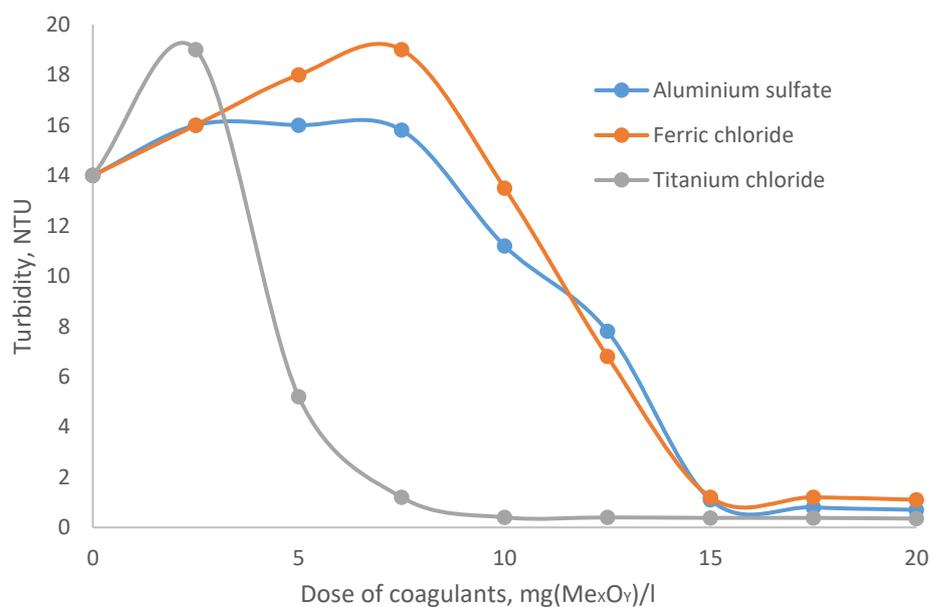
Aqueous solution of titanium tetrachloride ( $\text{TiCl}_4$ ) produced by Merck (Sigma-Aldrich)

Aqueous solution of aluminium sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ) produced by Kemira (Finland)

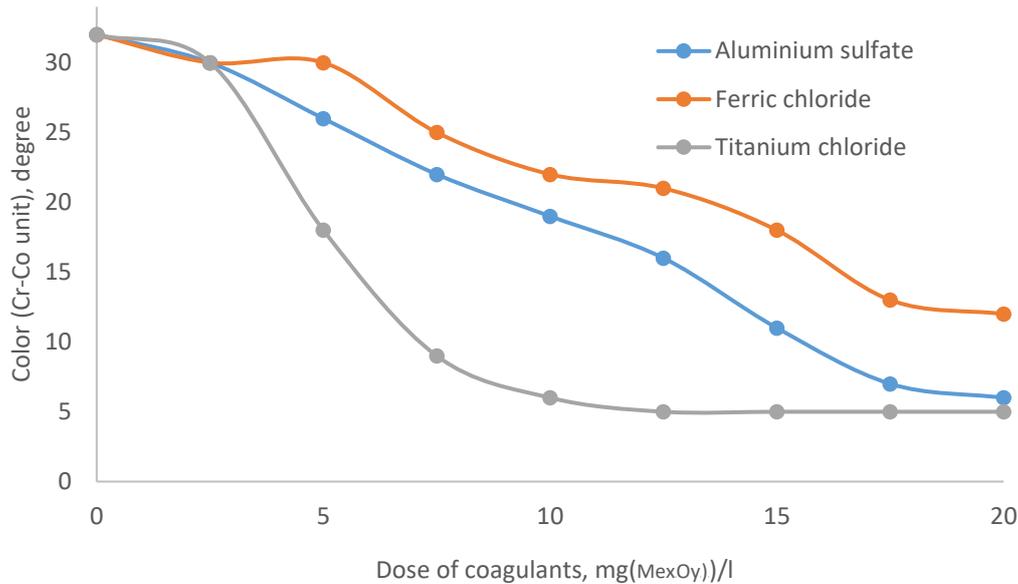
Aqueous solution of ferric chloride ( $\text{FeCl}_3$ ) produced by Kemira (Finland)

## 3. Results and discussion

At the first stage of experiments, a comparison was made of the efficiency of reducing color indices (content of dissolved organic substances) and river water turbidity. Data on comparison of treatment efficiency are presented in Figures 3 and 4.



**Figure 3.** Turbidity reduction efficiency



**Figure 4.** Color index reduction efficiency

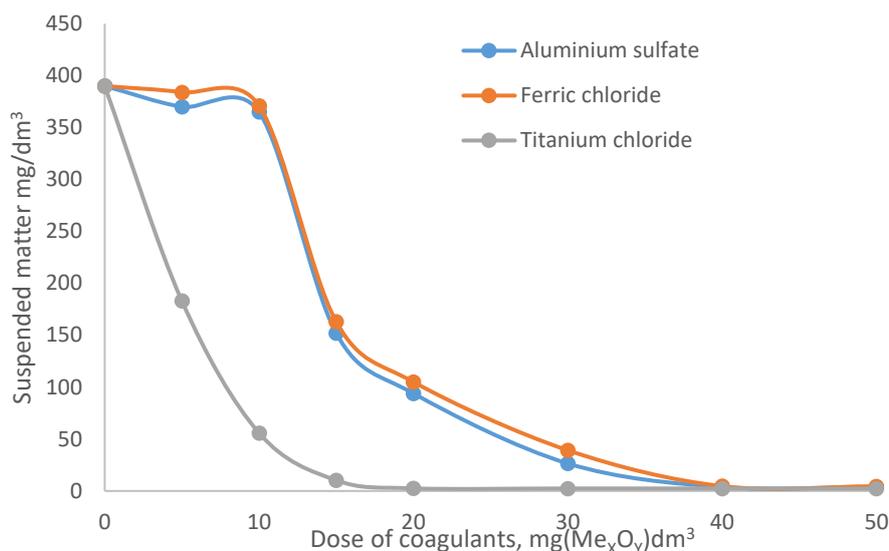
From the data in Figures 3 and 4 it is clear that titanium salts have higher efficiency than traditional reagents, while their dosage is on average 2.0 times lower ( $10 \text{ mg/dm}^3$  for titanium salts versus  $20 \text{ mg/dm}^3$  for aluminium and iron salts) than that of reagents based on aluminium and iron compounds. Residual turbidity of water treated with titanium tetrachloride was 0.38 NTU, while when using aluminium and iron salts this indicator was 0.8 NTU and 1.2 NTU, respectively. A minor increase in turbidity at the first stage of coagulation is accounted for by the specific phenomena of hydrolysis of coagulants. Residual color value when using the titanium coagulant was 1.2 times lower than that of aluminium salt and 2.0 times lower than that of iron compounds.

Decrease of residual concentrations of indicator pollutants will significantly improve the quality of recycling water and minimize the processes of abrasive wear (the influence of dispersed particles) and biofouling (dissolved organic substances).

An increased efficiency of titanium salts as a coagulant is due to its high surface charge, which is fully consistent with the Schultz-Hardy rule as well as specific hydrolysis phenomena and formation of complex products with a developed surface [21, 22].

The use of titanium salts in river water treatment processes is most preferable due to reduction in the dose of the coagulant reagent (2.0-fold) and minimization of residual concentrations of pollutants (on average 2.0 - 3.0-fold).

The next stage of experiments was evaluation of the efficiency of different reagents for treating wastewater from gas purification units in the process of production and use of titanium nanoparticles. Data on purification efficiency (residual concentrations of suspended matter) are presented in the graph (Figure 5).

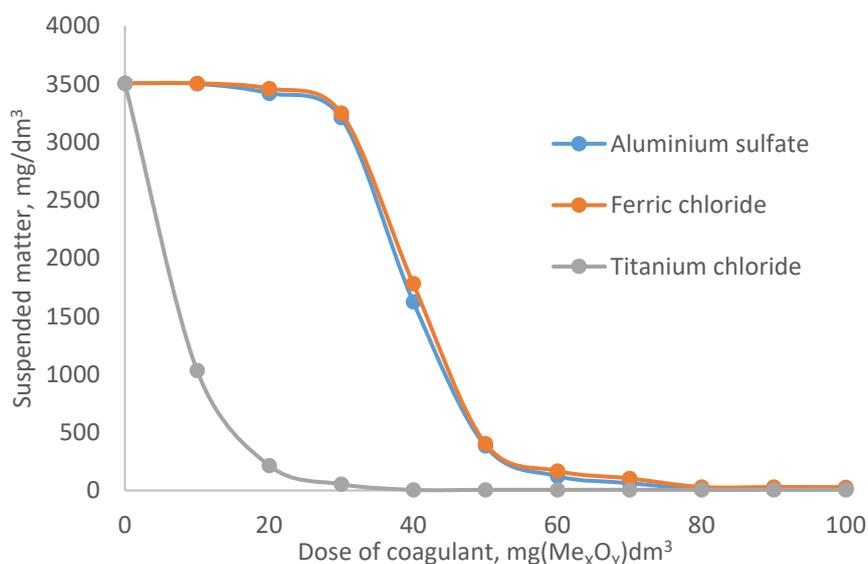


**Figure 5.** Wastewater from gas purification unit in the processes of production and use of titanium nanoparticles

From the data in graph 5 it is clear that water from gas purification process is characterized by a high content of suspended matter represented mainly by titanium nanoparticles. The efficiency of titanium tetrachloride as a coagulant was much higher than that of its analogues, and the minimum effective dose was approximately 2.0 times lower (20 mg/dm<sup>3</sup> for titanium tetrachloride versus 40 mg/dm<sup>3</sup> for aluminium and iron salts).

Treated water can be recycled in gas purification system (recirculating water supply of a wet scrubber), while the minimum content of suspended matter of 2.5 mg/dm<sup>3</sup> in water treated using titanium tetrachloride will allow reducing the abrasive wear of equipment) [23]. Residual concentrations of pollutants when using aluminium and iron salts were 3.5 mg/dm<sup>3</sup> and 4.7 mg/dm<sup>3</sup>, respectively.

At the next stage of experiments, the efficiency of different reagents was investigated on wastewater from the process of hydrotreating the surface of articles. Data on the efficiency of different reagents are presented in the graph (Figure 6).



**Figure 6.** Wastewater of hydrotreating of articles

The graph in Figure 6 clearly shows that the effective dose of titanium tetrachloride is on average 2.5 - 3.0 times lower than that of aluminium or iron salts (35 mg/dm<sup>3</sup> for TiCl<sub>4</sub> versus 80-90 mg/dm<sup>3</sup> for aluminium sulphate and ferric chloride). At the same time, residual concentration of the dispersed phase represented by highly abrasive iron compounds was minimal and amounted to 5.8 mg/dm<sup>3</sup> (28 mg/dm<sup>3</sup> for an iron-containing coagulant and 12.5 mg/dm<sup>3</sup> for an aluminium-containing coagulant).

High efficiency of titanium coagulant can be accounted for by the fact that partially hydrated iron oxides carry a positive charge on their surface, that is why their coagulation with negatively charged hydrolysis products of titanium compounds is highly intense due to electrostatic attraction of particles (charge neutralization, countercharge attraction).

The final stage of the experiments was the assessment of chemical composition forming in the process of coagulation purification of sludge and development of a concept direction for its further use. Data on the chemical composition of coagulation sludge are presented in Table 1.

**Table 1.** Chemical composition of sludge from water treatment processes

Chemical composition of sludge, wt. %	Titanium	Oxygen	Total carbon	Iron	Silicon
River water treatment					
Drying 105 °C, 12 hours	0.1	62.5	37.19	0.01	0.2
Baking 900 °C, 4 hours	21.2	34.5	0.1	2.1	42.1
Hydrocleaning of articles					
Drying 105 °C, 12 hours	0.5	29,85	-	69.65	-
Baking 900 °C, 4 hours	0.5	29.85	-	69.65	-
Gas purification of units for producing and applying nanoparticles (including a sieve)					
Drying 105 °C, 12 hours	96.3	3.7	-	-	-
Baking 900 °C, 4 hours	59.4	40.6	-	-	-

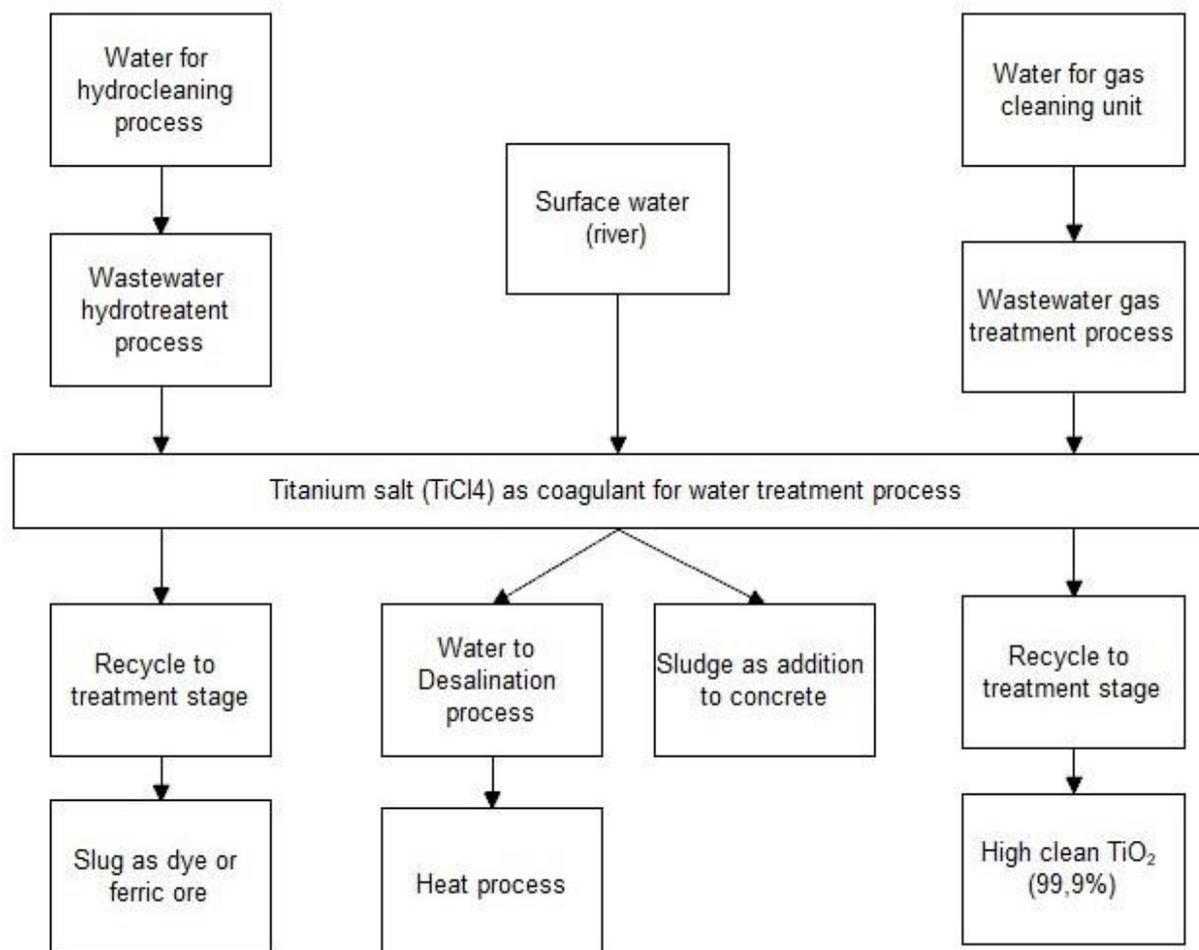
From the data in Table 1 it is clear that by its chemical composition (titanium:oxygen molar ratio), the sludge from wastewater treatment process at gas purification plants is titanium dioxide (rutile, according to X-ray diffraction data), while its purity exceeds 99%, which indicates a possibility of its processing with manufacturing of commercial products (for example, a compound for paint and varnish coatings or finishing materials) [24, 25].

Sludge from hydrotreating of articles largely consists of iron oxides. It is recommended to use this sludge after heat treatment as a raw material for the production of iron coagulants, pigments, or to transfer it to metallurgical plants as iron ore raw materials.

The chemical composition of sludge from water treatment process does not allow its use as titanium raw material, and this waste after heat treatment can be used as an additive to cement mixtures.

Reduction of the volume of waste disposal (decrease of environmental fees) as well as organization of waste recycling as secondary raw materials for different industries have pronounced environmental and economic effects [24, 25].

Based on experimental data, the main trends for using the titanium coagulants in additive manufacturing water treatment processes were formulated (Figure 7).



**Figure 7.** Additive manufacturing water balance optimization flowchart

#### 4. Conclusion

Proceeding from the data obtained as a result of the work, it was concluded that the use of coagulants based on titanium compounds offers better prospects in comparison with traditional reagents in wastewater treatment processes in additive manufacturing.

The key advantages of using titanium tetrachloride as a coagulant are a 2.0 - 3.0 fold reduction in the coagulant dose and minimization of residual concentrations of pollutants in treated water (higher treatment efficiency).

Treated water from hydrotreatment of the surface of articles and gas purification in the processes of producing and using titanium nanoparticles can be recycled to production for reuse in these processes (implementation of recycled water supply).

Natural water treated with coagulants based on titanium salts will be purified according to the traditional scheme of the plant, while the absence of iron salts in it and the minimum content of suspended matter (turbidity) and organic compounds (color index) compared to other reagents will significantly simplify and reduce the cost of further water treatment.

The use of waste from additive manufacturing wastewater treatment processes as secondary raw materials will not only reduce the volume of the waste stored (Zero Waste

concept), but also have a certain economic effect due to the use of cheaper raw materials (UN Sustainable Development Goal 12 “Responsible Consumption and Production”).

Decrease of residual concentrations of pollutants and improvement of the quality of treated/discharged water is included in the UN SDG 6 “Clean Water and Sanitation”.

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