



ORIGINAL ARTICLE

Study of the physical and mechanical properties of permeable concrete with the addition of TiO₂ for the treatment of sewage

Estudo das propriedades físicas e mecânicas do concreto permeável com adição de TiO₂ para o tratamento de esgoto sanitário

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Abstract: The sewage treatment stations (STSs), located in Teresina-PI, were designed to receive domestic sewage, however, in 2011 they began to receive unknown sewer from clean pit vehicles. This sewage is compromising the effluent treatment efficiency. The permeable concrete with the addition of titanium dioxide (TiO₂) presents itself as an alternative process to assist in the treatment of sanitary sewage due to its photocatalytic properties. Therefore, the objective of this work was to evaluate the mechanical, hydraulic, and microstructural properties of permeable concrete with the addition of 3, 6 and 10% of TiO₂. The results determined that the variation in the concentration of TiO₂ significantly influenced the properties analyzed in this research. The addition of TiO₂ to the permeable concrete to a concentration of 6% impairs its physical and hydraulic properties and improves its mechanical properties.

Keywords: mechanical properties, physical properties, permeability, microstructure, TiO₂.

Resumo: As estações de tratamento de esgoto (ETEs), situadas em Teresina-PI, foram projetadas para o recebimento de esgoto doméstico, porém, em 2011 começaram a receber esgoto desconhecido proveniente dos veículos Limpa Fossas. Este esgoto está comprometendo a eficiência do tratamento dos efluentes. O concreto permeável com adição de dióxido de titânio (TiO₂) apresenta-se como um processo alternativo para auxiliar no tratamento de esgoto sanitário devido suas propriedades fotocatalíticas. Com isso, o objetivo deste trabalho foi avaliar as propriedades mecânicas, hidráulicas e microestruturas do concreto permeável com a adição de 3, 6 e 10% de TiO₂. Os resultados determinaram que a variação na concentração de TiO₂ influenciou significativamente as propriedades analisadas nesta pesquisa. A adição de TiO₂ no concreto permeável até uma concentração de 6% prejudica suas propriedades físicas e hidráulicas e melhora suas propriedades mecânicas.

Palavras-chave: propriedades mecânicas, propriedades físicas, permeabilidade, microestrutura, TiO₂.

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1 INTRODUCTION

The disorderly growth of society, associated with the processes of degradation of water quality, has been creating serious problems of quantitative and qualitative water scarcity, in addition to conflicts of use, even in natural regions with excess water. Industrial and domestic activities release many aggressive agents in the air, water, and soil, generating consequences that society needs to resolve. The residues produced in generally contain toxic pollutants and

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are resistant to conventional treatment systems (coagulation/flocculation; adsorption with activated carbon; precipitation; biological degradation, among others) [1].

The sewage treatment stations in Teresina-PI were planned to receive domestic sewage, however, as of 2011, by the decision of the Government of the State of Piauí, they began to receive sewage transported by clean pit vehicles, which collect sewage from pits installed in regions that do not receive coverage from basic sanitation. The effluents, coming from the pit cleaners, possibly contain a complex mixture of agents that cause the mutagenic effect, which can compromise the efficiency of the treatment in the effluent treatment plants. Physical-chemical analyzes revealed that the collected waters and effluents have high concentrations of electrical conductivity, detergents and phosphorus, in addition to high levels of thermotolerant coliforms, requiring alternative processes to ensure greater efficiency of the treatment sewage station [2].

Currently, in the treatment of contaminated effluents, mainly with toxic organic compounds, Advanced Oxidative Processes (AOPs) have been highlighted. These processes can degrade organic compounds and can even break them down into mineral compounds. This capacity is due to the high oxidizing power of hydroxyl radicals (\bullet OH), which are produced during the entire treatment process. These AOPs can also destroy toxic organic loads or convert them into more biodegradable forms [3].

Photocatalysis is a chemical reaction induced by photo-absorption of solid material, or photocatalyst, which remains chemically unchanged during and after the reaction. Its performance is affected by environmental factors such as light wavelength, humidity, temperature, and concentration of the photocatalyst. Titanium dioxide (TiO_2) is one of the most efficient photocatalysts due to its high catalytic activity, being highly stable, economical, non-toxic (for environments and humans), containing strong oxidizing power and chemical resistance. Photocatalysis with TiO_2 is a popular research area and finds its application in several fields such as air purification, hydrophilic coating, self-cleaning devices, water disinfection, wastewater treatment [4].

TiO_2 concrete is already used in pavements, paints, concrete panels and tiles, when added to concrete, TiO_2 keeps the surface self-cleaning, eliminates biological organisms such as algae, bacteria, fungi and degrades airborne pollutants, such as nitrogen oxides (NO_x) [5].

Other factors that can affect the efficiency of TiO_2 photocatalysis, when applied to concrete, include porosity, type of aggregate, size of aggregate and method of application. The higher rate of voids and surface roughness, coupled with a larger surface area, can increase the bond, performance, and durability of TiO_2 applied to permeable concrete [6].

TiO_2 -permeable concrete can be used for the decomposition of natural and inorganic mixtures, removal of heavy metals and eliminating infectious microscopic organisms. It can be used in the same way to assist the decay in the concentration of humid substances [7].

The incorporation of nanomaterials, such as TiO_2 , in the concrete matrix or in the coating formulations, even in small quantities, results in greater resistance to biodeterioration and greater durability of the concrete structures used in sewage systems [8].

The addition of TiO_2 to the permeable concrete causes important changes at the macrostructural and microstructural level and its understanding is fundamental for the effectiveness in its application in the treatment of sanitary sewage [9]. The objective of this research was to study the influence of the addition of TiO_2 on the mechanical, physical and hydraulic properties of the permeable concrete and also to evaluate the microstructural modification on the surface of the permeable concrete with addition of TiO_2 .

2 MATERIALS AND EXPERIMENTAL PROGRAM

2.1 Materials

2.1.1 Cement

For the formulation of permeable concrete traces, PC-V ARI RS cement was used, following NBR 16697 [10]. This cement was chosen due to its property of resisting aggressive sulfated media, such as those found in sewage, wastewater or industrial networks, in seawater and some types of soils.

2.1.2 Coarse Aggregate

As a coarse aggregate, crushed stone of basaltic origin was used, sold commercially as gravel 0, with five different gradations: 2.36, 4.75, 6.30, 9.50 and 12.50 mm, with specific mass and unit mass. of 2810 kg/m^3 and 1400 kg/m^3 , respectively, verified, based on NBR NM-53 [11].

The granulometric analysis (Table 1) and the granulometry curve (Figure 1) were performed according to NBR NM-248 [12], where it was observed that the coarse aggregate has a maximum characteristic dimension of 9.50 mm.

The coarse aggregate used in this study fits after the upper limit of the 9.5/25 sieves and has a uniformity coefficient (Cu) equal to 1.5. According to Lima and Silva [13], the Cu of the aggregate must be between 1.4 and 1.6, to provide better filtering of particles suspended in the water, avoiding greater risks of loss of efficiency due to clogging. Therefore, the aggregates used in this research meet the specifications found in the literature for use in the treatment of sanitary sewage.

Table 1 - Granulometric analysis of crushed stone

Sieve Opening (mm)	Material retained in the sieve (g)	Material retained in the sieve (%)
25	0.00	0.00
12.5	10.00	1.00
9.5	415.40	42.54
6.3	499.80	92.52
4.75	25.90	95.11
2.36	47.20	99.82
Bottom	1.70	100.00
Maximum Characteristic Dimension	9.50 mm	

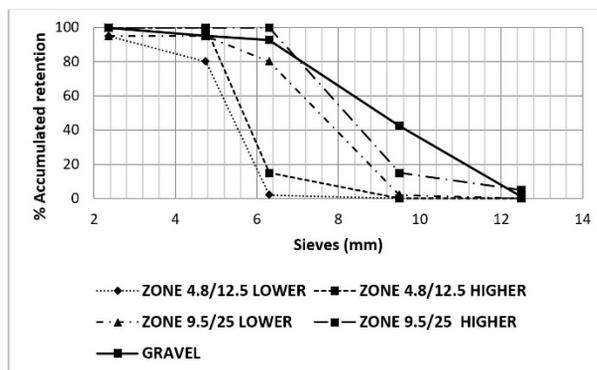


Figure 1 Granulometric curve of coarse aggregate.

2.1.3 Titanium Dioxide

To produce photocatalytic permeable concrete, titanium dioxide P25 was used as a catalyst. Its chemical composition was determined by X-ray fluorescence by dispersive energy (FRX), where 99.95% purity was observed. Mineralogical characterization to identify the crystalline phases present was performed using the X-ray diffraction technique (XRD), Figure 2.

According to the micrographs obtained by scanning electron microscopy (SEM), at point A, the TiO₂ samples (Figure 3a), present particles with uniform distribution, spherical morphology, and slight agglomeration. There were no significant variations in grain morphology. According to Casagrande et al. [14], TiO₂ powder tends to agglomerate, has a spherical shape, however, due to agglomeration, does not have a well-defined shape.

The graph of TiO₂ powder obtained by the dispersive energy spectroscopy (EDS) technique (Figure 3b), at point A, shows high titanium (Ti) and oxygen peak (O) peaks, which are the constituent elements of the TiO₂ nanoparticles [15]. The presence of these peaks in the sample confirming the purity found in the X-ray fluorescence analysis, observing a carbon peak (C) in the EDS, which corresponds to the metallization tape used.

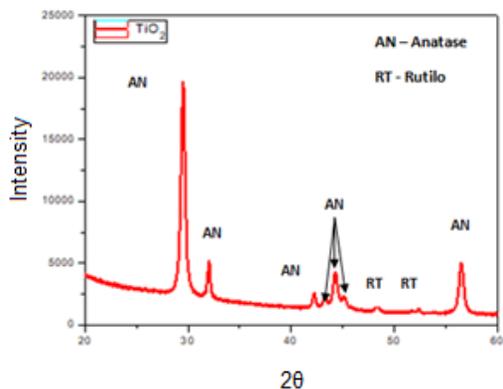


Figure 2 Titanium dioxide (TiO₂) diffractogram.

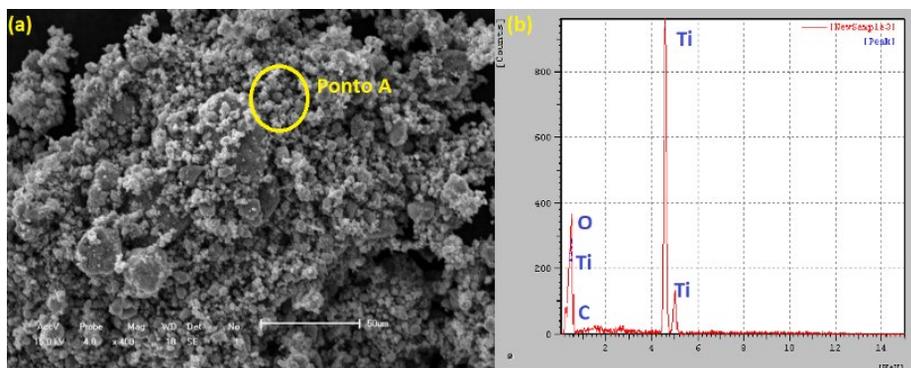


Figure 3 (a) Image obtained by SEM of the TiO₂ powder; (b) EDS image of TiO₂ powder.

2.2 Experimental Program

2.2.1 Permeable concrete characterization tests

The specific mass of the permeable concrete in the fresh state was determined according to NBR 9833 [16]. The porosity of the permeable concrete was determined according to Joshaghani et al. [17]. In the test to measure the permeability coefficient, the method described by the American Concrete Institute - ACI 522 R-10 [18] was used, which uses a variable load permeameter.

Permeable concrete samples were collected with and without TiO₂ to characterize its surface using the Scanning Electron Microscopy (SEM) method with Dispersive Energy Spectroscopy (DES).

2.2.2 Molding of specimens

Two types of specimens were prepared: cylindrical and prismatic. The molding of cylindrical specimens was performed according to NBR 5738 [19] with dimensions of 10 cm in diameter and 20 cm in height, being used in permeability and compression resistance tests, whereas the prismatic specimens were made from the recommendations of NBR 16416 [20], with dimensions of 10 cm × 10 cm × 40 cm, being used in the flexural strength test.

2.2.3 Permeable concrete dosage

Eighteen types of samples were produced, where they are identified as reference concrete (RC), using gravel 0 and permeable concrete (PC) in their composition, using aggregate with single granulometry (12.5; 9.5; 6.3; 4.75; 2.36 mm), water/cement ratio (0.25, 0.30 and 0.35) (Table 2).

Table 2 Proportion of materials in the samples.

Samples	Ratio water/cement	Cement (kg/m ³)	Aggregate (kg/m ³)	Water (kg/m ³)
RC.0.25.B0	0.25	487.45	1462.35	121.86
RC.0.30.B0	0.30	390.41	1561.66	117.12
RC.0.35.B0	0.35	325.59	1627.99	113.96
PC.0.25.12.5	0.25	481.82	1445.47	120.45
PC.0.30.12.5	0.30	385.60	1542.42	115.68
PC.0.35.12.5	0.35	321.42	1607.10	112.49
PC.0.25.9.5	0.25	399.66	1598.66	99.91
PC.0.30.9.5	0.30	331.92	1659.60	99.57
PC.0.35.9.5	0.35	458.94	1376.84	160.63
PC.0.25.6.3	0.25	337.12	1685.64	84.28
PC.0.30.6.3	0.30	470.37	1411.12	141.11
PC.0.35.6.3	0.35	378.80	1515.23	132.58
PC.0.25.4.75	0.25	398.65	1594.60	99.66
PC.0.30.4.75	0.30	331.04	1655.21	99.31
PC.0.35.4.75	0.35	457.94	1373.82	160.27
PC.0.25.2.36	0.25	338.33	1691.67	84.58
PC.0.30.2.36	0.30	471.78	1415.34	141.53
PC.0.35.2.36	0.35	380.02	1520.11	133.00

This procedure resulted in 108 specimens for the determination of compressive strength (18 samples x 6 repetitions), tested at 28 days; 108 specimens for flexural tensile testing (18 samples × 6 specimens), tested at 28 days and 108 specimens for calculating porosity, density and permeability (18 samples × 6 specimens). The RC.0.25.B0 to RC.0.35.B0 samples have particle sizes ranging from 2.36 to 12.50 mm and PC.0.25.12.5 to PC.0.35.2.36 single particle size, as shown in Table 3.

Table 3 Sample granulometry, in percentage.

Sample Identification	Granulometry (mm)				
	12.50	9.50	6.30	4.75	2.36
RC.0.25.B0	5.26	28.86	48.4	12.59	4.89
RC.0.30.B0	5.26	28.86	48.4	12.59	4.89
RC.0.35.B0	5.26	28.86	48.4	12.59	4.89
PC.0.25.12.5	100	0	0	0	0
PC.0.30.12.5	100	0	0	0	0
PC.0.35.12.5	100	0	0	0	0
PC.0.25.9.5	0	100	0	0	0
PC.0.30.9.5	0	100	0	0	0
PC.0.35.9.5	0	100	0	0	0
PC.0.25.6.3	0	0	100	0	0
PC.0.30.6.3	0	0	100	0	0
PC.0.35.6.3	0	0	100	0	0
PC.0.25.4.75	0	0	0	100	0
PC.0.30.4.75	0	0	0	100	0
PC.0.35.4.75	0	0	0	100	0
PC.0.25.2.36	0	0	0	0	100
PC.0.30.2.36	0	0	0	0	100
PC.0.35.2.36	0	0	0	0	100

2.2.4 Mechanical tests

The compressive strength test was performed according to the NBR 5739 standard [21] and the flexural strength test was performed by the standard NBR 12142 [22].

2.2.5 TiO₂- permeable concrete

After the tests with the permeable concrete, one of the eighteen compositions was chosen and TiO₂ was added to the cement, before the concrete production, for a determined time of two hours in the ball mill, to guarantee a greater homogeneity between the two materials. With the obtaining of the previous mixture, gravel and water were added to the 150-liter concrete mixer to obtain the concrete.

This choice was made considering the feature that best suits the conditions of durability and performance for use in sewage systems. According to Noeiaghahi [8], the concrete used in sewage systems must have a water-cement ratio lower than 0.45 and have high resistance, because concretes with low resistance reduce the durability of the sewage system, increasing the repair cost and maintenance throughout the life of the system.

Four samples were used to analyze the addition of TiO₂ in the permeable concrete, a control sample, without TiO₂ and three samples containing 3, 6, and 10% of TiO₂, in substitution of the cement, by mass. The concentrations of TiO₂ in the permeable concrete were adopted based on the work of Melo et al. [23], where the efficiency of the incorporation of TiO₂ in paving blocks was evaluated. The samples of concrete permeable with TiO₂ were subjected to the same tests, physical and mechanical, carried out on permeable concrete without TiO₂.

The tests resulted in 24 specimens for compression (4 samples × 6 repetitions), tested at 28 days; 24 specimens for traction in flexing (4 samples × 6 repetitions), tested at 28 days and 24 specimens for calculating porosity, density, and permeability (4 samples × 6 specimens).

Samples of TiO₂-permeable concrete were collected from the broken specimens from the compressive strength test to characterize its surface using the Scanning Electron Microscopy (SEM) method with Dispersive Energy Spectroscopy (EDS).

2.2.6. Statistical analysis

The data obtained in the tests were treated statistically, through the analysis of variance (ANOVA) to check the significant effects at a 95% confidence level, in addition to the test of multiple comparisons of means (Tukey's test), to check which averages showed statistical differences at the level of 5% probability.

3 RESULTS AND DISCUSSIONS

3.1 Porosity and specific mass

The average values of specific mass and porosity obtained in this study vary from 1565.53 kg/m³ to 2082.29 kg/m³ and 15.25% to 31, which can be verified in Figures 4 and 5. By the Tukey Test, admitting if a p-value ≤ 0.05 it can be seen that there was a difference between the eighteen samples.

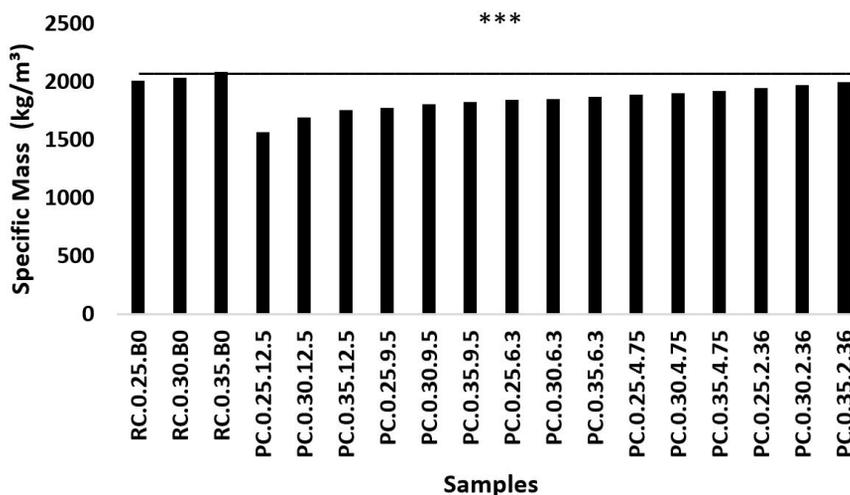


Figure 4 Average samples results of specific mass tests. *** Significant statistical difference by the Tukey test p <0.001.

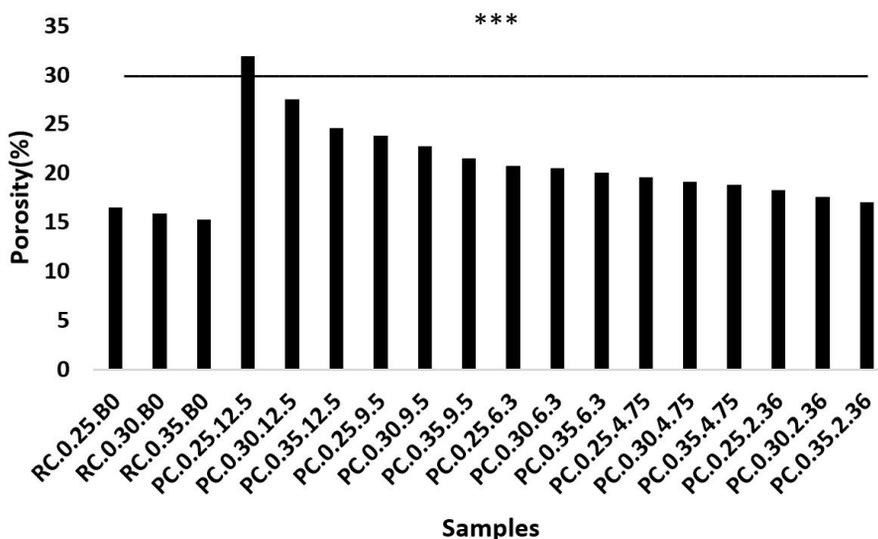


Figure 5 Average samples results of porosity tests. *** Significant statistical difference by the Tukey test $p < 0.001$.

The samples PC.0.35.B0 and PC.0.25.12.5 obtained the highest and lowest specific mass, respectively, concerning the eighteen samples analyzed in this study. This indicated that the increase in the granulometry of coarse aggregates, with a lower water-cement ratio, offered more resistance to compaction, which decreased the specific mass and increased the porosity, which according to Ibrahim et al. [24], as the ratio cement-aggregate increases, the volume of intergranular void decreases due to the decrease in the resistance to compaction offered by the reduced amount of aggregates, which was evidenced by the tests performed.

The mixtures that had in their composition varied granulometry (PC.0.25.B0, PC.0.30.B0 and PC.0.35.B0), presented the highest specific masses because the voids generated by the aggregates with larger particle sizes (12.5 mm), it may have been sufficient to accommodate the smaller aggregates (4.75 and 2.36 mm), resulting in a greater compaction factor, which had already been verified by Ibrahim et al. [24] where the values of specific mass, obtained in different water-cement ratios, are functions of the compaction method and the degree of lubrication of the sample.

3.2 Permeability

It is observed that the average permeability values obtained in this study vary from 0.74 to 18.68 mm/s (Figure 6). By the Tukey test, assuming a value of $p \leq 0.05$, it can be observed that there was a difference between the eighteen samples.

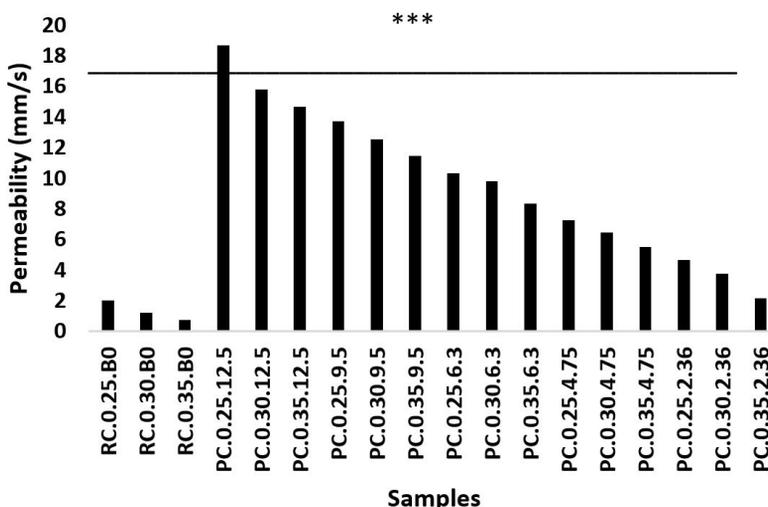


Figure 6 Average samples results of permeability tests. *** Statistically significant difference by the Tukey test $p < 0.001$.

The permeability of the mixtures that present in their composition coarse aggregates with a single size (PC.0.25.12.5 to PC.0.35.2.36) reached a rate above that recommended by the ACI 522R-10 standards [18], which establishes a minimum value of 1mm/s for permeable concretes. Neptune and Putman [25] verified in his study about the effect of the size of the coarse aggregate in permeable concrete mixtures that, the highest permeability values were obtained in the dosages that had coarse aggregates of one size.

The permeable concrete mixtures that used coarse aggregates with dimensions of 12.5, 9.5, and 6.3 mm (PC.0.25.12.5 to PC.0.35.6.3), obtained a higher permeability due to the smallest surface area of the aggregates. The samples with coarse aggregates with dimensions of 4.75 and 2.36 mm (PC.0.25.4.75 to PC.0.35.2.36) had a larger surface area of aggregates, decreasing porosity and permeability, but it was observed enough cement paste just to coat them.

The samples PC.0.25.B0, PC.0.30.B0, and PC.0.35.B0, composed of aggregates of size ranging from 2.36 to 12.5 mm, obtained greater compaction, requiring more cement paste to coat the aggregates. Chandrappa and Biligiri [26] found that permeable concretes that contain coarse aggregate in their composition with continuous graduation, require greater amounts of cement paste to coat the aggregates, with this, they present a lower permeability, because a part of this cement paste fills the voids intergranular, reducing porosity. This was evidenced in the sample PC.0.35.B0, where the permeability was below the specification of the ACI 522R-10 standard [18].

According to Kia et al. [27], the permeability of permeable concretes is related to the porosity of the material, since the greater the porosity, the greater the permeability. Still in this context, the compaction procedure must be selected and applied with care, since, even the material having high porosity, the use of an inadequate compaction procedure can cause the reduction of interconnectivity between the pores, impairing the permeable capacity of the material.

3.3 Compressive strength

The average values of compressive strength obtained in this study ranged from 9.55 to 22.17 MPa (Figure 7). By the Tukey test, assuming a value of $p \leq 0.05$, it can be observed that there was a difference between the eighteen samples.

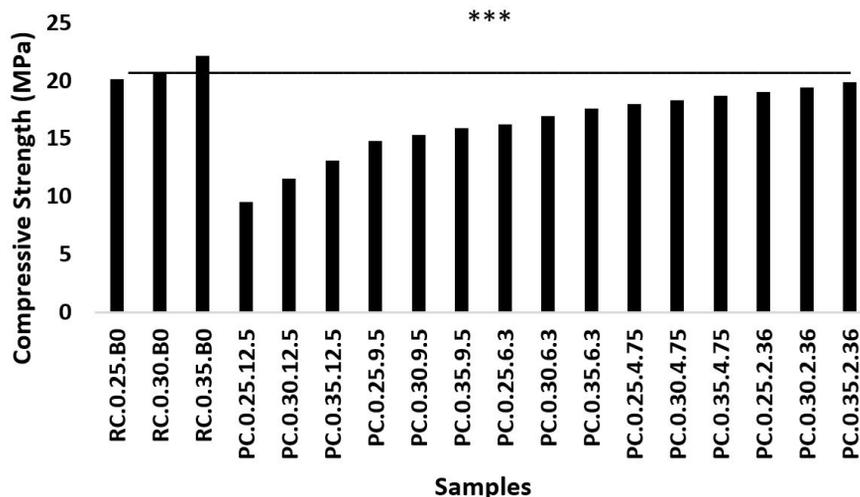


Figure 7 Average samples results of compressive strength tests. *** Statistically significant difference by the Tukey test $p < 0.001$.

average compressive strength after 28 days of curing (22.17 MPa). When the water-cement ratio was less than 0.35, for the same size of coarse aggregate, the compressive strength decreased in all samples analyzed. The PC.0.25.12.5 mixture with a water-cement ratio of 0.25 and a single coarse aggregate of 12.5 mm produced the lowest average compressive strength of 9.55 MPa, at 28 days.

Yeih et al. [28] studied the use of slag from the electric arc furnace as aggregate for permeable concrete and found that the lowest compressive strength was recorded for the mixture produced from a single type of aggregate, with a dimension of 12.5 mm, and the water-cement ratio that guaranteed greater resistance in the samples was 0.35, corroborating with the current study.

Figure 8 shows the relationships between porosity, compressive strength, and permeability for permeable concrete. This figure can be used to estimate the porosity required for mixtures that have specifications for use in terms of permeability and strength of permeable concrete. As an example, with 30% porosity, the permeable concrete will have a permeability of 20.00 mm/s and compressive strength of 10.0 MPa.

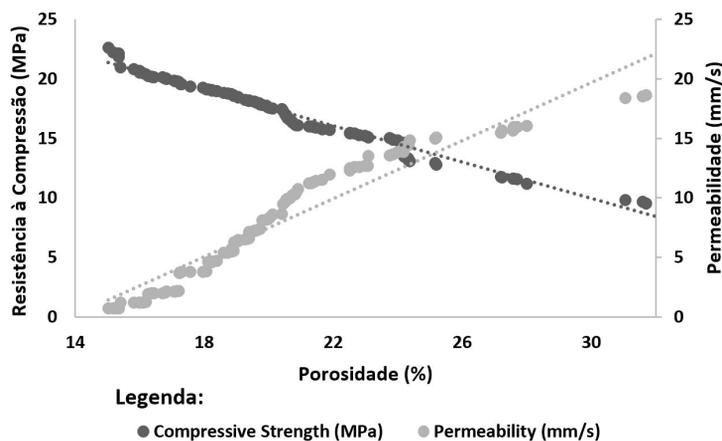


Figure 8 Relationship between Porosity, Compression Resistance and Permeability.

3.4 Flexural tensile strength

It is observed that the mean values of flexural tensile strength obtained in this study vary from 1.22 to 4.82 MPa (Figure 9). By the Tukey test, assuming a value of $p \leq 0.05$, it can be observed that there was a difference between the eighteen samples.

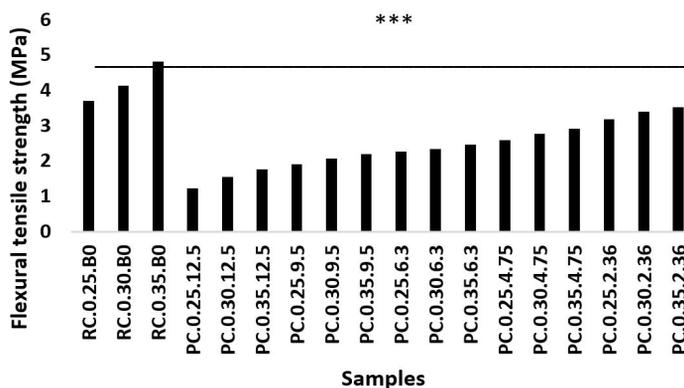


Figure 9 Average samples results of flexural tensile strength tests. *** Statistically significant difference by the Tukey test $p < 0.001$.

It was observed that the ratio between the flexural strength and the compressive strength ranges from 0.12 (PC.0.25.12.5) to 0.21 (RC.0.35.B0), this relationship increases as the porosity decreases. Yeih and Chang [29] assessed the influences of the type of cement and curing conditions on the properties of permeable concrete and found that the ratio between flexural strength and compressive strength ranges from 0.16 to 0.26. As the sample porosity increases, a greater reduction in compressive strength compared to flexural strength has occurred.

The size of the aggregate affects the tensile strength in flexion in all types of samples analyzed. The mixture PC.0.35.B0, using in its composition coarse aggregates ranging from 2.36 to 12.5 mm, reaches the maximum average tensile strength in flexion of 4.82 MPa corresponding to the lowest porosity and a water factor cement of 0.35. However, the PC.0.25.12.5 mixture, which has a single aggregate size of 12.5 mm, has the lowest average tensile strength in flexion of 1.22 MPa due to the greater porosity and a water-cement factor of 0.25.

According to Brake et al. [30], the coarse aggregate grain size and the water-cement ratio significantly affect its flexural strength. The larger size of the aggregates and a lower water-cement ratio results in decreasing the specific mass of permeable concrete. Therefore, the contact forces between the aggregates become weaker, which leads to a reduction in the permeable concrete strength. Joshaghani et al. [17] found that the permeable concrete that contains coarse aggregates with unique sizes in its composition, showed a reduction in tensile strength in flexion as the coarse aggregate size increased.

3.5 Addition of TiO₂ to permeable concrete

Following the recommendations of Noeiaghahi [8], the PC.0.35.2.36 mixture was chosen to add TiO₂, since the concrete used in sewage systems must have a water-cement ratio lower than 0.45 and have high resistance, therefore, concrete with low resistance reduces the durability of the sewage system, increasing the cost of repair and maintenance throughout the system's useful life.

Four permeable concrete samples were produced, the detailed experimental proportions are provided in Table 4. The water-cement ratio remained constant with a value of 0.35. Yeih et al. [28] found that water-cement ratios equal to 0.35, in permeable concrete, improve their mechanical properties.

Table 4 Proportion of materials in the samples.

Sample Type	Water/cement ratio	Cement (kg/m ³)	Aggregate (kg/m ³)	TiO ₂ (kg/m ³)	Water (kg/m ³)
PC	0.35	380.00	1520.11	0.00	133.00
PC.3.TiO ₂	0.35	368.60	1520.11	11.40	130.00
PC.6.TiO ₂	0.35	357.20	1520.11	22.80	126.00
PC.10.TiO ₂	0.35	342.00	1520.11	38.00	121.00

3.5.1 Porosity and specific mass

Figures 10 and 11 show the average porosity and specific mass of the samples. The higher the concentration of TiO₂ in the permeable concrete, the lower the porosity and the higher the specific mass, up to a concentration of 6%. For a 10% concentration of TiO₂, the porosity of the permeable concrete increases and the specific mass decreases. By the Tukey test (Figures 10 and 11), assuming a p-value ≤ 0.05 , it can be observed that there was a difference between the four samples. The addition of 3, 6 and 10% of TiO₂ decreased the porosity by 10.86, 15.79, and 11.80% respectively and the specific mass increased by 5.17, 8.81 and 2.00%, respectively, in relation to the PC sample. Chen et al. [31] studied the porosity in cement mortars with the addition of TiO₂ and found that the addition of TiO₂ in the cement paste can decrease the porosity and increase the specific mass, since the TiO₂ particles fill the voids, mainly the capillary pores. Besides, it was found that TiO₂ does not have pozzolanic activity, being inert in the mortar and can be used as fine aggregate.

According to Magesvari and Narasimha [32], the voids between coarse aggregates cannot be filled by a cement paste, the use of fine aggregate can increase the bonding area between cement paste and coarse aggregates, resulting in less porosity and greater specific mass, but it is necessary to control the addition of the fine material so as not to compromise the permeability considerably.

The PC.10.TiO₂ sample showed an increase in porosity and a decrease in specific gravity in relation to the PC.6.TiO₂ sample, the TiO₂ content made the mixture less workable, providing greater resistance to compaction, resulting in greater porosity and less mass-specific.

3.5.2 Permeability

Figure 12 shows that, with the increase in the percentage of TiO₂ in the permeable concrete mixture, there is a gradual decrease in the permeability value. The greatest reduction in permeability was in the PC.10.TiO₂ sample, with a decrease of 12.5% about the PC sample. However, all samples were above that required by ACI 522R-10 [18], which establishes a minimum permeability value of 1mm/s for permeable concretes. Using the Tukey test (Figure 12), assuming a p value ≤ 0.05 , it can be observed that there was a difference between the four samples.

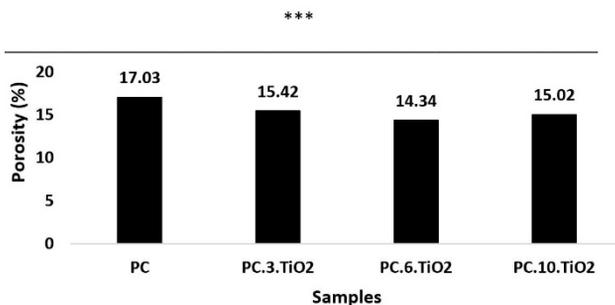


Figure 10 Average samples results of porosity tests. *** Statistically significant difference by the Tukey test $p < 0.001$.

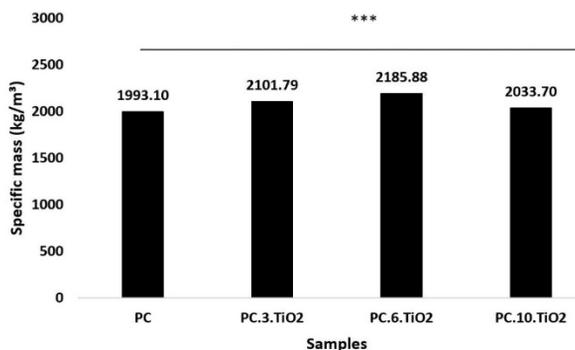


Figure 11 Average samples results of specific mass tests. *** Statistically significant difference by the Tukey test $p < 0.001$.

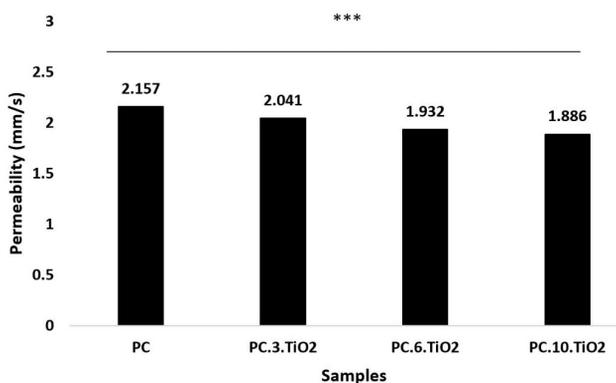


Figure 12 Average of samples obtained in the Permeability test. *** Statistically significant difference by the Tukey test $p < 0.001$.

In his study, Bolt et al. [33], adding 10% of TiO_2 to a permeable concrete mixture that had 45% of the aggregates passing through the 4.75 mm number sieve, reduced its permeability by 11.29% and the addition of 15% of TiO_2 , permeability of permeable concrete decreases by approximately 47%, compromising its permeability.

In his research, Lian et al. [34] found that permeability depends on the size of coarse aggregates, the thickness of cement paste, water/cement ratio, as well as the addition of fine aggregates. Permeability increases with the use of aggregates of greater particle sizes. However, it decreases with the increase of fine aggregate content. Thus, the addition of TiO_2 to the permeable concrete must be carried out in such a way that it does not compromise its permeability.

3.5.3 Compressive strength

According to Figure 13, the PC.3. TiO_2 and PC.6. TiO_2 samples increased their compressive strength, compared to the PC sample, the increase in the concentration of TiO_2 in the mixture, resulted in an increase in compressive strength by 9, 56 and 22.8%, respectively. With the addition of TiO_2 , the contact area between the

cement paste and the coarse aggregate increases, making the permeable concrete more resistant. By the Tukey test (Figure 13), assuming a p-value ≤ 0.05 , it can be observed that there was a difference between the four samples.

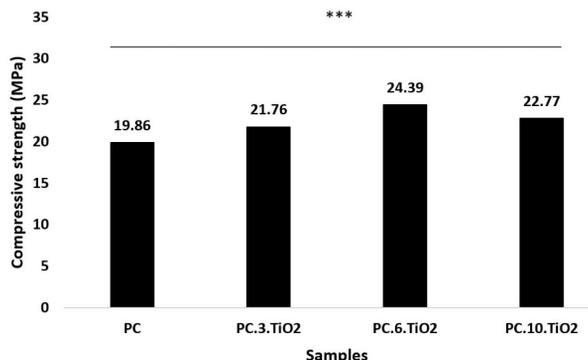


Figure 13 Average samples results of Compression Resistance tests. *** Statistically significant difference by the Tukey test $p < 0.001$.

Manoj Kumaar et al. [35] studied the influence of the addition of 2% TiO_2 on the compressive strength of permeable concrete, using a single aggregate with a size of 10 mm. A 7.64% increase in compressive strength was observed. Andrade et al. [36] found that the addition of TiO_2 to autoclaved cellular concrete reduces the porosity of the cement paste, improving its mechanical properties.

The PC.10. TiO_2 sample showed a decrease in compressive strength of 6.92% compared to the PC.6. TiO_2 sample, this may have occurred due to the less workability of the mixture. Senff et al. [37] reported that the increase in the concentration of TiO_2 in cement mortars decreases its workability, impairing the mechanical properties of the mortar. Meng et al. [38] studied the influence of the addition of TiO_2 in cement pastes and observed that the addition of 10% of TiO_2 decreases the workability by 40%, thus the compressive strength decreased by 9% concerning the sample with 5% of TiO_2 .

3.5.4 Tensile strength in flexion

Figure 14 shows the average tensile strength in the flexion of the samples. The higher the concentration of TiO_2 in permeable concrete, the greater the increase in tensile strength in flexion, up to a concentration of 6%. For a concentration of 10% of TiO_2 the tensile strength in the permeable concrete flexion decreases. Using the Tukey test (Figure 14), assuming a p value ≤ 0.05 , it can be observed that there was a difference between the four samples.

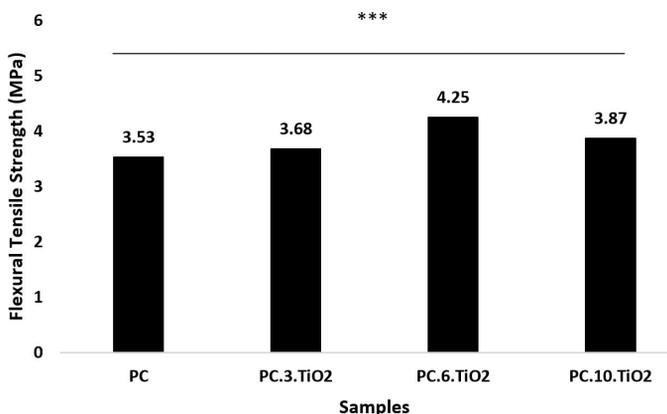


Figure 14 Average of the samples obtained in the Flexural Tensile Strength test. *** Statistically significant difference by the Tukey test $p < 0.001$.

The permeable concrete samples PC.3.TiO₂ and PC.6.TiO₂ increased the tensile strength in flexion by 4.25 and 20.39%, respectively, in relation to the sample PC. Zade et al. [39] used a concentration of 5% of TiO₂ in the permeable concrete with coarse aggregate ranging from 6, 10 and 20 mm and obtained an increase in the tensile strength in flexion of 18.86%. This relationship can be compared to the addition of fine aggregate to the permeable concrete. According to Lian and Zhuge [40], the fine aggregate is generally excluded from permeable concrete, but adding a small fraction, up to 7%, increases the tensile strength in flexion, compression, and specific gravity.

The flexural tensile strength decreases by 8.70% in the PC.10.TiO₂ sample, compared to the PC.6.TiO₂ sample. According to Jalal et al. [41], the increase in the concentration of TiO₂ in the cement paste decreases the content of calcium hydroxide Ca(OH)₂ responsible for the formation of hydrated calcium silicate (CSH), which is responsible for the strength gain of the concrete.

3.6 Characterization of permeable concrete

Figure 15a shows the SEM of the permeable concrete surface of the PC sample, where there is a rough and irregular region with the presence of many pores. Figure 15b, at point A, verified the DES of the PC sample, where the peaks of the elements, aluminum (Al), silicon (Si), oxygen (O) and calcium (Ca), characteristic for the formation of oxides in the cement paste, which give rise to hydrated silicates (CSH) and calcium hydroxide (Ca(OH)₂), for example (MEHTA, 2014). Observing a carbon peak (C) in the DES, which corresponds to the metallization tape used.

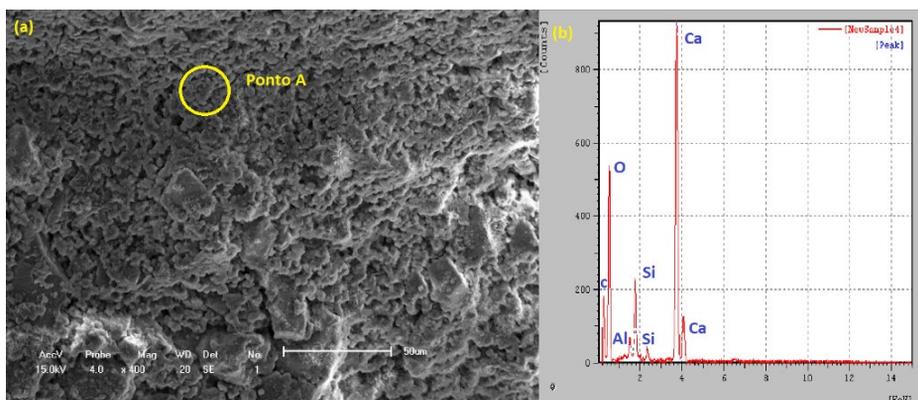


Figure 15 (a) SEM images of the permeable concrete surface increased 400 times; (b) DES analysis of the permeable concrete surface.

Figures 16a, 16b and 16c correspond to samples PC.3.TiO₂, PC.6.TiO₂ and PC.10.TiO₂, respectively. The change in the concentration of TiO₂ changed the surface of the permeable concrete, influencing the decrease in the porosity of the cement paste that surrounds the coarse aggregates in the permeable concrete, when the higher the concentration of TiO₂, a less porous surface is observed. It was not possible to identify the TiO₂ particles by SEM images because the particles in the concrete were similar to the TiO₂ particles. According to Shen et al. [6], the permeable concrete particles have a shape similar to the TiO₂ particles and their rough texture helps to camouflage the TiO₂ particles, in addition, the porosity and roughness of the permeable concrete surface allow more TiO₂ particles to have contact with UV lights and thus improve its photocatalytic properties.

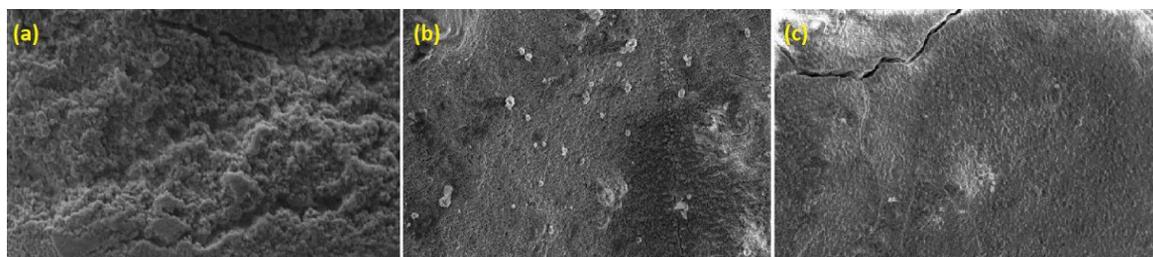


Figure 16 SEM images of the permeable concrete surface: (a) 3% TiO₂; (b) 6% TiO₂; 10% TiO₂.

DES (Figure 17) confirmed the presence of TiO_2 on the permeable concrete surface, showing peaks of titanium (Ti), calcium (Ca), oxygen (O), aluminum (Al), silicon (Si), carbon (C) and niobium (Nb). In this analysis, the metallized tape used had the chemical element Niobium in its composition, hence the presence of peaks in the DES.

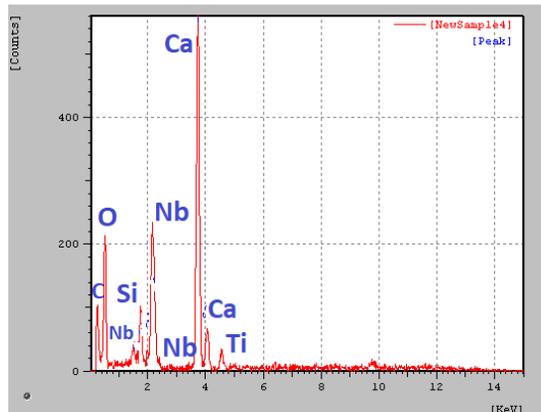


Figure 17- DES analysis of the permeable concrete surface with 10% TiO_2 .

4 CONCLUSIONS

This research studied the addition, in different concentrations, of TiO_2 in the permeable concrete to evaluate its mechanical, hydraulic, and microstructural properties to use it in the sanitary sewer system. Based on the results presented, it is concluded that:

- (a) With the increase in coarse aggregate granulometry, in mixtures containing single aggregate size, there is an increase in the value of porosity, permeability and a reduction in specific gravity, resistance to compression and flexural tensile strength;
- (b) Samples with varying granulometry, due to greater compaction, an increase in specific gravity, compressive strength, tensile strength in flexion and a decrease in permeability and porosity;
- (c) As the concentration of TiO_2 increases, up to a concentration of 6%, in the permeable concrete dosage, there is an increase in the compressive strength, flexural tension and specific mass, and a reduction in porosity. This fact occurs due to the expansion of the connection area between the cement paste and the coarse aggregate, with the addition of TiO_2 ;
- (d) The permeable concrete samples, which had 10% TiO_2 in their mixture, showed a lack of workability, with this, there was a reduction in compressive strength, flexural traction, specific mass, and an increase in porosity;
- (e) For all TiO_2 concentrations studied in this research, in permeable concrete, there was a reduction in permeability in relation to the sample containing 0% TiO_2 . However, all samples were above that required by ACI 522R-10, which establishes a minimum permeability value of 1mm/s for permeable concretes;
- (f) The increase in the concentration of TiO_2 , changes the surface of the permeable concrete, leaving the cement paste, which involves the coarse aggregate, less porous.

The permeable concrete with the addition of TiO_2 presents itself as an alternative process to assist in the treatment of sanitary sewage, but it is necessary to control its addition in order not to considerably compromise the permeability and the mechanical properties of the permeable concrete.

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