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Efficiency of titanium salts as alternative coagulants in water and wastewater treatment: short review

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ABSTRACT

Coagulation is a fundamental process of water treatment. Its main purpose is to remove colour and turbidity from water and it plays a role in ensuring the safety of the water supply systems. It can also be an intermediate stage of industrial wastewater treatment and is usually used before applying more complex treatment methods. The protection of water resources, which will re-enter the water cycle, is of vital importance. Research conducted in recent years indicates the possibility of using coagulants containing Ti^{4+} compounds as an alternative to traditional coagulants. In addition, the use of titanium coagulants provides the opportunity to recycle reagents, as it is possible to recover titanium from the resultant sludge. A review of available literature data on the use of titanium salts in the coagulation process was carried out in the paper. The work covers both issues of water and industrial wastewater treatment. The results of tests conducted using various parameters of the coagulation process were considered. The research on the coagulation of synthetic water and river water as well as synthetic sewage and sewage from various industrial processes was collated and analyzed.

Keywords: Coagulation; Titanium coagulants; Water treatment; Wastewater treatment; Titanium tetrachloride; Flocculation

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1. Introduction

Water, due to its physicochemical properties, is a natural environment in which many physical processes and chemical reactions take place. In addition, water is a universal, readily available and cheap solvent for many inorganic and organic substances, and therefore is widely used on an industrial scale. It is also used as a refrigerant in industrial cooling systems. Due to the extensive use of water in many technological processes, it is often heavily polluted and therefore requires purification, before its re-introduction into the natural environment. Taking into account rapid social economic growth, the significance of water pollution and water scarcity remains very important and current. In addition, the demand for high quality of water is constantly increasing, resulting in significant interest from many scientists, particularly regarding the issue of the sustainable development of water resources [1–3]. To a large extent, the issues of the presence and removal of potentially harmful chemicals concern not only water, but also industrial wastewater. In the latter case, the concentrations of chemical compounds present can be very high. These problems relate to, for example, wastewater from the electroplating and electronics industries, due to the presence of heavy metal ions [4–6], and the textile industry, which uses many dyes of varying chemical structures, including toxic azo dyes, which may adversely affect aquatic organisms by preventing the penetration of light and oxygen into the deeper layers of water and thus may adversely affect the proper functioning and development of aquatic organisms [7–10]. Other examples include the coke industry which produces polluted wastewater by, for

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example, oils, tars, phenols, ammonia, thiocyanates, cyanides, sulphides and PAHs [11–13], the tanning industry [14] and many others. For both water and industrial wastewater, one of the basic technological processes used for their treatment is coagulation, in which the particles of the dispersed colloid phase form larger aggregates creating a continuous phase, with a complicated and irregular spatial structure. Coagulation is a basic process of water and industrial wastewater treatment. In addition to processes such as sedimentation and filtration, due to its simplicity and cost-effectiveness, it is widely used either as a pre- or a post-treatment step [15]. In this respect, it plays a part in ensuring the security of water supply systems. Coagulation can also be an intermediate level of industrial wastewater treatment. In this case, it is usually used before exerting more advanced methods of purification, such as: advanced oxidation processes (e.g., the Fenton method) or biological processes (e.g., use of activated sludge) [13,15]. In this aspect, coagulation has a special connection with the protection of water resources. For coagulation of impurities present in water or wastewater, coagulants containing iron(II), iron(III) and aluminum salts or a mixture thereof [15,16] are often used. Studies carried out in recent years have shown, that pre-hydrolyzed coagulants such as: polyaluminum chloride (PAC), iron(III) and aluminum chloride, polyferrous sulphate (PFS), polyferrous chloride, may in some cases be more effective than conventional coagulants [17]. Similarly, new coagulants containing titanium compounds are, under certain conditions, more effective in decreasing colour, turbidity, total suspended solids, refractive organic substances (UV_{254}), dissolved organic carbon (DOC) and chemical oxygen demand (COD) than conventional coagulants. These properties of titanium-based coagulants probably relate to different mechanisms of their action, mainly consisting of physical immobilization of colloid particles in sediments, resulting from the hydrolysis of titanium salts and their adsorption, while in the case of conventional coagulants, bridge aggregation and adsorption are the dominant mechanisms [18]. Despite the fact that their effectiveness and usefulness in water and wastewater technology is recognised, they are not common, not manufactured and they are not used on a large scale, unlike Al-based and Fe-based coagulants. Nevertheless, the results of the studies obtained [30] so far indicate that they may, at least in some cases, be a promising alternative or increase the effectiveness of currently used coagulants. In this regard, titanium coagulants can be treated as alternatives to the iron and aluminum coagulants currently used.

There is a lack of complex reviews in the technical literature to allow comparison of existing research results in this area (e.g., type of the medium, parameters of the medium before and after treatment, parameters of the coagulation process, removal efficiency of individual indicators of pollution). Therefore, the purpose of this work is to critically analyze the available literature data on titanium salts and their applicability in water and wastewater technology, taking into account technical and technological conditions. This paper will provide the most up to date research and data on titanium coagulants. It indicates future avenues of research and will enable practitioners to make more informed decisions regarding the choice of coagulant.

2. Titanium coagulants – general properties

The use of conventional coagulants, containing iron or aluminum salts, in the technology of water or industrial wastewater treatment is associated with two major challenges: (1) the toxicity of residual coagulant remaining in water after the coagulation process and (2) the quantity of precipitate produced [19,20]. While the first plays a minor role in wastewater treatment processes, it is very important when considering water intended for human consumption. The problem of the amount of sludge generated in the coagulation process is particularly important in the context of further storage, disposal or potential management opportunities. The last aspect is related to circular economy, in which special attention is paid not only to minimizing the consumption of raw materials but also to the amount of generated waste, emissions or energy losses as a result of creating so-called closed-loop processes, unlike traditional linear economy. The undoubted advantage of circular economy is the concept of using process waste as raw material in other processes to produce valuable products, which would result in a reduction of primary raw materials and the amount of unusable waste due to its composition or physicochemical properties [21]. The use of titanium salts in water and wastewater coagulation processes fits the circular economy model, because it is possible to apply a thermal treatment to the final precipitate, in order to receive the remaining titanium dioxide (TiO_2), which is impossible when using conventional coagulants [19,22]. Titanium dioxide is widely used in catalysis, photocatalysis, paint production, cosmetics and solar cells, and its electrical, optical and morphological properties make it preferable for environmental applications. In addition, the nanomaterials produced by using TiO_2 have been classified as the most promising photocatalysts, especially for environmental reclamation, such as air and water purification or hazardous waste disposal. This is mainly due to their non-toxicity, cost-effectiveness, stability and availability, as well as appropriate photocatalytic properties [23–26]. Therefore it is possible to reuse nanocrystalline TiO_2 for photocatalytic water treatment or wastewater treatment in advanced oxidation processes, in which a wide spectrum of organic compounds are chemically degraded to harmless products such as H_2O, CO_2 and inorganic ions [27]. All of this makes it possible to fulfill one of the circular economy postulates regarding the reuse of waste raw materials. In the case of titanium salts, the toxicity of the supernatant after using $TiCl_4$ as the coagulant is very low, and the residual concentration of titanium salts in treated water usually meets the World Health Organization guidelines for drinking water standards (0.5–15 μg Ti/L) [28,29]. However, as the study of water coagulation with titanium compounds indicates, the final Ti concentration in water may slightly exceed these values and amount to about 0.018 mg/L [30]. Tests of the dependence of Ti concentration in water on the coagulation pH, carried out with the use of $TiCl_4$ solutions, showed that the concentration of titanium in water after the coagulation process varies in the range of 0.007–1.200 mg/L, at pH 2–10 with application of a dose of Ti 100 mg/L [13]. In addition, titanium and its compounds are biologically inert, and therefore, water containing titanium compounds is safe, and residual concentrations greater than the maximum acceptable concentration are safe and are not a risk factor for Alzheimer's disease or hemochromatosis, as is the case (under certain conditions) when using aluminum and iron coagulants [31]. Epidemiological studies (an 8-year follow-up study) confirmed the hypothesis that Al^{3+} ions present in drinking water are a risk factor for Alzheimer's disease (adjusted relative risk of dementia 2.20, 9% confidence interval (CI) 1.23–3.34; compared with risk for Si (≥11.25 mg/L) 0.75, 95% CI 0.58–0.96). However, this risk occurs for water with an aluminum concentration above 0.1 mg/L [32]. In the case of Fe^{3+} ions (more rarely Fe^{2+}), chronic iron overload results primarily from the genetic disorder which is hemochromatosis, and iron intake of 0.4–1.0 mg/kg body weight per day is unlikely, and therefore the likelihood of negative effects in healthy people is negligible. For drinking water, the iron concentration is usually <0.3 mg/L [33]. In addition, specific odour and flavour thresholds for titanium were 4.329 and 3.332 mg/L, respectively [34]. The oral toxicity assessment allowed to classify titanium as low-order according to the toxicity classification. In addition, no cumulative mutagenesis effect was demonstrated, and a chronic toxicity study on rats showed that the maximum safe Ti concentration was 1.08 mg/L. Therefore, it is suggested that the maximum allowable concentration of Ti in drinking water may be 0.1 mg/L [34]. In addition, titanium ions (Ti^{4+}) have a higher charge value than aluminum (Al^{3+}) or iron (Fe^{2+} or Fe^{3+}) ions and therefore are better coagulating agents. When the same doses of titanium coagulant and conventional coagulants are used under identical conditions, titanium coagulant should be more effective than conventional coagulants [31]. In addition, in the case of titanium salts, Ti^{4+} hydrolysis occurs at a lower pH than in the case of Al^{3+} ions, hence fluff formation in the coagulation process can occur at a pH 3 or even lower; in the pH range of 0.5–6.0, TiO^{2+}, $TiOOH^{+}$ and TiO_2 have been reported in water after using titanium salts [31]. However, Ti^{4+} compounds undergo very fast hydrolysis in water, which is due to the fact that the coagulant cannot be distributed quickly, which causes some technical problems when using full-scale titanium coagulants in water treatment plants [31].

3. Titanium-based coagulants manufacturing

Fig. 1 presents the block diagram of titanium-based coagulant manufacturing. In this manufacturing method [35], leucoxene ore is used, which consists of mainly rutile (TiO_2) and anatase (TiO_2) and contains in total about 9% titanium dioxide (TiO_2). In the preliminary production process, a leucoxene concentrate with high quartz content (45%–50%) is formed. The concentrate also contains 2.5%–3.5% Fe_2O_3, 3%–4% Al_2O_3, as well as rare (Nb, Ta, Zr) and rare-earth (Y, Nd, Gd, Sm, Eu) elements [36]. After mechanical treatment, involving the addition of pitch, coke, and ferrosilicon, the mixture obtained is treated using chlorine gas. After the condensation process $TiCl_4$ solution is obtained, which is subjected to distillation to obtain the pure titanium tetrachloride solution. Following synthesis processes, titanium tetrachloride is produced in paste form, which is then dried to obtain a powder product. The final titanium-based coagulant consists of titanium (and aluminum originating from

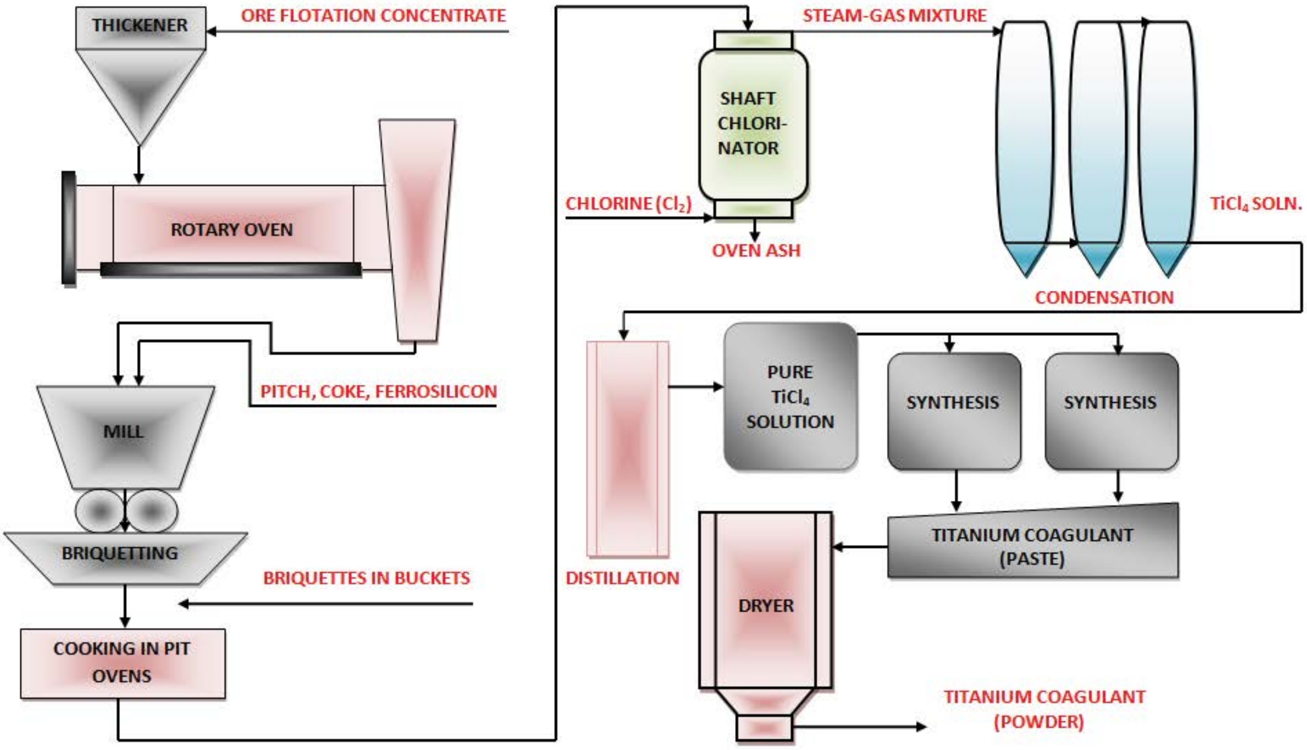

Fig. 1. Block diagram of titanium-based coagulant manufacturing (based on the study by Sittec [35]).

Al_2O_3) hydroxides, chlorides and oxyhydroxides (12 ± 2 titanium oxide) [35]. The Ti^{4+} salts (simple and polymeric) are prospective reagents for water and wastewater treatment. They show many interesting properties compared with conventional coagulants, among others: the possibility of using lower doses, lower pH dependence, biological inertness and the possibility of using at low temperatures [31].

4. Titanium coagulants in water treatment

Titanium salts may be used in the water purification process. Research is currently underway on the effectiveness of titanium chemicals in water coagulation. Table 1 illustrates the results of research measuring concentrations of Ti residues in distilled water after using titanium tetrachloride as a coagulant at various pH values. The studies using distilled water to determine the Ti concentration after the coagulation process showed that the lowest Ti concentrations were recorded at pH 4 (0.018 mg/L), pH 5 (0.007 mg/L), pH 6 (0.025 mg/L) and pH 7 (0.076 mg/L) [13]. When river water was used, the Ti concentration in the water after the coagulation process was 0.018 mg/L [30].

Table 2 presents the results of various studies on the effectiveness of titanium-based coagulants in water coagulation under different physicochemical conditions. Research was carried out on various types of water (synthetic water, river water). The list includes coagulant type, protocols of the coagulation process (usually mixing time and speed of mixing for different process phases), physicochemical parameters of water before and after treatment, and process efficiency.

In the studies, of which results are presented in Table 2, not only $TiCl_4$ was used but also polytitanium tetrachloride (PTC_0, PTC_{15}), polyferrotitanium chloride (PTFC), polytitanium silicate chloride (PTSC), polysilicate titanium salt (PST) and complex coagulants. The composition of these complex chemicals was determined by an appropriate patent, in which titanium compounds served as one of the components, in addition to the compounds Al, Si, S, Fe, Ca and Cl [30]. The protocols for coagulation used in the process were variable, but most often in the first phase the authors used rapid mixing (150–200 rpm) to accurately spread the coagulant throughout the liquid in a relatively short time (0.5–3.0 min). The second phase of the coagulation process involved slow mixing (30–40 rpm), which was required for the formation of optimum sized fluff, which required a longer time period (10–20 min). The third stage consisted of sedimentation of the formed flocs (15–30 min). The use of complex titanium coagulants was characterized by high efficiency of natural water purification in the temperature range of 3.0°C–10.5°C. The purification efficiency measured against the muddiness index was 99.4%, 98.5% and >81.8%, respectively, which corresponded to 0.1, 0.1 and <0.58 mg/L. The colour reduction efficiency (designated as the water colour index) was 61.7% and 82.8%, respectively, and the efficiency of removing organic compounds measured by changing the $KMnO_4$ index was 35.8% and 65.3%. In addition, the use of complex titanium coagulant reduced the concentration of metals in the tested water (Al, Fe and Mn) by 27.4% (residual concentration 0.098 mg/L), 89.1% (residual concentration 0.051 mg/L) and 69.4% (residual concentration 0.085 mg/L) [30]. Tests were also carried out using two polytitanium coagulants (PTC_0 vs. PTC_{15}), and the results of these tests, carried out using synthetic water, indicate the efficiency of UV_{254} and DOC removal at about 90% and 60%, respectively, with very low residual turbidity values, amounting to 1.2 and 1.8 NTU, respectively. The use of PTC_{15} for the purification of river water made it possible to achieve a reduction of UV_{254} by approx. 77%–78% (for 60 and 65 mg/L Ti), DOC by approx. 84% (for 60 mg/L Ti) with a residual turbidity of 1 NTU [37]. Thus, the use of titanium coagulants makes it possible to reduce the value of basic indicators of water pollution; however, the effectiveness of the coagulation process depends not only on the type and dose of coagulant used but also on the conditions of its application and the initial values of pollution indicators. The lowest Ti values in water, after using titanium coagulants, were within pH 4–7, which would indicate the highest efficiency of titanium salts in this pH range, however, the use of polytitanium tetrachloride indicates the possibility of obtaining higher efficiency at a pH range 8–9. Studies were also carried out on the coagulation effectiveness of PTC, polyferrotitanium chloride (PTFC) and polytitanium silicate chloride (PTSC)

Table 1
Results of determination of titanium residues in water depending on pH – own elaboration based on the study by Thomas et al. [13]

Coagulant type	Parameters of coagulation process	Physicochemical parameters of water	Final concentration of Ti in filtered water	Source
$TiCl_4$ acidified with conc. HCl Ti^{4+} conc. 100 mg/L	pH range 2–10, alkalization by using NaOH to a suitable pH value Initial Ti^{4+} conc. 100 mg/L	Distilled water pH 6.80 Conductivity 1.1 μS/cm Heavy metals (as. Pb) <0.1 μg/L	pH 2.00–1.20 mg/L pH 3.00–0.38 mg/L pH 4.000–0.018 mg/L pH 5.000–0.007 mg/L pH 6.000–0.025 mg/L pH 7.000–0.076 mg/L pH 8.00–0.22 mg/L pH 9.00–0.30 mg/L pH 10.00–0.21 mg/L	[13]

Table 2
Selected applications of titanium-based coagulants in water treatment

Coagulant type	Coagulation process protocol	Physicochemical parameters of water before treatment	Physicochemical parameters of water after treatment; process efficiency	Source
$TiCl_4$ 20%	Rapid mixing for 0.5 min at 200 rpm Slow mixing for 20 min at 40 rpm 20 min settling time Flocculation experiments at optimal dosage pH range 4–11	Synthetic water with humic acid and Kaolin Turbidity 15 ± 0.2 NTU UV_{254} 0.450 ± 0.01 cm^{-1} DOC 4.300 ± 0.5 mg/L pH 7.84–8.38	Optimum dosage 20 mg/L Turbidity removal 93.1% UV_{254} removal 98.4% DOC removal 84.3% pH 3.77 Largest floc size 801 µm	[18]
Polytitanium tetrachloride PTC_0, PTC_{15}	Rapid mixing for 1 min at 200 rpm Slow mixing for 15 min at 40 rpm 15 min settling time	Synthetic water Turbidity 4.8–5.3 NTU UV_{254} 0.331–0.344 cm^{-1} DOC 5.14–5.58 mg/L Zeta potential (–18) to (–19) mV pH 8.06–9.07 Alkalinity 50–70 mg $CaCO_3$/L	Optimum dosage 8 and 10 mg/L UV_{254} removal 80%–90% DOC removal 40%–60% Turbidity removal 66.0%–72.9% At pH 9 (optimum pH) Turbidity 66.0%–75.0% UV_{254} removal ≈ 90% DOC removal ≈ 60%	[37]
Polytitanium tetrachloride, PTC_{15}	Rapid mixing for 1 min at 200 rpm Slow mixing for 15 min at 40 rpm 15 min settling time	River water Turbidity 1.3–3.2 NTU UV_{254} 0.185–0.189 cm^{-1} DOC 7.76–9.28 mg/L Zeta potential (–15.3) to (–15.7) mV pH 7.46–8.03 Alkalinity 60–120 mg $CaCO_3$/L	Turbidity (≈1 NTU) for 30 mg Ti/L UV_{254} removal ≈ 77%–78% for 60 and 65 mg Ti/L DOC removal ≈84% for 60 mg Ti/L	[37]
Polytitanium chloride (PTC), polyferrotitanium chloride (PTFC), polytitanium silicate chloride (PTSC) prepared by using a slow alkaline titration method	Temperature 0°C, 5°C, 15°C, 20°C and 25°C pH range 3–9, in steps of 1 Basicity range of 0.5–2.5, every 0.5	Synthetic water sample Control sample and with coexisting ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, SiO_3^{2-}, $H_2PO_4^-$	Cr(VI) >90% for all tested coagulants up to pH 5 Temperature and coexisting ions with little influence on the coagulation effect Under weak acid conditions optimal removal efficiency of Cr(VI) over 95% for all tested coagulants and basicity 1.5	[38]

(Continued)

Table 2 Continued

Coagulant type	Coagulation process protocol	Physicochemical parameters of water before treatment	Physicochemical parameters of water after treatment; process efficiency	Source
Polysilicate titanium salt (PST) synthesized by using spent titanium solution and polysilicic acid (PSiA)	pH 3–12 Rapid mixing for 3 min at 200 rpm Slow mixing for 10 min at 40 rpm 30 min settling time	Sodium humate-kaolin water synthesized by sodium humate and kaolin (50 mg and 5 g, respectively, for 5 L deionized water) Turbidity 143 NTU COD 36.4 mg O_2/L pH 7.89	At pH 5, n(Ti):n(Si) 2:1 Turbidity removal 97.2% At pH 5, n(Ti):n(Si) 1:1 Turbidity removal 96.5% At pH 6, n(Ti):n(Si) 1:2 Turbidity removal 94.4%	[39]
Complex coagulant H_2O max. 7.4% Al_2O_3 max. 76.5% TiO_2 min. 10.6% SiO_2 min. 5% S, Fe, Ca, Cl, max. 0.5%	Temperature 10.5°C 15 mg/L as 20% soln. of powdered titanium coagulant	Temperature 10.5°C Water colour index 10.2° Al <0.04 mg/L Muddiness 16.1 mg/L	Muddiness removal 99.4% Al 0.06 mg/L (residue) Ti 0.018 mg/L (residue)	[30]
Complex coagulant H_2O max. 7.4% Al_2O_3 max. 76.5% TiO_2 min. 10.6% SiO_2 min. 5% S, Fe, Ca, Cl, max. 0.5%	Temperature 6°C 60 mg/L as 10% soln. of powdered coagulant Rapid mixing for 3 min at 180 rpm Slow mixing for 20 min at 40 rpm 30 min settling time	Temperature 6°C Water colour index 47° Muddiness 6.8 mg/L pH 7.79 $KMnO_4$-index 6.6 mg O_2/L	Colour removal 61.7% Muddiness removal 98.5% pH decreasing 2.2% (7.79) $KMnO_4$-index decreasing 35.8%	[30]
Complex coagulant H_2O max. 7.4% Al_2O_3 max. 76.5% TiO_2 min. 10.6% SiO_2 min. 5% S, Fe, Ca, Cl, max. 0.5%	Temperature 3°C 60 mg/L as 30% soln. of powdered coagulant Rapid mixing for 90 s at 150 rpm Slow mixing for 10 min at 30 rpm 20 min settling time	Temperature 3°C Water colour index 39.73° Muddiness 3.19 mg/L pH 7.25 $KMnO_4$-index 11.52 mg O_2/L Alkalinity 0.86 mg-eq/L Al 0.135 mg/L Fe 0.47 mg/L Mn 0.278 mg/L	Colour removal 82.8% Muddiness removal >81.8% pH decreasing 5.5% (6.85) $KMnO_4$-index decreasing 65.3% Alkalinity 30.2% Al removal 27.4% Fe removal 89.1% Mn removal 69.4%	[30]

in removing chromium(VI) from water against the control sample and in the presence of other ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, SiO_3^{2-}, $H_2PO_4^-$, using different temperature, pH and alkalinity values [38]. These studies have shown that due to the low impact of temperature and co-existing ions on the coagulation effect, polytitanium coagulants have a wider range of use than other coagulants. Studies [18] comparing titanium tetrachloride to conventional coagulants (aluminum sulphate $Al_2(SO_4)_2$, PAC, iron chloride ($FeCl_3$), PFS) showed that the use of an alternative coagulant allowed the highest removal of UV_{254} (98.4%) and DOC 84.3% (at the optimum dosage). In addition, $TiCl_4$ flocculation reduced turbidity from 15 to 1.03 NTU. The effluent pH after that process decreased to 3.77. It is important that this coagulant achieves the highest efficiency in the removal of UV_{254} and DOC, when the zeta potential was close to the isoelectric point at the optimum dosage. In alkaline conditions, this coagulant showed high and stable turbidity removal. Detailed research on flocculation [18] exhibited faster floc growth rate and larger floc size (801 μm) for the titanium coagulant compared with the previously mentioned conventional coagulants, which can reduce retention time and allows the use of compact tanks for mixing processes and sedimentation. It should be added, however, that the sludge requires careful handling due to the low recoverability of the aggregated flocs.

5. Titanium coagulants in wastewater treatment

Titanium chemicals could also be used in the treatment of various types of wastewater, as well as leachate from landfills. Table 3 presents the results of coagulation tests of synthetic wastewater, real wastewater from various industrial processes and rural domestic sewage with the use of different types of titanium-based coagulants.

The $TiCl_4$, polytitanium tetrachloride (PCT), polysilicate titanium salt (PST), $Ti(SO_4)_2$ and TiO_2-based coagulants were used for the research, and the results are presented in Table 3. Contamination coagulation processes were carried out (the same as in the case of water purification) in three stages, including rapid mixing (100–250 rpm, 1–1.5 min), slow mixing (10–40 rpm, 10–30 min) and flocs sedimentation (20–50 min). The studies were carried out using synthetic sewage, post-processing wastewater originating from experimental simulation of the underground coal gasification process, textile and coal mining wastewater, chrome tanning wastewater, rural domestic sewage and landfill leachate. Coagulated effluents were characterized by different pH values (4.0–11.8), turbidity (4.3–171.0 NTU), DOC concentrations (9, 10 and 1,954 mg/L), as well as low (61.1 mg O_2/L) and high COD values (998 and 3,050 mg O_2/L). Furthermore, in wastewater from experimental simulation of the underground coal gasification processes, a high colour value of this wastewater (3,320 mg Pt/L), TOC (910 mg/L) and the presence of phenols at a concentration of 1,360 mg/L were found. In wastewater from the textile industry, ammonia was also found in a concentration of 65 mg/L (Table 3). In synthetic sewage, a coagulant dose corresponding to 25–30 mg/L Ti, at a pH range of 3.2–3.4, reduced turbidity, DOC and UV_{254}, by 80%, 70% and 90%, respectively [41]. For wastewater from experimental simulation of the underground coal gasification processes, at pH 8.5, the turbidity removal efficiency was 90% (residual turbidity 16 NTU), colours 67.5% (residual colour 1,080 mg Pt/L), and phenols 17.3% (residual phenols 1,125 mg/L). The lowest effectiveness was found for COD and it was only 7.3%, which was associated with a decrease of this indicator from 3,050 to 2,828 mg O_2/L [13]. In real textile wastewater and synthetic textile wastewater (containing 100 mg/L reactive dye), the efficiency of colour removal was 68.0% and 98.4%, respectively and was therefore significantly higher for synthetic wastewater [42,45]. In the case of synthetic wastewater, representing biologically treated sewage effluent in a wastewater treatment plant, using $Ti(SO_4)_2$, 100% colour removal at all pH values with doses ≥50 mg/L was achieved [40]. Two coagulants, that is, PTC and $TiCl_4$, were used for coal mining wastewater treatment in optimal doses, 0.15 and 0.40 mmol/L, respectively. In the case of using PTC, the final pH value of the wastewater was much higher, than when using a $TiCl_4$ solution (pH 6.13 vs. 3.43), which was associated with the more acidic pH of the $TiCl_4$ solution and the higher dose applied. For both coagulant concentrations, similar reduction values of UV_{254} (86.0% and 85.9%, respectively) and turbidity (98.1% and 97.0%, respectively) were obtained, however, the efficiency of removing the compounds responsible for the DOC value was different and was 6.2% and 23.5% (for PTC and $TiCl_4$, respectively) [46]. Therefore, it is concluded that when using titanium or conventional coagulants, the effectiveness of removing organic pollutants, measurable by means of appropriate indicators, depends to some extent (in comparable conditions) also on the pH and total concentration of metal used as a coagulating agent. For the wastewater tested, a decrease in the pH value (pH 6.13 vs. 3.43) and an increase in the coagulant dose (0.15 vs. 0.4 mmol Ti/L) resulted in an almost four-fold increase in the efficiency of DOC removal (6.2% vs. 23.5%). The reason for significant differences in the effectiveness of DOC removal with $TiCl_4$ and PTC is probably associated with the various hydrolyzed forms of Ti found in the wastewater after the addition of coagulants. In the first case, $Ti(OH)_3^+$ and $Ti(OH)_2^{2+}$ complexes form complexes with negatively charged NMO particles and increase the efficiency of DOC removal. In the case of PTC, $Ti(OH)_3^+$ and $Ti(OH)_4^0$ complexes dominate, which results in unfavourable complexation with negatively charged NMO particles, and as a result leads to a reduction in process efficiency [37,46,48]. Floc sizes (d_{50}, μm) showed that the flocs formed in the hydrolysis process of both $TiCl_4$ and PTC are larger than the flocs obtained under the same conditions using $FeCl_3$ (843.3 and 899.5 vs. 796.2 μm), and the flow growth rate (μm/min) decreases in the order of PTC (285.3), $TiCl_4$ (219.0) and $FeCl_3$ (182.1), which allows to conclude that flocs formed as a result of Ti^{4+} hydrolysis are not only larger but also show faster growth rates than flocs as a result of Fe^{3+} hydrolysis [46]. Similar conclusions have been formulated previously [40]. These studies suggested that the floc size obtained in the processes using titanium salts is greater than using iron and aluminum salts. The particle size after flocculation with titanium salts ($TiCl_4$ and $Ti(SO_4)_2$) was in a range (17.2–176.0 μm) and (17.2–236.0 μm), respectively. The particle size after flocculation with conventional coagulants ($FeCl_3$ and $Al_2(SO_4)_3$) varied in the range of 13.9–153.0 and 5.8–73.8 μm, respectively. In the case of

Table 3
Selected applications of titanium-based coagulants in wastewater/landfill leachate treatment

Coagulant type	Coagulation process protocol	Physicochemical parameters of wastewater before treatment	Physicochemical parameters of wastewater after treatment; process efficiency	Source
$TiCl_4$ 1% soln.	Rapid mixing for 1 min Slow mixing for 30 min at 30 rpm 50 min settling time Doses 10–60 mg/L pH 4–10	Synthetic wastewater represents biologically treated sewage effluent in WTP Tannic acid 4.2 mg/L Sodium lignin sulphonate 2.4 mg/L Sodium lauryl sulphate 0.94 mg/L Arabic acid 5.0 mg/L Peptone 2.7 mg/L Beef extract 1.8 mg/L Humic acid 4.2 mg/L DOC 10 mg/L	At pH 4 and 6, optimal dose (30 mg/L)-residual turbidity ratio 0.23 At pH 8, optimal dose (40 mg/L)-residual turbidity ratio 0.24 At pH 10, optimal dose (50 mg/L)-residual turbidity ratio 0.29 At pH 4–10 minimum UV_{254} ratio 0.10–0.16 (doses 30–50 mg/L) At pH 4 and 6; minimum colour ratio 0.04 At pH 8 colour ratio 0.1 at dose 40 mg/L	[40]
$TiCl_4$ 10% soln.	Rapid mixing for 1 min at 100 rpm Slow mixing for 25 min at 10 rpm Settling time 45 min	Synthetic wastewater pH 6.8–7.2 Turbidity 4.3–4.5 NTU DOC 9–10 mg/L UV_{254} 2.90–3.10 cm^{-1}	At pH 3.2–3.4 with 25–30 mg Ti/L Turbidity removal 80% DOC removal 70% UV_{254} removal 90%	[41]
$TiCl_4$ 20% soln. in HCl	100 mg/L Ti^{4+} Rapid mixing for 1 min at 100 rpm Slow mixing for 10 min at 20 rpm Settling time 30 min	Synthetic wastewater (100 mg/L reactive dye), initial colour intensity measured at wavelength 380 nm was 1.245 Real textile wastewater (water from Citarum River, contaminated by the textile wastewater)	For synthetic wastewater: TSS removal 34.1% Colour removal 98.4% For real textile wastewater: TSS removal 34.1%	[42]
$TiCl_4$ 1.197 mol/L soln. in HCl	Rapid mixing at 250 rpm 200 mg/L Ti^{4+} pH 6.5, 7.5, 8.5 and 9.5 4 mL/L 0.025% anionic flocculant Filtering	Post-processing wastewater originating from the underground coal gasification process pH 7.5 Conductivity at 20°C 4,180 µS/cm UV_{254} (1:40) 0.437 Turbidity 171 NTU Colour 3,320 mg Pt/L COD 3.050 mg O_2/L TOC 910 mg/L Phenols 1.360 mg/L	At pH 8.5 UV_{254} (1:40) removal 32.0% Phenol removal 17.3% COD removal 7.3% Colour removal 67.5% Turbidity removal 90.6%	[13]
$TiCl_4$ 1,728 mg/L	pH 6 Dosage 600 mg/L	Landfill leachate Colour 4,253 mg Pt/L TSS 330 mg/L Ammonia 4.4 mg/L UV_{254} 0.017 cm^{-1}	At the optimal conditions: Colour removal 81.4% TSS removal 86.7% Ammonia removal 58.4% UV_{254} removal 76.5%	[43]

$TiCl_4$ soln.	10–60 mg/L pH 6.0–8.5 at presence of Na^+, Ca^{2+}, Mg^{2+}	Synthetic turbid wastewater containing *E. coli*	Turbidity removal 96.96% *E. coli* removal 4.69 log *E. coli* removal 4.85 log pH 8.5	[44]
$TiCl_4$ soln. in HCl	pH 6 300 mg/L Ti^{4+} Rapid mixing for 1 min at 250 rpm Slow mixing for 20 min at 30 rpm Settling time 30 min	Textile wastewater pH 11.8 COD 998 mg O_2/L Turbidity 159 NTU Colour 1,020 mg Pt/L TSS 540 mg/L Ammonia 65 mg/L	COD removal 28% Turbidity removal 97% Colour removal 68% TSS removal 98% Ammonia removal 28%	[45]
Polytitanium tetrachloride (PTC) and $TiCl_4$, 20% soln.	Rapid mixing for 1.5 min at 200 rpm Slow mixing for 20 min at 40 rpm Settling time 20 min.	Coal mining wastewater Turbidity 44.7 NTU Zeta potential –30.9 mV UV_{254} 0.281 cm^{-1} pH 7.34 DOC 1,954 mg/L	At the optimal dose of PTC (0.15 mmol/L): pH 6.13 Turbidity removal 98.1% UV_{254} removal 86.0% DOC removal 6.2% At the optimal dose of $TiCl_4$ (0.4 mmol/L): pH 3.43 Turbidity removal 97.0% UV_{254} removal 85.9% DOC removal 23.5%	[46]
Polysilicate titanium salt (PST) synthesized by using spent titanium solution and polysilicic acid (PSiA)	pH 3–12 Rapid mixing for 3 min at 200 rpm Slow mixing for 10 min at 40 rpm Settling time 30 min	Rural domestic wastewater collected from the Dianchi valley Turbidity 126 NTU COD 61.1 mg O_2/L pH 7.13	At pH 5, n(Ti):n(Si) 2:1 Turbidity removal 87.3% At pH 5, n(Ti):n(Si) 1:1 Turbidity removal 88.9% At pH 6, n(Ti):n(Si) 1:2 Turbidity removal 88.1%	[39]
$Ti(SO_4)_2$ 1% soln.	Rapid mixing for 1 min Slow mixing for 30 min at 30 rpm Settling time 50 min Doses 10–60 mg/L pH range 4–10	Synthetic wastewater represents biologically treated sewage effluent in WTP Tannic acid (4.2 mg/L) Sodium lignin sulphonate (2.4 mg/L) Sodium lauryl sulphate (0.94 mg/L) Arabic acid (5.0 mg/L) Peptone (2.7 mg/L) Beef extract (1.8 mg/L) Humic acid (4.2 mg/L) Initial DOC 10 mg/L	At pH 4 and 6, at the optimal dose 40 and 50 mg/L Residual turbidity ratio 0.27 At pH 8, at the optimal dose 50 mg/L Residual turbidity ratio 0.29 At pH 10, at the optimal dose (60 mg/L) Residual turbidity ratio 0.29 Minimum UV_{254} ratio 0.10–0.12 At pH 4–10 with doses ≥50 mg/L Removal of colour 100%	[40]
TiO_2-based coagulant	40 mg/L TiO_2-based coagulant Rapid mixing for 1 min at 200 rpm Slow mixing for 15 min at 40 rpm	Chrome tanning wastewater pH 10.4 Cr(III) 15.5 mg/L Turbidity 45.7 NTU	Cr(III) removal 74.2% Turbidity removal 96.8% pH 9.48	[47]

TSS: total suspended solids; COD: chemical oxygen demand.

titanium coagulants, the low effluent pH and fast hydrolysis limit the wide application of titanium salts. The prehydrolysis process in some cases can improve the coagulation efficiency, but narrow applicable dose and pH range remains problematic from a technological point of view. To avoid this, new formulations such as titanium-based xerogel (TXC) by using the sol–gel method are being developed. TXC compared with $TiCl_4$, PTC and PFS creates larger flocs that have better settling properties; also TXC offers a wider applicable coagulant dose/pH range. Additionally, corrosion problems can be avoided because pH value during coagulation does not significantly reduce. Moreover, TXC exhibited good coagulation performance for real wastewater, especially for low turbidity wastewater [49]. Additionally, the obtained results show that through the use of a Ti-based composition a much better degree of treatment could be achieved (even in complicated conditions), and an effective dose of Ti-based coagulant is several times less, than the necessary dose of Al-based coagulant. Therefore, because of lower dosage, the pH decrease is much less in the case of a Ti-based coagulant which can be applied to water with low alkalinity without the need to add lime [31]. Other studies have shown that titanium coagulants are valuable in treating water with alkalinity between pH 7 and 9, when aluminum sulphate is ineffective [50]. Therefore, it is possible to avoid lowering the pH value of water to some extent due to the use of lower doses of titanium-based coagulants. It is clear that in the case of industrial wastewater treatment, the problem of lowering pH is not very important because the wastewater usually requires pH correction, for example, to remove heavy metals [5]. The application of PTC solutions with different basicity values (i.e., OH/Ti molar ratio), prepared using a slow alkaline titration method, indicated that the water pH after PTC coagulation was significantly improved towards neutral pH [37]. The addition of chitosan to the titanium salts indicated the ability of chitosan foils to bridge the neutralized wastewater particles. For this reason, the use of low doses of Ti salt with chitosan was possible and had a positive impact on flocculation pH and resulted in 40% of Ti sludge reduction [41]. Titanium coagulants based on nano-encapsulation of titanium salts help obtain much better results than in the case of traditional coagulants, even under extreme conditions. They counteract the main disadvantages of titanium salts and titanium dioxide [31]. Thus, the apparent disadvantages of titanium coagulants can be eliminated at the stage of their development and chemical synthesis. Additionally, the mutual quantitative ratios of titanium and silicon in titanium coagulants (e.g., in polysilicate titanium salt, PST) play very important roles in terms of molecular structure stability and properties. In the case of PST, the Ti/Si molar ratio strongly determines its morphology and surface structure. The PST has a tendency to be a one-dimensional linear or two-dimensional sheet shape (when Ti content increases) or a three-dimensional spherical shape with larger secondary spherical particles (when Ti content reduces). The analysis of the variation in absorption peaks (FT-IR results) of PST shows that the intensities of both Si–O–Si and Ti–O–Si bonds experience rising process and then falling process when Ti content in compound increases. The polymerization of the titanium coagulants (PST in this case) can be strengthened and then weakened. Also, the variation of Ti–O–Ti and Si–O absorption peaks indicates that the inhibition of hydrolysis can be strengthened and then weakened as well [39]. The presented dependencies indicate that the regulation of the mutual quantitative ratios between Ti and Si enables the design of specific coagulant properties, for example, stability, the rate of hydrolysis and efficiency in removal of undesirable compounds from water and wastewater. In the case of PST, the excellent performances were attributed to the special structure, which has a large number of stable Si–O–Ti bonds [39]. The conventional coagulants (Fe and Al-salts) are widely used because of their price and effectiveness even though ferric salts generate a large volume of chemical sludge. However, titanium-based coagulants offer a more attractive and cost-effective solution to the sludge disposal approach. The early study on titanium tetrachloride showed that a medium-size wastewater treatment plant (25,000 m^3/d) could produce an average of 446.5 kg TiO_2 photocatalysts per day and the performance of recycled TiO_2 was found to be higher than the commercially available TiO_2 [19,51].

6. Conclusions

Both natural waters and wastewater (especially industrial) contain many inorganic and organic chemical compounds, with different physicochemical properties and toxicity to aquatic organisms, and therefore they must undergo many purification processes before they are intended for human and for industrial purposes or introduction into the environment (treated wastewater). These processes use the phenomenon of coagulation, which uses many types of conventional coagulants containing mainly Fe^{2+}, Fe^{3+} and Al^{3+} salts. The research carried out in recent years indicates that coagulants containing Ti^{4+} compounds may be an alternative to conventional coagulants. The use of titanium coagulants provides the benefits of circular economy, because it is possible to recover TiO_2 from sludge generated in coagulation processes by using titanium compounds. The benefits of titanium coagulants are their low toxicity, low residual concentration in water, high Ti concentration values for taste and smell thresholds and the maximum allowable concentration in drinking water suggested by some authors (not higher than 0.1 mg/L), but the concentration is usually lower (using, among other things, the appropriate pH value and dose of Ti^{4+}). Titanium coagulants in the form of titanium chloride, as well as products containing Ti(IV) compounds, were used to treat water (including river water), synthetic wastewater, textile wastewater, wastewater from underground coal gasification processes and coal mining wastewater. In addition, application at low temperatures (even 3°C) is possible. Furthermore, these coagulants were characterized by a high efficiency of reducing water or wastewater parameters (e.g., colour, turbidity, UV_{254}, etc.), and the residual Ti concentration (also dependent on the initial Ti concentration used for coagulation of impurities) in the appropriate process conditions was low (0.007–0.076 mg/L at pH 4–7 (starting dose 100 mg Ti/L)) and 0.018 mg/L (starting dose 15 mg Ti/L) for coagulation of river water. Therefore, titanium coagulants can be an alternative to commonly used iron and aluminum coagulants; however, it is necessary to take appropriate action to introduce legal regulations regarding the maximum residual Ti concentration in drinking water and quality guidelines for titanium coagulants, including limit values of physicochemical parameters, especially those regarding permissible concentrations of pollutants, as well as methods of their determination, as is the case with aluminum coagulants. Despite many benefits of titanium-based coagulants, the amount of published research is still low. For instance, there is a lack of research on the effectiveness of titanium coagulants used for the treatment of different municipal wastewater and/or industrial wastewater, that is, electroplating, cosmetic and tannery wastewater. In the scientific literature, despite references to the production and application of titanium coagulants, there is little in-depth economic analysis of their use for various wastewater treatment plants and their availability, in the context of highly used, commonly available and affordable conventional coagulants. In fact, titanium-based coagulants in some cases show higher efficiency than conventional coagulants but their wider application requires more research. Based on the analysis of the presented research, it can be concluded that current research is not carried out systematically, on media with different initial parameters, and moreover the parameters of the coagulation processes are different. In addition, the number of tests on real water samples is still insufficient. Therefore, there is a need for a systematic approach on the effectiveness of titanium coagulants. It would be highly recommended to develop an extensive research program on these type of coagulants.

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