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Granulometric analysis of TiO_2 particles in the aspect of membrane filtration

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ABSTRACT

The paper presents a granulometric analysis of the size of particles of Aeroxide® P25 and P90 titanium oxides in the context of their retention in low-pressure membrane processes (microfiltration, ultrafiltration). Measurements of the particle size using a laser granulometer showed that the particle size of TiO_2 Aeroxide® P25 dispersed in water is in the range from approx. 0.3 μm to approx. 150 μm. The particles with dimensions smaller than 1.0 μm constituted about 7.0%, and the largest particles, with dimensions above 30 μm, constituted about 0.9% of the volume of all the particles in the suspension, respectively. In the case of TiO_2 Aeroxide® P90, a double curve of grain size distribution was observed. For the main curve, the particle size ranged from approx. 0.3 μm to approx. 18.7 μm. The particles with dimensions smaller than 1.0 μm constituted approx. 3.0% by volume of all particles in the sample. The second curve, which can be described as oversized/supersized grains, was comprised of particles ranging in size from about 21 to 170 μm, and they accounted approximately for 3.9% by volume of the total particles in the sample. The specific surface area for the samples was 0.56 m^2/g for TiO_2 P25 and 0.48 m^2/g for TiO_2 P90. It was found that the observed large particle sizes of titanium oxide particles in aqueous solutions may be the result of their agglomeration, which gives one hundred percent certainty that they will be retained by ultrafiltration and microfiltration membranes with pore sizes above 0.3 μm.

Keywords: Titanium(IV) oxide; Particle size; Microfiltration; Ultrafiltration

1. Introduction

Titanium oxide is a nanomaterial widely used in environmental engineering. Among other things, it is widely used as a photocatalyst in heterogeneous oxidation processes (photocatalysis) because it is characterized by high photocatalytic activity and remains stable in repeated catalytic cycles, while being an environmentally friendly substance [1]. These properties of titanium oxide make it possible to use it in water treatment and wastewater treatment. In the scientific literature, one can find many works on this subject, for example for the degradation of pharmaceutical drugs [2,3], pesticides [4], humic substances [5–7] etc.

An interesting option in water treatment are membrane photocatalytic reactors, in which titanium oxide is used in the form of a suspension and is being continuously separated from the treated water using membranes, in particular microfiltration and ultrafiltration.

In the own research [6,7] and in other scientific works [8,9] it was emphasized that titanium oxide is completely retained by microfiltration membranes, despite the fact the average size of TiO_2 particles is about 25 nm (given by the producer [10]), which is much smaller than pore size of microfiltration membranes (the smallest pores are approx. 0.1 μm).

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As a result, research was undertaken, the purpose of which was to perform granulometric characteristics of two titanium oxide powders with different specific surface areas and to analyze the obtained test results in terms of separation of titanium oxide particles by micro and ultrafiltration membranes.

2. Materials and methods

2.1. TiO_2 powders

Two titanium dioxide powders with symbols P25 and P90 from Evonik Degussa GmbH (Germany) were used in the tests. The characteristics of TiO_2 powders given by the producer are shown in Table 1.

2.2. Scanning electron microscopy analysis

Scanning electron microscopy (SEM) images were obtained using a high-resolution scanning electron microscope SEM Supra 35 by ZEISS (Germany); parameters such as secondary electron detection (SE) at an acceleration voltage of 20 kV and a maximum magnification of 20,000× were applied.

2.3. Methodology of granulometric analysis

To measure sizes of particles the laser diffraction particle size analyzer Mastersizer 2000 (Malvern Instruments Ltd., UK) equipped with a standard dispersion units Hydro 2000MU was used. The measuring range of the analyzer is between 0.02 and 2,000 μm. The instrument uses two laser lights: red and blue one. The measuring technique is based on the laser diffraction phenomenon (LALLS – low angle laser light scattering [11]). The laser beam which passes through a sample is scattered by particles dispersed in solution. Determination of particles sizes is an indirect result of the calculation of their volume. The instrument provides results as particle size distribution which illustrated percentage share of particles with equivalent diameter in relation to the total volume of all particles in the sample (by volume) [11–13]. The equivalent diameter is defined as the diameter of the sphere with the same volume as the measured particle. The measurements were taken with following settings: particle = titanium dioxide, refractive index = 2.741, absorption index = 0.1; dispersant = water, refractive index = 1.330; analysis model = general purpose; sensitivity = normal. Measurement time for each laser light (red and blue) equaled 5 s, whereas single measurement took in total approximately 16 s. 6 measurements were taken for each sample.

In addition to the particle size distribution, characteristic values such as d_{10}, d_{50} and d_{90} were calculated, as well as the largest and smallest particles observed during the measurement. The characteristic values (d_{10}, d_{50}, d_{90}) are defined as: d_{10} – particles of this and smaller diameters constituting 10% of the total volume (mass) of all particles in the sample, d_{50} (average particle size) - particles of this and smaller diameters constituting 50% of the total volume of all particles in the sample and d_{90} - particles of this and smaller diameters constituting 90% of the total volume of all particles in the sample. Water was constantly circulating in the granulometer measuring cell. The study was carried out using a standard dispersion units Hydro 2000MU integrated with mixing system and an built-in ultrasonic probe to aid breaking agglomerates up.

The mixing system consisted of 1 L glass beaker and automatic stirrer (with adjustable stirring speed) connected with centrifugal pump which role is to deliver a sample to the analyzer. After passing the measuring cell the sample went back to the beaker (water with resin suspension was flowing in the closed circuit). In order to conduct the measurements a small sample volume was added to about 0.7 L of water and mixed at 2,000 rpm. The measurement was started approximately 1 min after the sample was introduced. After the measurement the sample was sonicated for 2 min to break up agglomerates, and the measurements were repeated.

Each time the term dimension or size of particles is mentioned in this study, it means the equivalent diameter of the particles which value is the average of the measurement interval with the range of approximately ±7% of given value.

3. Results and discussion

3.1. SEM analysis TiO_2 particles

The vast majority of single TiO_2 grains visible in the SEM images have relatively regular, spherical shapes (Fig. 1). Single nanoparticles have the following diameters: for Aeroxide® P25 from 18 to 49 nm (Fig. 1A), and for Aeroxide® P90 from 18 to 39 nm (Fig. 1B), while both materials are dominated by grains with a diameter of 23–29 nm (although this is quite a subjective assessment). The particles visible in the SEM images seem to form agglomerates, but it cannot be ruled out that they are only loose clusters of unstable primary nanoparticles. It is also impossible to determine on the basis of SEM images the size of possible agglomerates, as it is difficult to ascertain whether the observed structures are stable homogeneous agglomerates, or whether they

Table 1
Characteristics of TiO_2 P25 and P90 [10]

Properties	Aeroxide® TiO_2 P25	Aeroxide® TiO_2 P90
Specific surface area (BET)	50 ± 15 m^2/g	90 ± 20 m^2/g
pH-value in 4% dispersion	3.2–4.5	3.2–4.5
Tamped density (acc. to DIN EN ISO 787/11 Aug. 1983)	100–180 g/L	Approx. 120 g/L
Crystal structure	88% anatase, 12% rutile	86% anatase, 14% rutile
Crystal size	16 nm anatase, 18 nm rutile	12 nm anatase, 18 nm rutile
Isoelectric point (pHIEP)	6.4	6.6

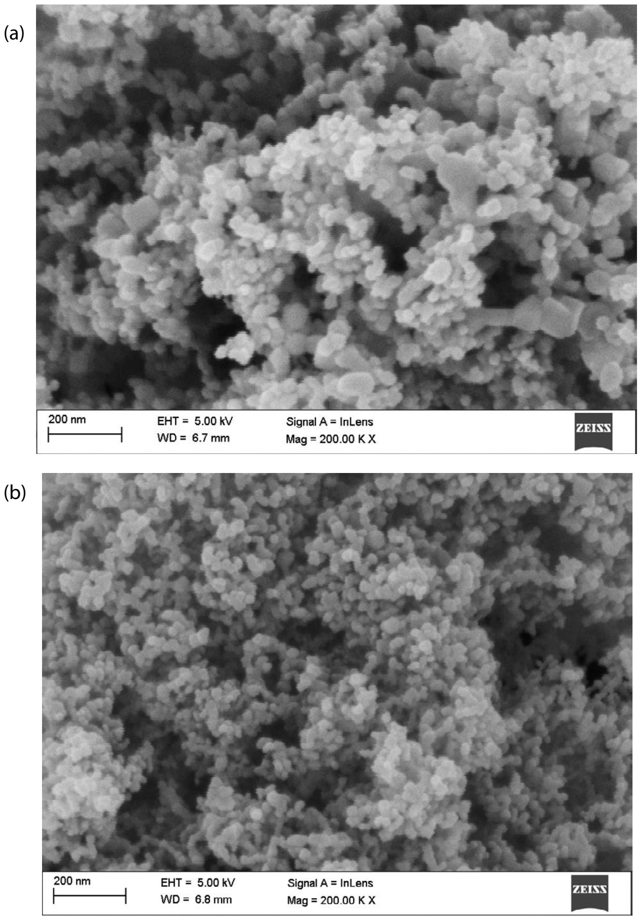

Fig. 1. Scanning electron microscopy images of Aeroxide® P25 (A) and Aeroxide® P90 (B) titanium dioxide fresh material particles.

are only smaller particles touching each other, or overlapping images of smaller particles. The stability of the visible agglomerates cannot be assessed on the basis of the SEM images either. It cannot be ruled out that after introduction into water and vigorous stirring, the visible structures will break down into smaller particles or individual nanoparticles.

The agglomerates visible in the SEM images have irregular shapes and a very expanded and complex morphology. Clumped spherical nanoparticles create porous structures with an extended surface.

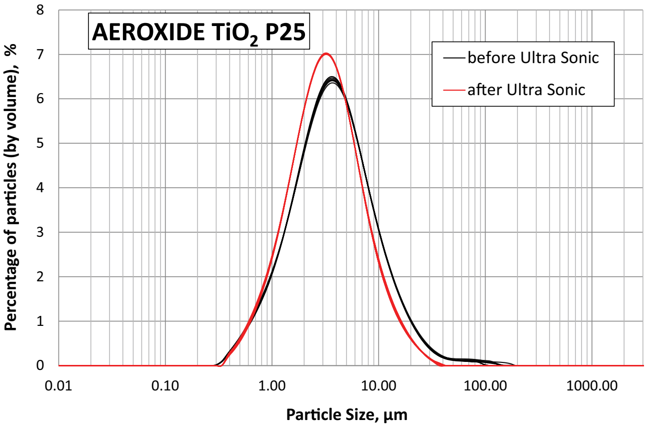

Fig. 2. Particle size of Aeroxide® P25 titanium dioxide suspension in water.

Table 2
Characteristic dimensions of TiO_2 suspension particles - Aeroxide® P25 and P90

	Substitute diameter (µm)					SSA[a]
	d_{min}	d_{max}	d_{10}	d_{50}	d_{90}	m²/g
TiO_2 - Aeroxide® P25						
	0.29	170.2	1.2	3.7	11.7	0.56
After US	0.34	37.2	1.1	3.2	8.9	0.61
TiO_2 - Aeroxide® P90						
	0.30	170.2	1.6	3.6	8.2	0.48
After US	0.45	257.6	1.4	3.1	7.4	0.55
TiO_2 - Aeroxide® P90 (without super-grain)						
	0.30	18.7	1.6	3.4	7.2	0.50
After US	0.45	18.7	1.3	3.0	6.2	0.58

[a] Specific surface area calculated for the spherical particle and density model 4.26 g/mL [14].

3.2. Granulometric analysis TiO_2 Aeroxide® P25

Measurements of the particle size with the use of a laser granulator showed that the particle size of Aeroxide® P25 titanium dioxide dispersed in water ranges from about 0.3 µm to about 170 µm (Fig. 2). Characteristic dimensions were respectively d_{10} approx. 1.2 µm, d_{50} approx. 3.7 µm, and d_{90} approx. 11.7 µm (Table 2). The particles with dimensions smaller than 1.0 µm constituted approx. 6.7% (by volume) of all the particles in the suspension. On the other hand, the smallest particles, with dimensions below 0.5 µm, constituted about 0.8% by volume of all particles in the suspension. The largest particles, with dimensions above 30 µm, constituted about 0.9% of all particles by volume. Particles with sizes larger than 50 µm accounted for about 0.35%, which means that they were single particles only (e.g., for one particle with an equivalent diameter of 50 µm, there are approx. 125 thousand particles with a diameter of 1 µm, with the same total volume).

The 2-min ultrasound treatment of the suspension resulted in relatively small changes in the particle size distribution. The particle size distribution curve has shifted slightly to the left (towards smaller particles), with larger particles being shifted more than the smallest particles. The d_{90} dimension has decreased by about 23.4%, the average particle size has decreased by about 13.5% and the smallest particle size, the d_{10} dimension has decreased by about 3.9% only. Mainly there have "disappeared" particles larger than 40 µm. This indicates that the particles with a size greater than 40 µm were created by agglomeration of smaller particles by relatively weak forces. Despite the disintegration of the particles, no particles smaller than the smallest particles (approx. 0.3 μm) observed in the suspension not subjected to the ultrasound effect appeared in the suspension. This means that the agglomerates were relatively stable, and the decomposition concerned mainly the largest particles, and the smallest particles did not disintegrate at all.

3.3. Granulometric analysis TiO_2 Aeroxide® P90

In the case of Aeroxide® P90 dispersed in water, a double grain size distribution curve was observed. For the main curve, the grain size ranged from about 0.3 μm to about 18.7 μm (Fig. 3). The second curve, which can be described as oversize, was about 21 to 170 μm in size, with the amount of oversize being about 3.9% by volume of all particles in the sample. For the main particle size distribution curve, the characteristic dimensions were respectively d_{10} approx. 1.6 μm, d_{50} approx. 3.4 μm, and d_{90} approx. 7.2 μm (Table 2). The particles with dimensions smaller than 1.0 μm constituted approx. 1.8% (by volume) of all particles in the sample. The particles larger than 50 μm accounted for about 2.1%.

2-min sonication of Aeroxide® P90 suspension, as with Aeroxide® P25, resulted in relatively little change in particle size distribution. The particle size distribution curve shifted slightly to the left, and, unlike P25, the shift was similar to all particles in the suspension smaller than 19–20 μm. Probably the difference was due to the fact that the P90 suspension had fewer most stable particles with the smallest size (less than 1.0 μm). Overall, for the main distribution curve, the average particle size was reduced by about 14.5%. As in the case of P25, no particles smaller than the smallest particles (approx. 0.3 μm) observed in the suspension not subjected to ultrasound influence appeared in the P90 suspension. On the other hand, in contrast to P25, in the case of P90 after the application of ultrasound, the super-grain distribution curve (particles larger than 20 μm) practically did not change, which means that the largest particles were relatively stable grains or it was a contamination of the sample with another material.

The particle size distributions of Aeroxide® P25 and Aeroxide® P90 are different (Fig. 4). Although both materials are dominated by particles with sizes 3.0–4.0 μm, significant differences can be seen in the ranges of the smallest and the largest particles. In the P90 material, there are definitely fewer particles smaller than 1.0 μm. In the P25 material, particles with dimensions smaller than 1.0 μm constitute by volume approx. 6.7% of the total particles, while in the P90 material, such particles constitute only approx. 1.8%. In both materials, the smallest observed particles are about 0.3 μm, however in the case of the P90 material, the particles smaller than 0.5 μm are only 0.3%, while in the P25 material they account for about 0.8% of all particles in suspension.

For both P25 and P90, particles larger than 20 μm are observed, but for P25 the curve is homogeneous over the entire particle size range, while for P90 the particle size distribution consists of two curves for particles smaller than and larger than 20 μm. Moreover, in the P25 material, the largest particles, with a size greater than 40 μm, disintegrated after the application of ultrasound (which indicates that they were TiO_2 agglomerates), while for P90, the ultrasounds did not break the particles with a size range of 20–200 μm.

The fact, that for Aeroxide® P90 particles larger than 20 μm form a separate curve, as well as that they are more durable than the others (they did not break down when exposed to the ultrasound suspension), may indicate that these are separate particles with different properties and thus it cannot be ruled out that it is a contamination with another material.

The large particle sizes of TiO_2 Aeroxide® P25 and Aeroxide® P90 (Table 2) observed in aqueous solutions, much larger than the size of nanoparticles declared by the manufacturer, may be the result of their agglomeration. This agglomeration could take place in an aqueous environment or earlier, during storage of the material in a dry form. Many authors indicate the agglomeration of TiO_2 in aqueous solutions [15,16]. At the same time, it is indicated that the rate of agglomeration may depend on the composition of water, including the concentration and type of electrolytes dissolved in water [15]. The presence of Ca^{2+} divalent calcium ions in the solution led to the destabilization of TiO_2 nanoparticles more effectively than monovalent sodium ions Na^+ [15].

It is difficult to assess whether the agglomeration took place after the material was introduced into water or the

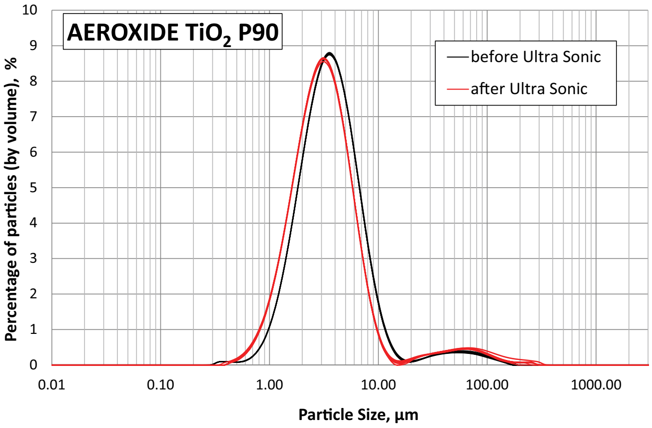

Fig. 3. Particle size of Aeroxide® P90 titanium dioxide suspension in water.

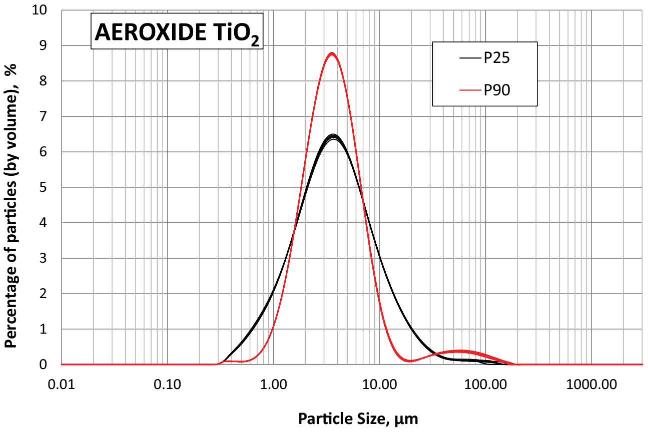

Fig. 4. Comparison of particle sizes of TiO_2 Aeroxide® P25 and P90 in aqueous suspension.

agglomerates had formed earlier, for example, during storage. However, the observations made during the measurements, including the observations of the particle size at different times from the introduction of the sample into the water and the high stability of the agglomerates may indicate, that they formed earlier, before the introduction of the samples into the water. The particle size measurements were made about 1 min after the moment, when the samples were introduced into water and stirred vigorously. Then the measurements continued for another 2 min. There were no significant differences between the particle size at the beginning of the measurements and at their end (Figs. 2 and 3) (Figs. 2 and 3 show the particle size distribution curves formed by 6 practically overlapping distribution curves for subsequent measurements made in intervals of 20 s).

In the case of measurements of materials that agglomerate (flocculate) after introducing them into water, each subsequent measurement shows larger and larger particles during the first few minutes [17]. It is unlikely that the agglomerates were formed within the first few tens of seconds after the material was introduced into the water, and for the next few minutes of mixing (with the same intensity) they did not change their size. This applied to both the smallest and the largest particles in the mixture of both Aeroxide® P25 and P90.

Moreover, the formed agglomerates were relatively stable, which would not be expected in case of freshly established structures. Both Aeroxide® P25 and P90 agglomerates did not disintegrate during the vigorous agitation of the slurry used during the measurements, as evidenced by the fact that subsequent measurements taken at 20 s intervals did not show any reduction in particle size (Figs. 2 and 3). In addition, the 2-min ultrasound treatment of the suspension (used in standard granulometric test methodology to break up unstable agglomerates) caused only relatively small changes in the particle size distribution (Figs. 2 and 3).

While a reduction in particle size in the suspension was observed, it was only about 15%. Moreover, the appearance of primary titanium dioxide nanoparticles (about 25 nm) was not observed in the suspension at all. After treatment with ultrasound, the smallest particles observed in the suspension were practically the same as the smallest particles observed in the untreated suspension. The smallest particles were more than ten times larger than the original particles of the P25 and P90 materials. The high durability of the agglomerates as well as the lack of particles in the suspension with sizes similar to the primary particles of the tested titanium dioxide may also indicate that the agglomerates were formed before the samples were introduced into the water.

These results are confirmed by the observations of the scanning electron microscope images, which show that Aeroxide® P25 and Aeroxide® P90 titanium dioxide stored in dry form create agglomerates.

Regardless of the mechanism of agglomeration formation, the fact is that Aeroxide® P25 and P90 titanium dioxide particles in aqueous solutions have a much larger size than the original nanoparticles. It may also be important in terms of the properties of material used in water purification processes including its photocatalytic activity and in the process of its separation from aqueous solutions.

As the titanium dioxide agglomerates did not break down due to the mixing used in the measurements it means that the agglomerates are relatively stable and will not break down during the usual mixing processes used in water treatment technology.

From the point of view of photocatalytic reactions, one of the most important parameters is the specific surface area of the material. The surface area of the samples suspended in water, calculated using a spherical agglomerate particle model and a density of 4.26 g/mL [14], was 0.56 m^2/g for TiO_2 Aeroxide® P25 and 0.48 m^2/g for TiO_2 Aeroxide® P90. These values were much smaller than the specific surface area declared by the manufacturer, determined by the adsorption method Brunauer–Emmett–Teller (BET), about 90 times less for P25, and about 190 times less for P90 [10]. These differences may indicate significant porosity of the TiO_2 Aeroxide® P25 and Aeroxide® P90 materials. This is confirmed by the analysis, the analysis of SEM images, indicating the complex and extensive morphology of agglomerates and their porous structure, what indicates/suggest that the actual specific surface of the tested titanium dioxide has a much larger specific surface than that calculated for spherical agglomerate particles.

The particle size of the suspension is important from the point of view of membrane separation. The smallest particles in the mixture are the most important in this respect. On the basis of the particle size distribution of the tested titanium dioxide suspensions it is possible to evaluate the separation efficiency through the use of specific membranes. For example, using microfiltration membranes with 0.45 μm pore size theoretically more than 99.5% Aeroxide® P90 particle removal efficiency and approximately 98% Aeroxide® P25 particle removal efficiency can be expected. Many scientific works emphasize that titanium dioxide in aqueous solutions is 100% retained by microfiltration membranes, despite the fact that in some studies the average size of TiO_2 particles is approx. 25 nm, which is much smaller than the pore size of microfiltration membranes (>0.1 μm) [6–9].

Despite the high efficiency of separation of these materials with the use of microfiltration, the use of membranes with pore size >0.3 μm (the minimum particle size observed in the tested samples) in longer period may result in permanent, irreversible blocking, because particles with sizes comparable or slightly smaller than membrane pores can penetrate deep into the pores and there. It should also be remembered that the determined particle size is the so-called equivalent diameter, meaning that also particles with an equivalent diameter larger than the pores of the membranes, may in fact be one dimension smaller than the pores of the membrane used and thus penetrate the membranes leading also to irreversible fouling.

4. Conclusions

- The TiO_2 Aeroxide® P25 and P90 particles in the aqueous solution were in the form of a suspension of stable agglomerates one to three orders of magnitude larger than the original titanium dioxide nanoparticles.
- The agglomerates were 0.3–170 μm with 80% of the material being 1.2–11.7 μm for Aeroxide® P25 and 1.6–8.2 μm for Aeroxide® P90.

- The analysis of the images obtained with SEM and the results of granulometric tests shows that the agglomerates were formed during the storage of the material in a dry form (before introducing the material into water).
- The agglomerates are relatively stable and do not break down during the usual mixing processes used in water treatment technology.
- Agglomerates are characterized by complex and extensive morphology, high porosity, and a large specific surface area.
- The use of microfiltration with a pore size of >0.3 μm should be effective in separating TiO_2 Aeroxide® P25 and P90 suspensions from aqueous solutions.

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References

[1] G. Marcì, E.I. García-López, L. Palmisano, Chapter 20 – Fine Chemistry by TiO_2 Heterogeneous Photocatalysis, F. Parrino, L. Palmisano, Eds., Titanium Dioxide (TiO_2) and Its Applications, 2021, pp. 609–635.

[2] R. Krakowiak, J. Musial, P. Bakun, M. Spychała, B. Czarczynska-Goslinska, D.T. Mlynarczyk, T. Koczorowski, L. Sobotta, B. Stanisz, T. Goslinski, Titanium dioxide-based photocatalysts for degradation of emerging contaminants including pharmaceutical pollutants, Appl. Sci., 11 (2021) 8674, doi: 10.3390/app11188674.

[3] S.J. Olusegun, T.G.F. Souza, G. de O. Souza, M. Osial, N.D.S. Mohallem, V.S.T. Ciminelli, P. Krysinski, Iron-based materials for the adsorption and photocatalytic degradation of pharmaceutical drugs: a comprehensive review of the mechanism pathway, J. Water Process Eng., 51 (2023) 103457, doi: 10.1016/j.jwpe.2022.103457.

[4] A. Bazargan, Ed., Photocatalytic Water and Wastewater Treatment, IWA Publishing, London, 2022.

[5] C.S. Uyguner-Demirel, N.C. Birben, M. Bekbolet, Elucidation of background organic matter matrix effect on photocatalytic treatment of contaminants using TiO_2: a review, Catal. Today, 284 (2017) 202–214.

[6] M. Rajca, NOM (HA and FA) reduction in water using nano titanium dioxide photocatalysts (P25 and P90) and membranes, Catalysts, 10 (2020) 249, doi: 10.3390/catal10020249.

[7] M. Rajca, The effectiveness of removal of NOM from natural water using photocatalytic membrane reactors in PMR-UF and PMR-MF modes, Chem. Eng. J., 305 (2016) 169–175.

[8] W. XI, S.-u. Geissen, Separation of titanium dioxide from photocatalytically treated water by cross-flow microfiltration, Water Res., 35 (2001) 1256–1262.

[9] C. Ullmann, F. Babick, M. Stintz, Microfiltration of submicron-sized and nano-sized suspensions for particle size determination by dynamic light scattering, Nanomaterials, 9 (2019) 829, doi: 10.3390/nano9060829.

[10] Ewonik Industries AG, Essen, Germany, Product Information, Aeroxide® P25 and P90.

[11] S.J. Vitton, L.Y. Sadler, Particle-size analysis of soils using laser light scattering and X-ray absorption technology, Geotech. Test J., 20 (1997) 63–73.

[12] G.B.J. de Boer, C. de Weerd, D. Thoenes, H.W.J. Goossens, Laser diffraction spectrometry: Fraunhofer diffraction versus Mie scattering, Part. Part. Syst. Charact., 4 (1987) 14–19.

[13] G. Bushell, Forward light scattering to characterise structure of flocs composed of large particles, Chem. Eng. J., 11 (2005) 145–149.

[14] https://www.sigmaaldrich.com/PL/pl/product/aldrich/718467 (Acc. July 2023).

[15] D. Lin, S. Drew Story, S.L. Walker, Q. Huang, P. Cai, Influence of extracellular polymeric substances on the aggregation kinetics of TiO_2 nanoparticles, Water Res., 104 (2016) 381–388.

[16] F. Xu, Review of analytical studies on TiO_2 nanoparticles and particle aggregation, coagulation, flocculation, sedimentation, stabilization, Chemosphere, 212 (2018) 662–677.

[17] R.T. Bray, K. Fitobór, Sizes of iron hydroxide particles formed during ferric coagulation processes, Desal. Water Treat., 64 (2017) 419–424.