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Improvement of Compressive Strength of Concrete Prepared from High Sulfur Super Soft Cement by Using Biosynthesized Titanium Oxide Nanoparticles

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A R T I C L E I N F O

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A B S T R A C T

Abstract: Green approach of nanoparticles has received great interest for the synthesis of metal oxide. The aim of this research included the biosynthesis of titanium oxide nanoparticles using Bacillus cereus, and investigation the feasibility of using different concentrations of nanoparticles (0.5%, 1%, 5%) to improve the performance of concrete. In this work we also prepared concrete without nanoparticles as a control. The results showed that the compressive strength of concrete was increased as the dosage of titanium oxide nanoparticles increased through 7 and 28 days compared with the control sample.

1. Introduction

Nanotechnology is one of the developing and newest technologies that deal with the understanding and control of matter at the Nanoscale range between 1-100 nm which gives a result of high surface/volume ratio. This science consults different central points for many fields such as medicine, chemistry, physics, biology and engineering (Shahrokhinasab *et al.*, 2021). Nanomaterials have been used widely in civil engineering in different novel applications and also to provide materials with unique physical and chemical properties. To enhance the mechanical properties of concrete, nanoparticles were incorporated into the matrix which become a promising research field. Nanoparticles are characterized by a high surface area-to-volume ratio. They employed many types of materials which exist in the organic & inorganic modules capable to produce by different routes which can be utilized and applied widely in many fields (Mughal *et al.*, 2021). Different techniques for synthesis of nanoparticles can occur including various methods, but scientists paid more attention to using green methods or (biological synthesis), the natural eco-friendly, cost-effective and non-hazardous (Ghosal & Chakraborty, 2021).

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These nanoparticles are capable to interact with various biological molecules in different ways due to their wide choice surface functionalization and high specific area. Bacteria have a notable ability for reducing metal ions and become one of the most remarkable nominees for nanoparticle biosynthesis (Capuzzo, 2021).

Titanium dioxide (TiO2) is one of the most important chemically stable nanoparticles which received the most attention as photocatalyst and adsorbents in removing pollutants from wastewater (Verma *et al*.,2022). These nanoparticles can be biosynthesized by some microorganisms such as bacteria as a nanofactories reducing agents for development of nontoxic ecofriendly methods to produce nanoparticles. Mainly, TiO2 nanoparticles have been used as a catalyst in the organic reaction, decomposition of organic waste in water. Biosynthesis of Tio2 NPs by using bacteria has a great interest because of their unique properties and they have less aggregation behavior due to presence of more repulsive forces (Hamza and Yaaqoob,2020).

Concrete is one of the most used construction materials worldwide which involve a mixture of cement, fillers (sand and aggregates) with water (Mahmood & Kockal, 2021). Durability of concrete plays an important role when exposed to varying climate conditions, then many ways were created to improve the structure and service the life of the concrete. Using nanoparticles as additive supplementary cementations material in concrete in order to enhance permeability and compressive strength (Metaxa *et al*., 2021).

The aim of our study is to biosynthesis of TiO2 NPs using *B.cereus* and incorporated it in cementitious composites to improve their performance and enhancing the compressive strength of concrete.

2. Materials and Methods

Bacterial strains:

In this study *B.cereus* (a gram-positive bacteria) was used for biosynthesis of TiO_2 NPs. This bacterium was obtained from Bacterial Strains Bank Unit in Biology Department / College of Science / Mosul University / Mosul / Iraq .

Biosynthesis of TiO_2 NPs:

Bacterium was cultured in nutrient broth medium for 24 hrs. at 37^{o}c in an orbital shaker. Then, by using cooling centrifuge, a broth culture was precipitated at 5000 rpm for 20 min, the supernatant was filtered by Whatman filter paper no.1. 100 ml of supernatant bacteria was mixed with 20 ml of 0.025 M TiO_2 in flask and began to stirred for 60 min then the solution was heated at 60^{o}c for 30 min. A visible white deposit formed at the bottom of the flask that indicated TiO_2 NPs forming. A positive control was prepared by incubating the culture of the bacteria with deionized water while negative control contained TiO_2 solution only Figure (1). TiO_2 NPs were centrifuged at 5000 rpm for 30 min in order to study their characterization. Pellet nanoparticles were washed many times with 70% ethanol and deionized water and then dried at 70^{o}c in the oven.

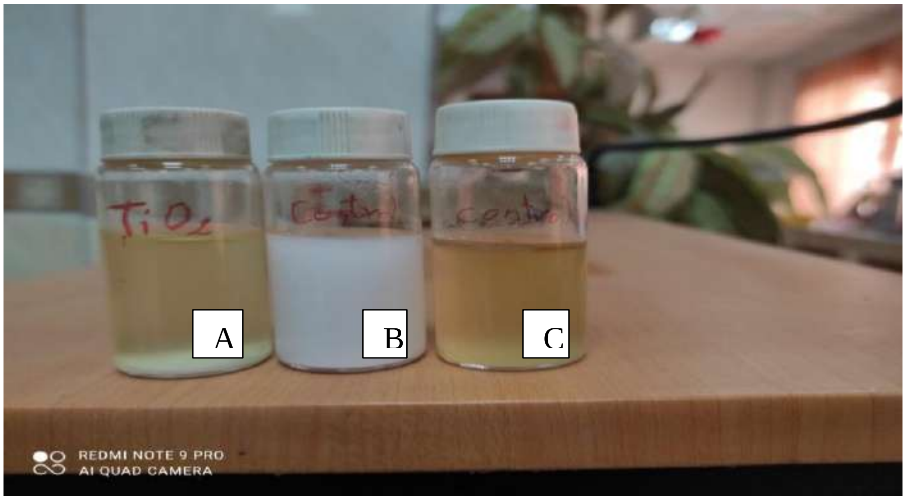


Fig. 1: Biosynthesis of TiO_2 NPs by using Bacillus cereus

A: TiO_2 NPs B: negative control (TiO_2 solution only) C: positive control (the culture with deionized water)

Characterization of TiO_2 NPs:

To study the morphology, shape, surface size and distribution of TiO_2 nanoparticles many instrumental analyses were used as follows:

Ultra Violet Visible Spectrophotometry Optima (UV spectroscopy):

Nanoparticles were emphasized by determining their absorption peaks of mixture reaction at the range (190-1100) nm using UV-light visible spectrophotometer (Hasan *et al*.,2022). Molecules absorb light at specific wavelength depends on structure, chemical nature and transition metal ions.

Scanning Electron Microscope (SEM) analysis:

Morphological and size characterization of nanoparticles, scanning electron microscopy (SEM) was used (FEI, QUANTA-250 FEG). TiO_2 NPs was examined at the University of Kofa/ faculty of Science/ Unit of Electron Microscope. Specimen were prepared by grinding or sonication of TiO_2 NPs, making a colloidal suspension of TiO_2 NPs, and adding a droplet of the suspension on fixing matrix. Sample dock then dried and examined, the imaging was at an accelerating voltage of 12.5-15 KV, low vacuum mode, a spot size 5 and working distances 5-10mm with different magnification powers.

Energy dispersive spectroscopy (EDS) analysis

Titanium nanoparticles compositional analysis was carried out with energy dispersive spectroscopy (EDS) at the faculty of Science/ University of Kofa. Point and mapping compositional analysis were examined at an accelerating voltage of 12.5-15 KV, low vacuum mode, a spot size 5 and working distances 5-10mm condition.

Atomic Force Microscope (AFM) analysis:

To study the shape of surface morphology and diameter of TiO_2 NPs AFM was used. A sufficient amount of TiO_2 NPs was sent for atomic force microscopy (AFM) at Nanotechnology Research center/ University of Technology/ Baghdad. TiO_2 NPs samples were prepared for AFM microscopy by 5 min incubation of 10 ul TiO_2 NPs with 1cm2 of freshly cleaved mica, modified by 20 min incubation with deposited of 100 µL of 0.01% APTES (3- amino propyl tri ethoxysilane) solution. After the mica was six times rinsed with 2 mL nanopore water and dried by compressed nitrogen, and placed in the AFM fluid cell holder for imaging. X- Ray Diffraction (XRD) analysis:

This pattern was recorded by using x-ray diffractometer (XRD, MiniFlex 600 Rigaku) with CuK radiation at 40 KeV in 20 range of 10-80 nm. Titanium nanoparticles were sent to Nanotechnology Research center/ University of

Technology/ Baghdad for X-ray diffraction (XRD) investigation. XRD is a common analytical technique that used for the study of both crystal and molecular structures, quantitative resolution of chemical species, measuring the degree of crystallinity, isomorphous substitutions, and identification the sizes of nanoparticles.

Fourier Transform Infrared Spectroscopy (FTIR):

This technique was performed to identify the functional groups of nanoparticles which was recorded on (Shimadzu IR-Affinity spectrophotometer), and determines the nature and crystallization activity by collecting data of the maximum values at specific lambda from absorption and reflection spectra table (1).

Table (1) The popular functional groups and their Frequencies

Functional Group	Group Frequency (cm^{-1})
-C-H (stretch)	2850-2960
=C-H (stretch)	3000-3100
≡C-H (stretch)	~3300
C=C (stretch)	1620-1680
C≡C (stretch)	2100-2260
-O-H (alcohols, H-bonded, stretch)	3200-3600
-O-H (carboxylic acids, H-bonded, stretch)	2500-3000
-N-H (stretch)	3300-3500
-N-H (bend)	~1600
C=O (stretch)	1670-1820
C≡N (stretch)	2220-2260
-S-H (stretch)	2550-2600
-S-S- (stretch)	470-620
Si-O-Si (stretch)	1020-1095
Si-O-C (stretch)	1080-1110
-N=N- (stretch)	1575-1630

3. Materials and Experimental program

Materials:

High Sulfur Resistant (HSR) super soft cement was used which manufactured by Al-Hadbaa Cement Factory. Table 1 represents the chemical composition analysis of this cement (as given by the supplier).

Table 1: The chemical composition analysis of HSR (WT.%)

MgO	SO_3	CaO	SiO_2	Al_2O_3	Fe_2O_3	L.O.I.	Total	Free lime	L.S.F.	C_3S	C_2S	C_3A	C_4Af
22.74	11.80	662.60	220.43	4.57	5.25	2.40	99.79	1.53	92	49.85	21.24	3.23	15.96

Aggregates:

Two types of aggregates were used: fine aggregates (sand) with a size 5 mm and coarse aggregates (gravel) with a size 20 mm.

Nanoparticles:

Biosynthesized TiO_2 NPs by *B.cereus* which prepared in a previous study was used.

Variables and Mix Proportions:

In total, four different mixtures were intended with different TiO_2 NPs concentrations:

0.0wt% (as a control), 0.5wt %, 1wt % and 5wt% of the total weight of the cement. The rate amount of mixture was 1wt% cement: 2wt% sand: 4wt% gravel with water-to-cement ratio (w/c) of 0.4. These mixtures were divided into two groups according to the time of measure of the compressive strength. TiO_2 NPs were added in potable water and sonicated for 10 min. The dry materials were mixed and then sonicated TiO_2 NPs was added to the mix gradually before the fresh mixtures were poured into the cube molds (10cmx10cmx10cm size). Demolding the specimens after 24 h. at room temperature and were cured in a water until the testing day .

Compressive strength test of concrete:

The compressive strength of each mortar was tested after 7 & 28 days of curing according to the standard BS 1881-116 (Minkwan *et al*., 2017), using a Toni Technic instrument (Germany).

Results and Discussion:

Biosynthesis of TiO_2 NPs:

The results showed that the TiO_2 NPS were successfully biosynthesized by the formation of a visible white deposit at the bottom of the reaction flask after 25 min of heating at 60°c as showed in figure (4). The exact mechanism of bio formation of TiO_2 NPs remains unclear (John *et al*.,2017), while (Chuc *et al*.,2022) suggest that production of TiO_2 NPs may be due to the negative electro kinetic potential which may easily attract the cations, this step may be the basis of the mechanism of biological synthesis. The proteins in the culture supernatant could have mediated the hydrolysis of anionic complexes which result in the nanoparticles synthesis (Vian *et al*.,2021). A similar study was done by Ibrahim and his authors who used *Lactococcus lactis* to biosynthesis of TiO_2 NPs, also TiO_2 NPs were biosynthesized by *Staphylococcus aureus* using $Ti(OH)_2$ 0.0025 M (Hasan *et al*.,2021).

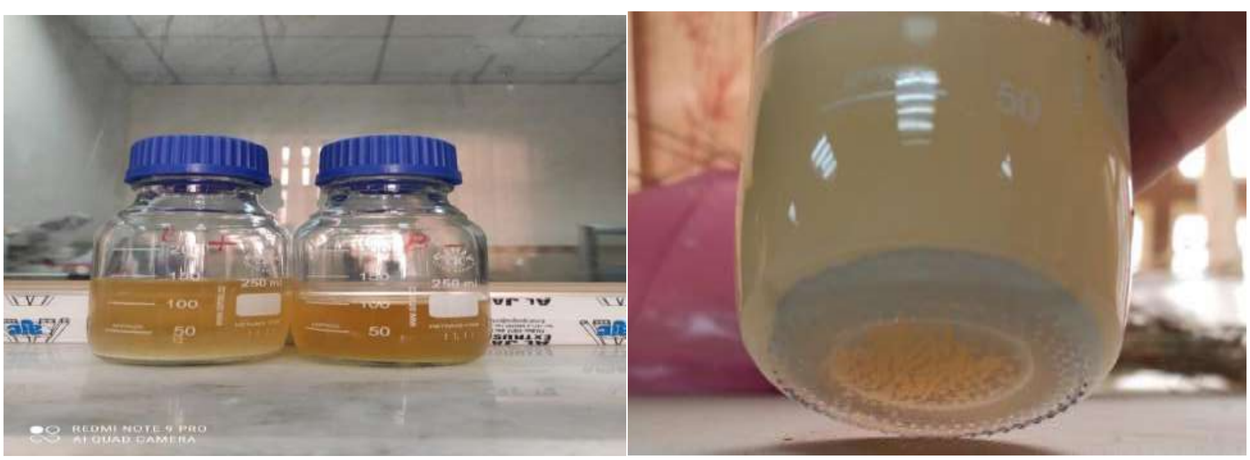
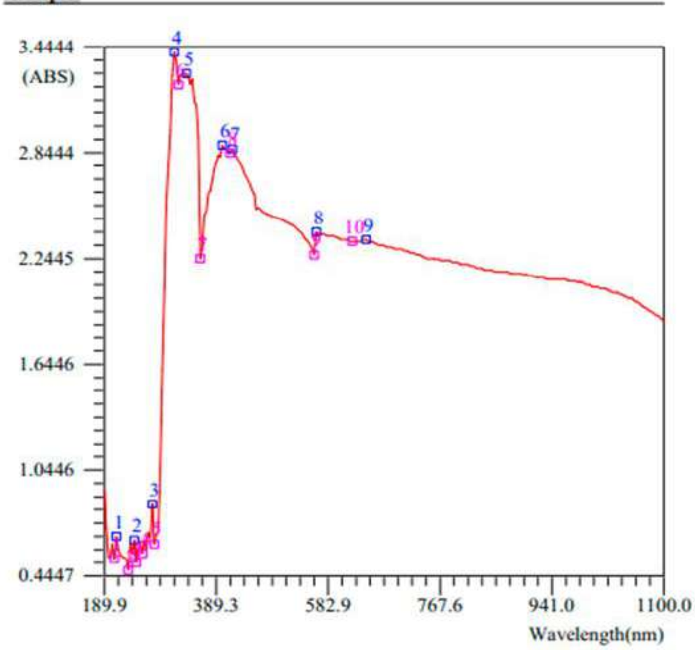


Fig. 4: TiO2 NPs Biosynthesis by *Bacillus cereus*

UV visible spectroscopy analysis:

UV analysis results showed that biosynthesis of TiO_2 NPs by using *B. cereus* was occurred Figure (5). There are many absorption peaks but the highest were at wavelength 315.12 and 336.32 nm with the values 3.4149 and 3.2966 respectively. This represents the formation of TiO_2 NPs in the reaction flask. This result was agreed with the study of (Hasan *et al*.,2022) who observed that TiO_2 NPs biosynthesis by *Staph. aureus* showed UV spectra confirming absorption peak at 324 nm., while Swathi and his colleagues suggest that UV spectra of TiO_2 NPs using *Cassia fisula* at wavelength of 350 nm. (Bekele *et al*.,2021).

Graph



Parameter settings

Function = SPECTRUM
Start wavelength = 190.0 nm
Stop wavelength = 1100.0 nm
Measure mode = ABS
Low value = 0.0000 ABS
High value = 3.0000 ABS
Scan speed = 2000 (nm/min)
Accessory = Single cell

Track data

No.	Lambda	Value	No.	Lambda	Value

Peak data

No.	Lambda	Value	No.	Lambda	Value
1	211.39nm	0.6688	2	243.71nm	0.6514
3	275.93nm	0.8546	4	315.12nm	3.4149
5	336.32nm	3.2966	6	399.93nm	2.8839
7	417.40nm	2.8629	8	562.45nm	2.3944
9	646.65nm	2.3469			

Fig. 5: UV visible spectrum analysis of TiO_2 NPs biosynthesis from *B. cereus*

SEM and EDS analysis:

Analysis of SEM revealed that TiO_2 NPs appeared in spherical shapes and agglomerated in crystallite rods as in figure (6). TiO_2 NPs was distributed uniformly with combined a smooth and rough surface. This agrees with other studies reported that suggested TiO_2 NPs were spherical or oval in shape by using *Lactobacillus* spp. (Elghwas,2018), also similar result was shown by (Hasan *et al*.,2022) who used *Staph. aureus* for biosynthesis of TiO_2 NPs.

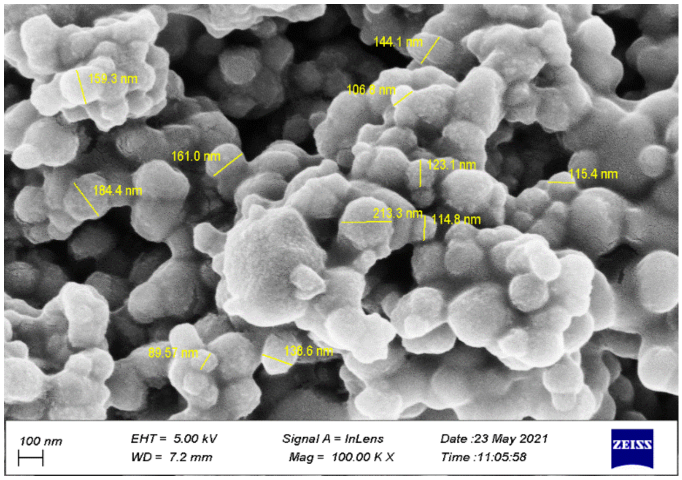


Fig.6: SEM analysis of TiO_2 NPs fabricated by Bacillus aureus

The EDS results confirm the presence of TiO_2 NPs in the suspension. The spectrum analysis revealed the appearance signals of titanium and oxygen regions. (Figure 7). Similar result was obtained by (Albukhaty *et al*.,2020) who mentioned that biosynthesis of TiO_2 NPs showed elemental composition which are identified as titanium and oxygen molecules.

Spectrum: Acquisition

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Oxygen	K-series	27.71	55.38	78.79	8.46
Titanium	K-series	22.33	44.62	21.21	1.07
	Total:	50.04	100.00	100.00	

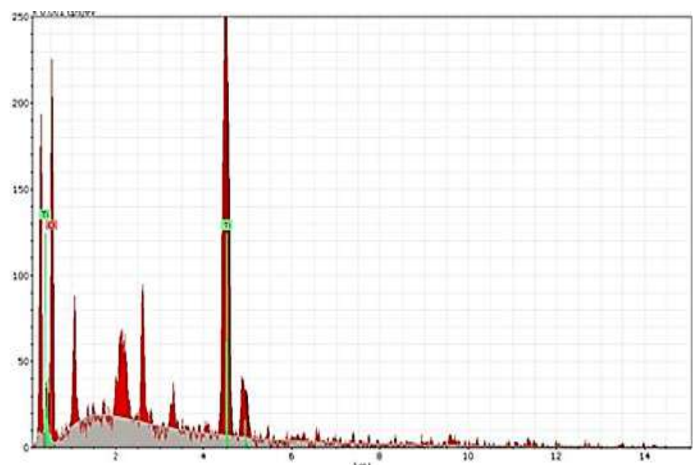


Fig. 7: EDS point analysis spectrum showing availability of TiO_2 NPs

AFM analysis:

Atomic force microscope image of TiO_2 NPs showed the data of three dimension (figure 8). It measures the height of NPs, length and width, in addition to other physical properties (morphology and surface textile) which appear to be smooth. The image displays that the photochemical are capped on the surface of the nanoparticle, therefore, it gives us the best understanding of topography and roughness of nanoparticle

(Hamza & Yaqoob,2020). The strong crystalline nature can be showed in the form of diagonal formations with ridges as show in figure (5). AFM analysis revealed that the TiO_2 NPs was in the size of 7.101 nm.

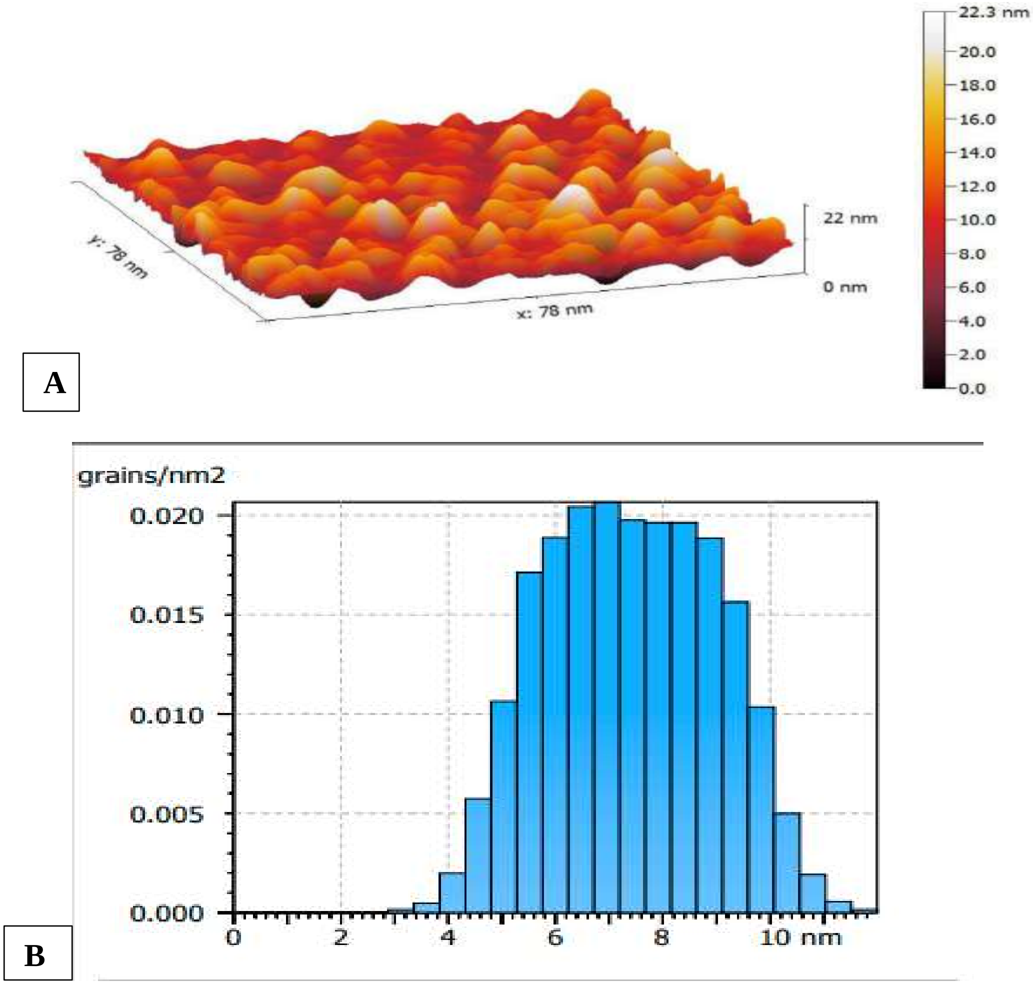


Fig. 8: AFM analysis of TiO_2 NPs fabricated by *Bacillus cereus*

A: 3D characterization B: granularity and Cumulation distribution chart.

XRD analysis:

X-ray diffraction pattern of TiO_2 NPs synthesized by B. cereus as showed in figure (9), indicates a high purity, small size, and crystallinity of sample. The intense peaks at 2θ= (25.3, 28.1, 32.4, 45.2) corresponding to around the lattice planes 101, 103, 021 and 112 respectively, that indexed as anatase phase of TiO2. This result was agreed with (Araoyinbo *et al*.,2018) who indicated that nano particle structure was correspond to anatase crystalline.

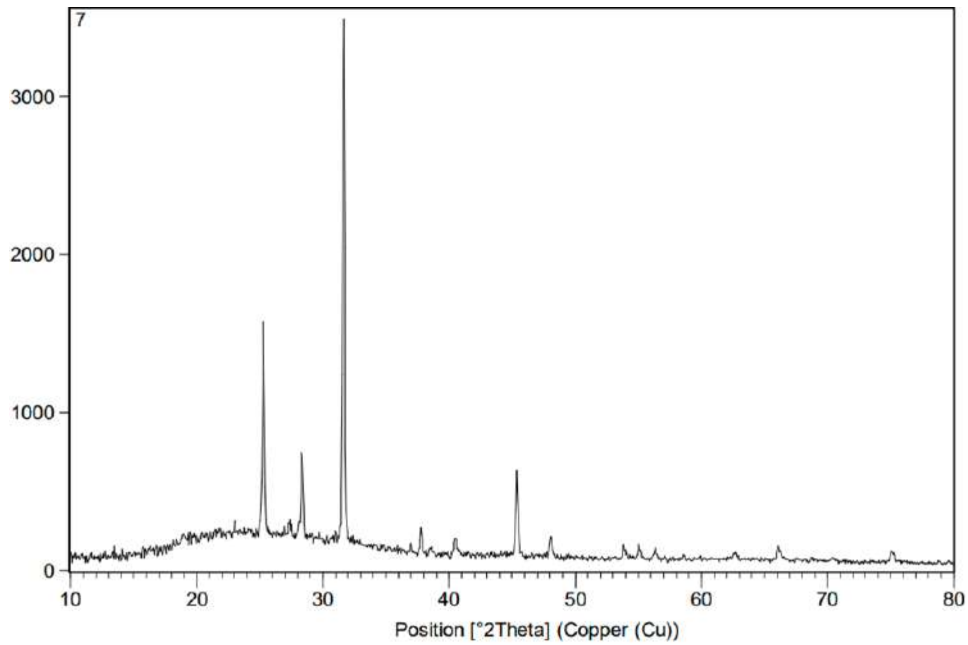


Fig. 9: XRD analysis of TiO_2 NPs

FTIR analysis:

As showed in the table (2) there are (11) different peaks which represents the presence of a broad band and many functional groups. The peak of 3851.56 cm-1 corresponds to the phenol group. Peak at 3799.04 corresponds to O-H group, while alcoholic group at the peak of 3436.24 cm-1. At 4,5,6,7 peaks the results showed the presence of many bonds of protein and peptide with nanoparticles which produced by the bacteria, while amino groups and C=C groups were due to carbohydrate and lipids. Finally, Ti-O-Ti bond was present at the last peak. Through the free amine's groups proteins which bind with nanoparticles or might help in the nucleation of nanoparticles formation figure (10).

Table (2): Peaks position of FTIR analysis of TiO_2 NPs

Peak Number	X (cm-1)	Y (%T)
1	3851.56	69.60
2	3799.04	68.97
3	3436.24	8.52
4	2956.43	56.58
5	2923.95	54.30
6	2854.13	62.71
7	2075.83	65.63
8	1633.51	26.70
9	1461.68	66.30
10	1377.08	68.04
11	710.68	55.03

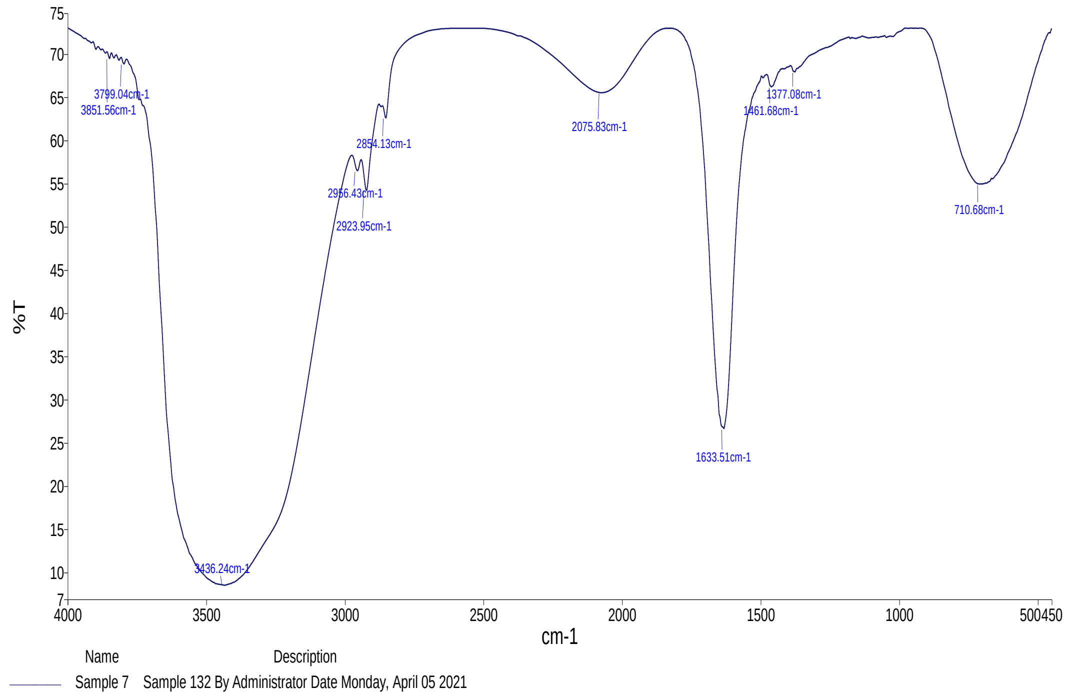


Fig. 10: FTIR analysis of TiO_2 NPs

Compressive strength test:

As showed in table (3) the compressive strength of mortars was increased as IONPs increase dosage and the best concentration was at 5wt% for both 7 & 28 days of curing. Compressive strength test was done in college of engineering/university of Mosul.

Table (3) Compressive strength of cementitious containing different dosage of TiO_2 NPs at 7 & 28 days.

Mixing mortar	7 days	28 days
Control	172 KN/mm2	235
0.5% TiO_2 NPs	235	294
1% TiO_2 NPs	265	311
5% TiO_2 NPs	305	352

TiO_2 NPs increased the compressive strength significantly by filling the gap between cement particles. These results were agreed with the results of Bhatia & Mishra (2018) who used nano iron oxide and nano silica within Portland cement for manufacture of concrete to be stronger, Kongsat and his colleagues referred that adding 1% TiO_2 NPs caused effective accelerators for cement and can enhanced its compressive strength (Sorathiy *et al*., 2017), while (Vallejos *et al*., 2021) concluded that using nano modified cement mortar composites containing 5% of TiO_2 NPs exhibited the highest compressive strength when they used different mortar composites. The TiO_2 NPs have more attention because of its highly interaction with calcium hydroxide of the cement, which result in forming hydration product to enhances the mechanical properties of the concrete. Magnetic nanoparticles considers as a key role of accelerators the hydrating the cementitious product.

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