An- Najah National University

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Graduation Project II

Enhancement of porcelain and synthesis of a new composites

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Submitted to Chemical Engineering Department in Partial Fulfilment of the requirements for Bachelor's Degree in Chemical Engineering

December ,2021

ABSTRACT

The issue of solid waste disposal is one of the most important concerns facing us in the modern era, especially those that occupy a rather large space and are difficult to dispose of. Eggshell and damaged porcelain are wastes that are produced in large quantities every year- the quantites cannot be identified because of the large types of porcelain and different load times and different quantities according to the time loading. As for eggs, a clear study of the quantities did not find, and according to the market study that conducted, the quantities differ according to the restaurant and according to the days of the week, and that summer has more consumption than winter and other considerations-. As for dental porcelain, it has become one of the most famous and most advanced fields, so that specialists in the field are always striving to find a new developed material that meets the needs. In this project, the two previous issues were combined, so that eggshell were treated by washing them, then passing through the stages of drying and grinding. The porcelain was also treated using both nitric acid by adding nitric acid to porcelain powder then drying at 120 ˚C, and treatment by adding polyethylene glycol and water to porcelain then drying at 1100˚C for 4 h, after it was ground using the Los Angeles device. Ball milling 1 and 2 was just physical mixing between porcelain treated by nitric acid and PEG – porcelain 1 and 2, respectively, TiO_2 and $CaCO_3$-EB. As for ball milling 2 and 3 they pass through 2 stages, the first stage was to produce CaO using direct thermal process, adding NaOH drop wise to $CaCO_3$-EB with stirring at 1300 rpm to get a precipitate when pH reaches 11.4 that indicates of getting $Ca(OH)_2$-, the product were filtered then calcined at 650˚C for 1h. The second stage was to mix ball milling 3 by adding porcelain treated by nitric acid and PEG – porcelain 1 and 2 respectively, TiO_2 and CaO-EB. FTIR (Fourier-transform infrared spectroscopy) analysis was made and the results showed a bonding between treated porcelain, eggshell based calcium components and TiO_2 were a different peak show a new bonding in treated porcelain. TGA (Thermogravimetry analyzer) also made for the 4 samples to analyze organic and inorganic material in different samples. The density of ball milling 1 have the higher value and also ball milling 1 have the best color compared with the other samples. Swelling test show that the samples not affected by moisture. So, in this study, synthesis of new porcelain is achieved, the best sample was ball milling 1 and

preference based on density, color and higher value of hardness, were the density was 1.43g/ml and hardness is 13.08N and 13.12N with the addition of KBr. New tests must be applied to confirm whether the porcelain is successful or not.

ACKNOWLEDGMENT

First of all, we thank God for the most mercy for enabling us to end this project in the best form that we wanted to be, we would like to thank our supervisor of this project, Dr. Amjad Elqanni for his valuable help and advice to come out with this project. We thank our faculty and doctors that provided us with all the knowledge. Most of all we are all thankful for our families for their endless love, assistance, support and encouragement. And for our friends for their understanding and support for us to complete this project.

DISCLAIMER

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Abbreviation

Porcelain 1	Porcelain treated with nitric acid
Porcelain 2	Porcelain treated with PEG
Ball milling 1	Porcelain 1 + TiO_2 + $CaCO_3$ from eggshell
Ball milling 2	Porcelain 2 + TiO_2 + $CaCO_3$ from eggshell
Ball milling 3	Porcelain 1 + TiO_2 + CaO
Ball milling 4	Porcelain 2 + TiO_2 + CaO

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2.1.INTRODUCTION

The issue of economic growth and industrialization in recent decades has brought an increase in waste generation either urban, construction, or industrial. Despite the advanced waste management and policies which have been established at the local and international levels. The impact of inappropriate waste disposal and management from various manufacturing sectors have contributed negatively to the environment resulting in soil, water, noise, and air pollution, all these add to the environmental implications (Swain et al., 2018).

A considerable quantity of solid waste is generated, some of which is partially recycled but the majority of which is disposed of in landfills, badly affecting the environment. An example of this waste is waste from tiles and eggshell that can be reused in several fields (Rivera et al., 2018).

Porcelain tiles generated solid wastes as a result of their various manufacturing methods. Recycling these wastes as raw materials is a more environmentally friendly waste management method. Because of their great technical features (Peng & Qin, 2019).

Ceramics have several unique properties that metals and other materials do not, such as a high melting point, chemical stability, brittleness, high-temperature stability, and heat and electrical insulating capacity. As a result, ceramics have a wide range of applications in the recent time, including biomedical applications (artificial bones and teeth) (Hossain & Roy, 2020).

Eggshell waste its potential use as a source of calcium (Ca) has been demonstrated since it contains $CaCo_3$. This eggshell could promote cell differentiation and increase bone mineral density, giving its potential in the treatment and prevention of certain bone diseases (Mayta-Tovalino et al., 2021)

The abundance of this amount of eggshell waste has a significant potential to be converted an use it in a different applications with a lower production cost such as medical applications (Rahim et al., 2020)

As an additive ,TiO2 nanoparticles have a high bioactivity, which promoting bone tissue proliferation on on nanoparticles and tissue adhesion to the biomaterial

interface. Because it comprises a bio-inert phase and can also be osteo-integratable to nearby tissue, titanium oxide (TiO_2) has a wide range of applications in the food, cosmetics, aerospace, and biomedical fields (Farhan et al., 2018).

Hence, in this study, the present work aims to evaluate the reuse of polished tile residues in the manufacture of dental porcelain after treatment using mechanical performance, and improvement of its properties by using Nano-titanium dioxide (TiO_2) and calcium components based from eggshell as an additive.

~~3.~~2.LITERATURE REVIEW

2.1. PORCELAIN

The manufacture of ceramic materials is one of the ancient industries that developed with the development of man, which began with pottery, which was one of the most important materials in every home, and reached the tiled tiles that we see today in several shapes and colors. Several attempts to imitate pottery, but they were not successful due to the distinctive chemical composition that gave the ceramics its distinctive interface, which was based on sand, soda and lime (Tomalino & Tulyaganov, 2021).

Porcelain is one of the building materials that have distinctive characteristics of durability, resistance to chemicals, and high hardness (Ke et al., 2016).

With the increasing need for the production of porcelain and its production in large quantities, this led to the production of large quantities of waste for porcelain, which is considered to have a great impact on the environment in terms of its difficult disposal due to the large volume of its waste.

There are several sources of irregularities from porcelain, some of which result from manufacturing processes so that it can be produced with tiles that do not conform to specifications and standards and are destroyed, or what results from transportation and distribution operations, or what results from demolition operations (Keshavarz & Mostofinejad, 2019).

The presence of such waste has led to the thought of getting rid of it, as it is considered a large waste that is difficult to deal with and affects the health and aesthetic aspects of the environment.

As for the detailed composition of the porcelain material, it consists of feldspar ($MOAl_2O_3.6SiO_2$ – M: K, Ca or Na) and kaolin, which has several properties, including that it is soft with water and hardens when it dries to the release of water from it, and it gives a glassy appearance in addition to high hardness. It also consists of SiO_2 and $MgCa(CO_3)_2$ which give porcelain the ability to melt. As for the calcite ($CaCO_3$)

compound, it gives the ability to contract when CO_2 is released from it (Hossain & Roy, 2020).

It is also known that porcelain is used in the field of dentistry, as it is a material with several compounds used to treat cosmetic or pathological conditions. Porcelain has made a revolution in modern medicine because of its great prospects for use. Therefore, the studies are seriously seeking to find new compounds that compete with the compounds circulating in the market in terms of improving the characteristics, appearance, or economic competition in terms of their price.

The composition of dental porcelain is very similar to the material of porcelain tiles, with the difference in the manufacturing process of each.

The dental porcelain material consists of clay that gives plasticity to the mixture, quartz/alumina that work as fillers and feldspar as a flux agent (Alonso-De la Garza et al., 2020).

The various processes of processing porcelain tiles may open many horizons for the use of the damaged ones in the manufacture of a new composite of dental porcelain, so that we touched on the waste resulting from the tiles, which is an economic wealth that should not be neglected.

Among the processing methods used in tiles are nitric acid treatment (Ding et al., 2021) and polyethylene glycol treatment (Ke et al., 2016).

According to PEG treatment, Shajun Ke, et al illustrated the method were the porcelain mixed with water and PEG 35% wt and 0.5% wt respectively. After that the mixture mixed 30 min then it sintered in muffle furnace at 1100-1180 for 10 min (Ke et al., 2016).

Nitric acid treatment is beginning with putting the sample in water path at 55˚C for 5 min then cleaned using distilled water and finally drying in oven at 120˚C for 4h (Ding et al., 2021).

A new composite of porcelain is tending to synthesis in this study. The Composite that consist of treated porcelain, TiO_2, and eggshell based components.

2.2. EGGSHELL

Eggs are consumed in large quantities, according to (FAO,2009) in 2008 the world egg production was almost 62 million tons, so the highly consumption leads to the accumulation of a large amount of waste. Important ingredient of an eggshell is calcium carbonate which can be potentially used in various material applications (Tangboriboon et al., 2012).

$CaCO_3$- EB can act as a reagent in carrying heavy metals from water and soil (Liao et al, 2010), eggshells are also used in the biodiesel production process by using it as a solid catalyst in the transesterification of vegetable oils with methanol (Wei et al, 2009).

So, eggshell can be used as a raw material in many applications so that reuse reduces the risks of pollution and reduces the costs of disposal, also it can be used as a cheap raw material so that calcium carbonate can be extracted and replaced with those taken from non-renewable sources (Laohavisuti et al., 2021).

2.3. NANO TITANIUM DIOXIDE IN DENTAL APPLINATION

TiO_2 have a good interest in medical field according to the different using and it have an antimicrobial effect (Gad & Abualsaud, 2019).

Nanotechnology can be defined in general as changing atomic or partial dimensions to dimensions at the nanoscale through a change in structures or systematic processing. It was defined in this book that the nanoscale ranges between 1 - 100 nanometers and in this range, nanotechnology is known (Schmalz et al., 2018).

The use of nanotechnology is increasing day by day in various fields of industrial, food, medical life, and many other fields. The use of nanotechnology provides ease of dealing with molecules, understanding their structure, and analyzing methods of chemically linking their molecules (Priyadarsini et al., 2018).

It was noted in Klaus Jandt and David Watts's research that the use of nanotechnology in the field of dentistry has increased significantly and the commercial nanomaterials used in this field have diversified (Jandt and Watts, 2020).

Interest in these materials is due to their distinctive chemical, physical and biological properties. Among the characteristics mentioned in Parel Branda et al report are long-lasting glass, improved polishability, and wear resistance (Priyadarsini et al., 2018).

So in this study, we seek to use the waste of each of the damaged ones from transporting and loading the porcelain and the waste of eggshell and treating them to make a new compound of dental porcelain compounds by adding titanium dioxide (TiO_2) using a physical method in synthesizing.

3. OBJECTIVES AND LIMITATIONS

3.1. OBJECTIVES

The objectives went to achieve by this project are:

- To treat porcelain and eggshell.
- To synthesis EB- TiO_2 porcelain composite.
- Make physical and mechanical tests.
- Ensure the success of using the physical technique by using FTIR analysis.
- Check if the samples contain organic sample using TGA analysis.

3.2. LIMITATIONS

- The obstacles are summed up in the fact that the project is new in Palestine and that there are no researches or specialists in depth in the field of porcelain in its field so that accurate numbers or clear examination methods can be obtained from them.
- The equipment needed to conduct the tests and synthesis not available.
- High prices for materials needed in the manufacturing process.
- It is unclear how many temperatures are needed in the hardening process.
- The use of porcelain tiles as an alternative to the porcelain used by dental technicians as an alternative to conducting experiments due to its high prices.
- Porcelain has many types, so it was difficult to compare the results with a specific type.
- The test approved through the dental ISO require a long time. (like absorption test, and swelling test).

4. DATA COLLECTION

4.1.EGGSHELL

Eggshell was used in the project as it constitutes a source of calcium carbonate (Habte et al., 2019). From the market study that will explained, there is a good percentage of the eggshell, which is considered organic waste so that it can be used in order for the project to be environmentally friendly. The study dealt with three governorates in the West Bank, where we took three restaurants from each governorate as a model for the study, Table 1 below illustrates the number of cartons used in each restaurant per day:

Table 1: Egg cartoons consumption in 3 cities in 1 day.

City	Number of cartoons use in 1 day		
Nablus	1-2	12-15	5-7
Jenin	3-4	2-4	2-3
Jerusalem	1-2	1-2	11-12

The calculations of the amount of waste resulting from the consumption of restaurants set in the table above are in appendix B.

4.2. PORCELAIN TILES

At the beginning of the project, the trend was to buy porcelain used by dentists, but due to its high price- 90ILS for 20gr of porcelain-, there was a need for an alternative to use it in experiments. The idea was to use the damaged tiles and treat them to obtain porcelain that is very similar to dental porcelain, so that we found that there is a great convergence between the components with different manufacturing process.

We conducted a study on tile stores, how many tiles are broken during the loading of one load, Table 2 show the numbers we obtained in each governorate:

Table 2: Waste porcelain tiles.

City	Number of tiles damaged in each load		
Nablus	112	80	68
Jenin	660	528	330
Jerusalem	8	66	12

There is a large gap between the cities taken in the study, so that Jenin is considered a city that produces and manufactures tiles. Both Nablus and Jerusalem are among the cities that depend on imports in the field of tiles. Therefore, the numbers of Jenin appeared much larger than those of the other two cities.

Therefore, the city of Jenin was taken as the main city in the study, so that the maximum percentage of damage from tiles was increased according to the increasing of manufacturing, and calculations were made accordingly.

5. MATERIALS AND METHODS

5.1.MATERIALS

Eggshells are organic waste; they used as a source of calcium carbonate. Eggshells were collected from a restaurant near the university. Waste porcelain tiles were used as raw materials, and they were obtained from a store in Nablus, and it was sourced from a Spanish company (Eco Ceramic Company).

Other materials were also used in synthesis, as shown in Table 3.

Table 3: The materials used in preparation

Materials	**Symbol**	**Manufacturer company**	**Purity (%)**
Sodium Hydroxide	NaOH	MERCK	99
Polyethylenglycol 300	PEG	MERCK-Schuchardt	99.9
Nitric acid	**HNO_3**	**Riedel-de Haen AG**	**65**
Titanium Dioxide	**TiO_2**		

5.2. METHODS

5.2.1. Waste treatment

5.2.1.1 Eggshell treatment

Eggshell are considered organic waste that is produced in large quantities, and this was observed from a statistical study that will be clarified in the previous section on the report. These wastes result in unpleasant odors and are considered a microbial pollutant to the environment. Eggshell contain calcium and magnesium compounds and other organic materials in different proportions. Calcium carbonate ($CaCO_3$) is 96% in chicken eggshell

(Tangboriboon et al., 2020), so it is economically feasible to use it as a natural and environmentally friendly source for obtaining various calcium compounds.

Chicken eggshells were collected from a restaurant near the university, then they were washed with warm water and acetic acid, and they were also cleaned with deionized water, after that eggshell drying in the drying oven at 120˚C for 24h. After the water was removed from the shells and dried for a whole day, they were ground using the manual grinder and electric spice grinder. The last step was sieving with 106µm sieve size. Figure 1 below shows the processing steps that the eggshell went through:

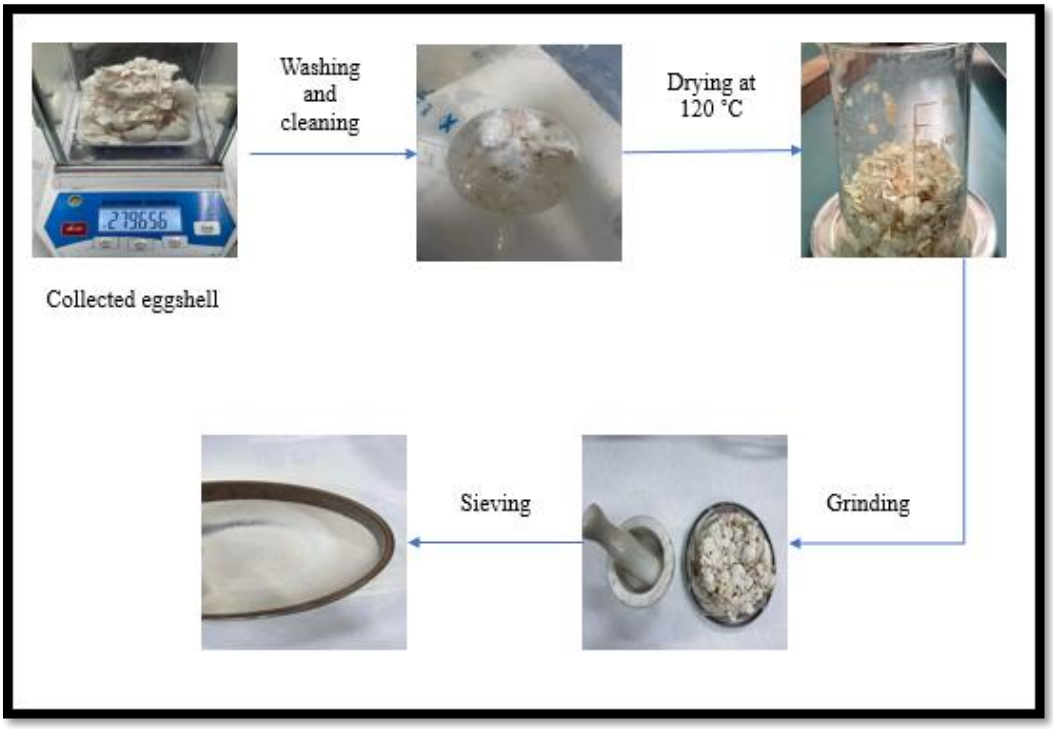

Figure 1: Schematic diagram showing eggshell treatment process.

5.2.1.2.Porcelain treatment

There are a large number of ceramic wastes from porcelain tile, which causes environmental problems. As a result, it is vital to recycle porcelain waste for the sake of the environment and to achieve a cleaner manufacturing process. the potential for using tile waste as a primary raw material.

In this project waste porcelain tiles were used as a source of porcelain, and because it contains impurities like gravel and sand, two methods of treatment for tiles were followed to study and compare which is the batter.

The aim of the treatment methods is to improve porcelain by removing impurities so that it can be used as an alternative to a material in the field.

5.2.1.2.1. Treatment of porcelain using nitric acid (HNO_3)

After the waste tiles were grinding using los angulous machine the powder produced used in the treatment methods.

As shown in Figure 2, 0.5mol/l nitric acid were added to porcelain powder, then they well stirred and agitated for 5 minutes at 55°C. after that, the powder was carefully washed with deionized water before being dried in a 120° C oven for 4h.

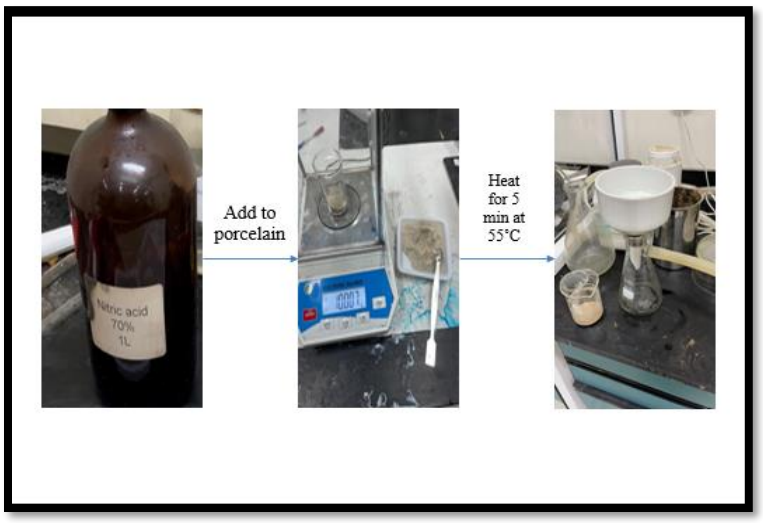

Figure 2: Schematic diagram showing the treatment steps for porcelain tiles with nitric acid.

5.2.1.2.2. Porcelain treatment with polyethylene glycol (PEG)

This sample prepared by milling the raw materials with 35 wt.% of water and 0.5 wt.% of polyethylene glycol. The sample was sintered in muffle furnace 1180°C for 10 min at a heating rate of 20 °C/min.

5.2.2 Methods of EB-TiO2 porcelain composite

5.2.2.1 Direct thermal

Many methods for preparing calcium hydroxide ($Ca(OH)_2$) were used, such as sol-gel, water in oil microemulsion, sonochemical and many other methods (Mirghiasi et al., 2014). These metods and other have many disadvantages that make them a bad method to synthesis $Ca(OH)_2$, as they take a lot of time to get the product and expensive as they need high temperature and special equipment. direct thermal decomposition recommended as a simple method which it do not need long time and can use in large scale (Mirghiasi et al., 2014).

CaO will be used to enhancement porcelain, so this method is happened as the reaction:

$$CaCO_3 + 2NaOH \rightarrow Ca(OH)_2 + Na_2CO_3$$

From the process that will illustrate a white precipitate appear ($Ca(OH)_2$). Fig 3 below shows how the process happened and when the reaction stopped, 0.5M $CaCO_3$ aqueous solution using eggshell as a source and 1M NaOH aqueous solution was prepared, the reaction happened with heating using hot plate at 80 ˚C and rapid stirring reach to 1300 rpm with N_2 flowing on the surface (Mirghiasi et al., 2014).

Figure 3: Schematic diagram shows direct thermal process and signs of end the reaction..

Upon preparation using direct thermal process, for getting the product, the steps are explained below through Figure 4:

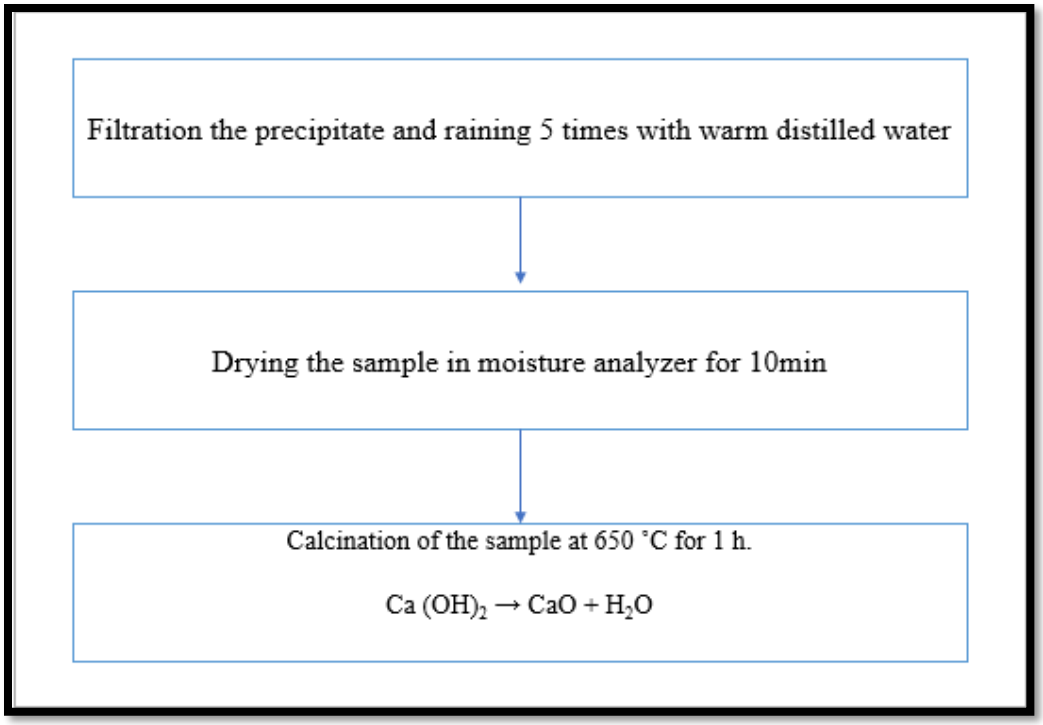

Figure 4: Sample preparation for calcium oxide production

After producing CaO ~~produced~~, ball milling method was the next step, an illustration of ball milling method will be in the next section.

Ball milling.

A typical comminution method for achieving sub-micron-sized powder, used in many industrial applications, it is a useful technology for synthesizing because its cost is low that depends on replacing expensive biomaterial products with less expensive alternatives, quick turnaround time, and simple method.

Physical mixing between all the ingredients went to achieve using this technique. Where the addition was according to the following proportions 10:3:1:1 for balls, porcelain, TiO_2, and $CaCO_3$ or CaO in arrangement. Fig

5 illustrate the 4 samples were applied by this method:

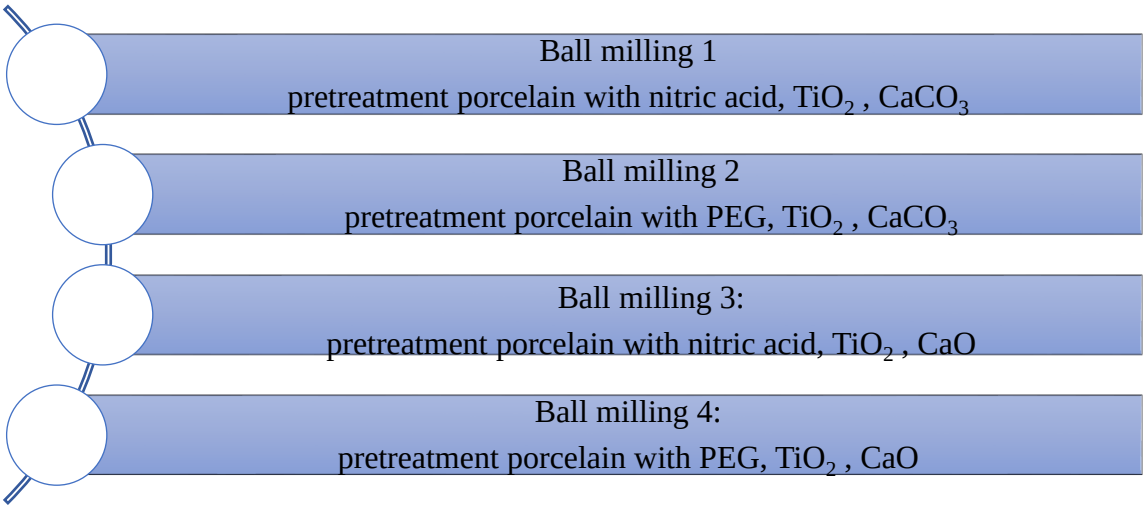

Figure 5: Ball milling samples prepared.

4 samples prepared by placing the required quantities and 10 stainless steel balls with a diameter of 10 mm inside a steel cylinder with an inner diameter of 100 mm, and after closing it we wrapped it well so that it does not open during the process, the cylinder put inside the available ball milling machine (los angelus machine)with an inner diameter of 710 mm, and set it at a rotation speed of 450 rpm for 15minutes.

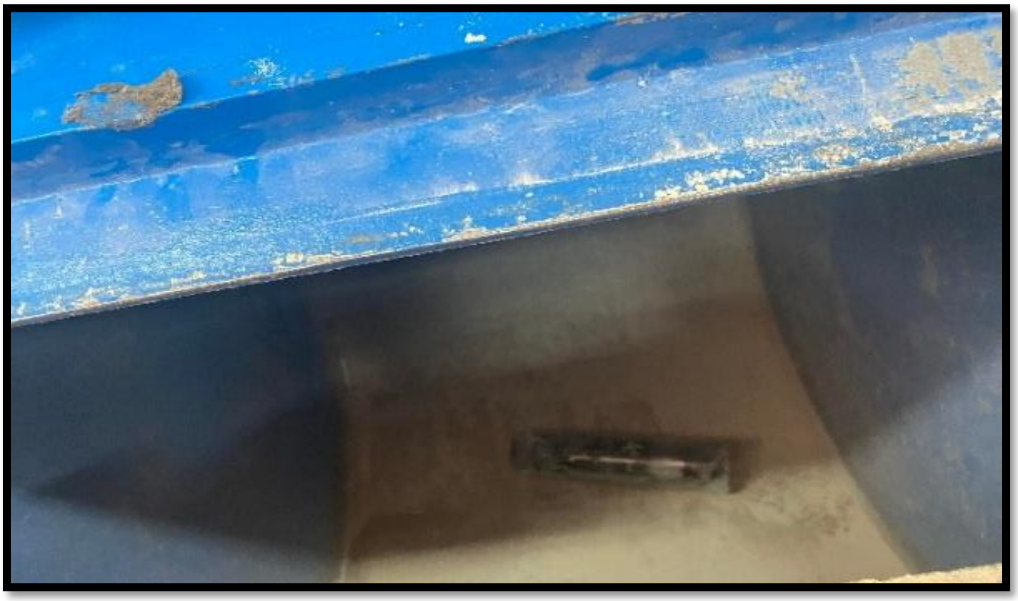

Figure 6: Steel cylinder inside ball milling machine.

5.2.3 FTIR and TGA analysis

5.2.3.1.FTIR

FTIR spectroscopy is a technique that depends on determining the interaction between IR radiation and a sample that can be solid, liquid or gaseous. It measures the frequencies at which the sample is sucked and the intensity of absorption. The frequencies help determine the chemical composition of the sample because the chemical functional groups are responsible for absorbing radiation at different frequencies. The concentration of the component can be determined based on the intensity of absorption. The spectrum is a two-dimensional diagram in which the axes are represented by the intensity and frequency of absorption of the sample (Farrukh, 2012)

FTIR is the preferred method for infrared spectroscopy for several reasons including: it does not destroy the sample, it is much faster than the old techniques, and it is more sensitive and accurate (Hospodarova et al., 2018).

5.3.2.2.TGA

Thermal gravimetric analysis is a technique by which a mass of a substance is monitored as a function of temperature or time as a sample is subjected to a controlled temperature program in a controlled atmosphere. Thermogravimetric analysis consists of a sample vessel supported by a fine balance. This pan is in the oven and is heated or cooled during the experiment (Zainal et al., 2021).

Its primary uses include measuring the thermal stability of a material, the filler content in polymers, the moisture and solvent content, and the percentage composition of the components in a compound (Zainal et al., 2021).

TGA is performed by gradually raising the temperature of a sample in the oven, where its weight is measured on an analytical balance that remains outside the oven. Mass loss is observed if the thermal event involves the loss of a volatile component. Chemical reactions such as combustion involve mass loss, while physical changes such as dissolution do not. The weight of the sample is plotted against the temperature or time to show the thermal transitions in the material (Menczel & Prime, 2009).

6. RESULTS AND DISCUSSION

First of all, the name of the project is changed We believe that the desired mechanical properties were not achieved and we could not examine them properly for reasons that will be clarified later, but we succeeded in making a new porcelain composite that can be developed in future projects.

6.1. FTIR ANALYSIS

The figures 7-10 below show the infrared spectra (IR) of treated porcelain 1 and porcelain 2 and the 4 ball milling composites. In Figure 6 ball milling 1 shows a new signal in 550 and 1400, that shows a new bond build in the composite, IR at 550 cm^{-1} could be assigned to the appearance of TiO_2(Al-Taweel & Saud, 2016)-, and the IR spectra at 1400 could be assigned to $CaCO_3$-EB (Jitjamnong et al., 2019). For ball milling 2 the same peaks appear in Figure 7 at 550 cm^{-1} and 1400 cm^{-1} because of the presence of TiO_2 and $CaCO_3$-EB, respectively. In addition,

Figure 8 shows ball milling 3 that contains porcelain 2, TiO_2 and CaO so the expectations is to see a peak for TiO_2 and CaO-EB and that was~~'s~~ evidenced~~true~~ in the IR signal~~fig~~ at 550 cm^{-1} for TiO_2 and signal at 1460 cm^{-1} for CaO-EB. The same expectations are for ball milling 4 where it has the same additions so the IR spectra in Figure 9 shows a signal at 550 cm^{-1} that could be for TiO_2 and a signal at 1460 cm^{-1} that show a new bond from CaO-EB (Al-Taweel & Saud, 2016) (Jitjamnong et al., 2019).

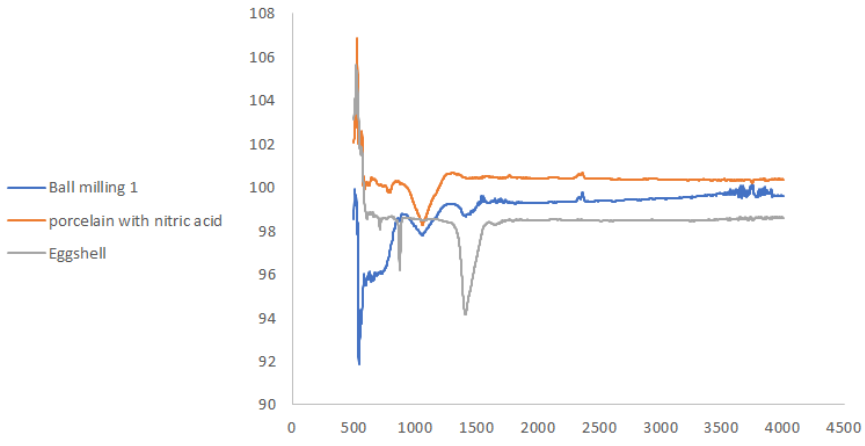

Figure 7: Infrared spectra of ball milling 1 composite.

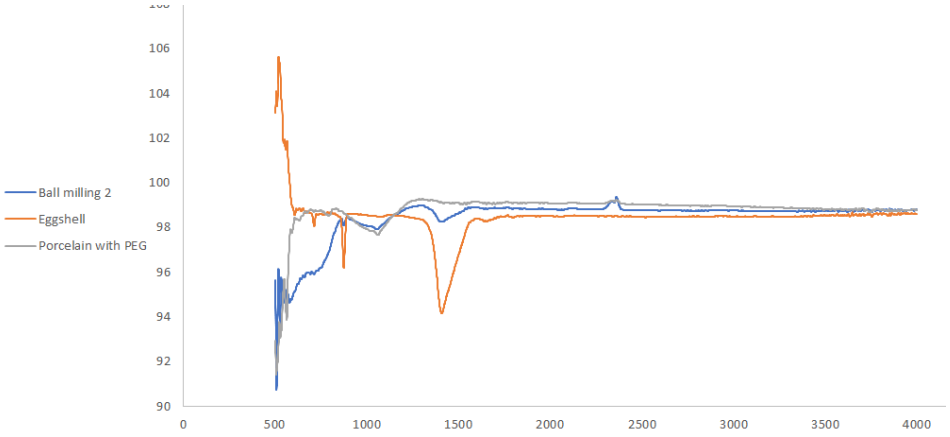

Figure 8: Infrared spectra of ball milling 2 composite.

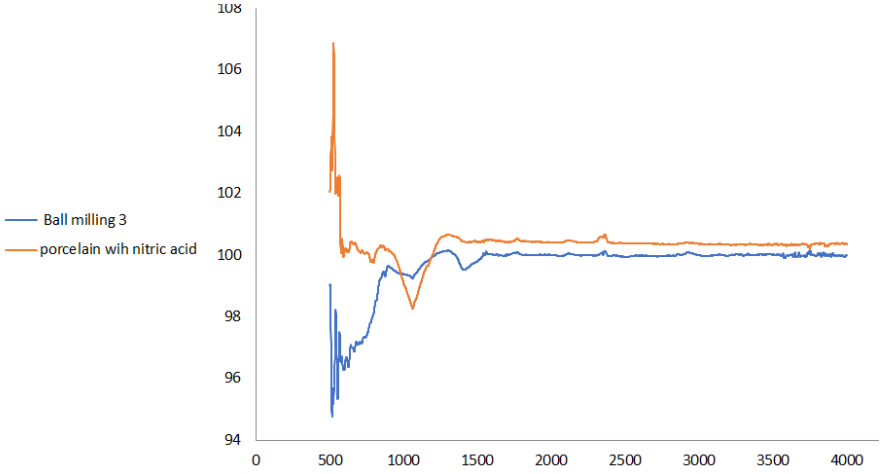

Figure 9: Infrared spectra of ball milling 3 composite.

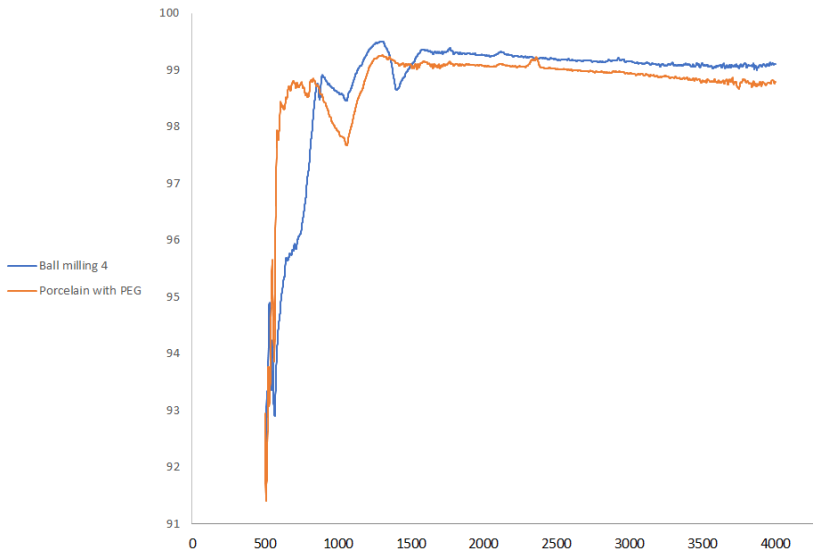

Figure 10: Infrared spectra of ball milling 4 composite.

The results of the FTIR analysis showed that the physical mixing – Ball milling- of the different compounds was successful, as the new compounds showed the presence of the added groups. As for Porcelain 1 and 2, it was expected that the functional groups of nitric acid would appear in Porcelain 1 and the appearance of PEG functional groups in Porcelain 2, but the high temperatures to which they were exposed led to a change in the composition of the two basic compounds, so that the treatment processes may have led to a change in the arrangements of the groups, but the desired physical mixing was achieved and the addition of the added compounds was linked (Xu et al., 2003) (Flores et al., 2013).

6.2.~~5.2.~~ TGA ANALYSIS

The thermal analysis results are shown in Fig 11. There were no clear differences between any of the four samples. In the TGA curve, mass decrease abruptly at any time, because it continued occurring along the path for each sample approximately from (12.1 to 700) C˚, that is why the determination of the thermal degradation range of each blend is complicated because of the overlapping of peaks of each original material. As the figure shows that the orange curve is the lowest among all the other three curves, and the reason is that there are more organic compounds (from PEG), and this led to a large loss in mass, where the mass percentage was from 100% in the beginning and reached 80.45% at the end of the analysis.

As for the rest of the curves, their mass percentage was as follows: In the blue curve, which expresses the treated eggshell, the mass percentage reached from 100% to 83.89%. In the gray curve, the mass percentage reached from 100% to 86.65%. Finally, the yellow curve, which expresses the lowest mass loss rate, has reached the mass percentage from 100% to 90.29%. So, the larger mass loss in porcelain treated with PEG and the additive is TiO_2 with $CaCO_3$ is an evidence of having more organic compounds than other samples due to the presence of PEG in the composite. Other samples show las losses which is expected as they contain more inorganic compounds in their structure.

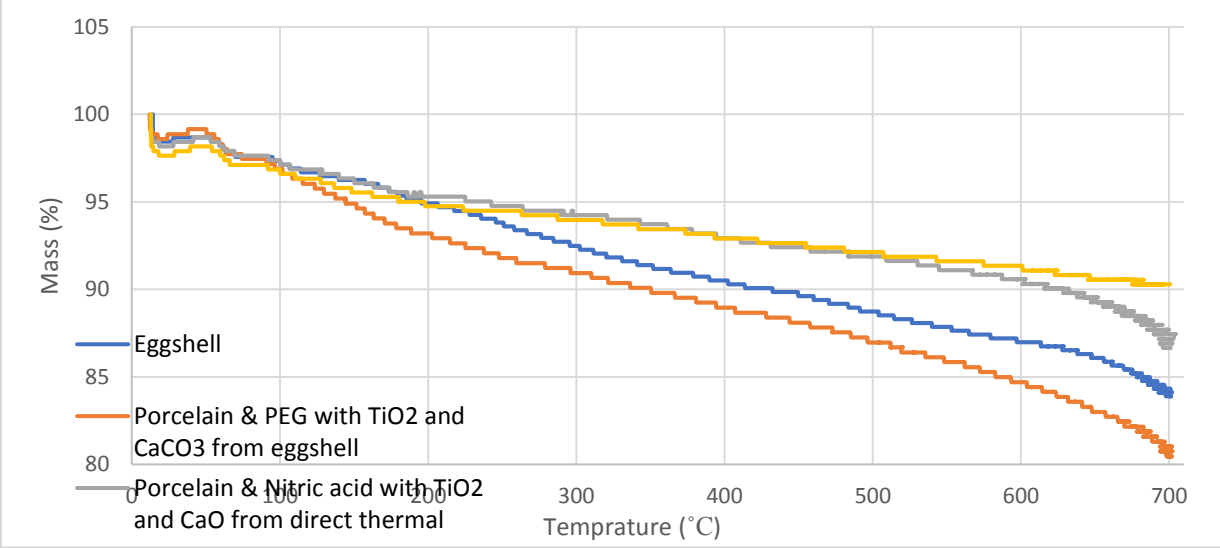

Figure 11: TGA curves of porcelain 2, eggshell, ball milling 2 and ball milling 3 at a heating rate of 10˚C/min.

6.3. PHYSICAL AND MECANICAL TESTS

The study of both physical and mechanical properties is an important part of observing the effects of this study and knowing whether this study has achieved the desired effects or not.

Among the physical properties that were chosen in this study were density and swilling. As for the study of mechanical properties, hardness have been studied, it considered important test for dental porcelain. There was a tendency to conduct the compression test, but the samples did not have sufficient hardness to conduct this examination, in addition to

the lack of a device for examining small disks, so that the disks on which the hardness was examined were 15 mm in diameter, and approximately 1 mm in thick. These tests and their characteristics will be clarified in later parts of the report.

6.3.1. Density

One of the physical properties that it is important to address in order to analyze the compounds produced is density.

Density was measured roughly by weighing the compounds approximately 5 gr for each sample, then placing them in a graduated tube and pressing them as much as possible, then measuring their volume so that:

$$\rho = \frac{mass}{volume}$$

Through Table 4 below show the density values that were practically obtained through the equation above:

Table 4: Mass and volume values for new composites.

Sample	Mass (g)		Volume (ml)	
	Trial 1	Trial 2	Trial 1	Trial 2
Ball milling 1	2.451	5.024	2.000	3.500
Ball milling 2	2.400	2.390	2.200	2.200
Ball milling 3	2.400	3.000	2.390	2.200
Ball milling 4	1.662	5.016	2.000	5.700
Porcelain	2.417	5.007	2.000	5.000

A weight was taken from each sample and placed in a graduated tube and pressured so that it does not have spaces and occupies a full space, which is considered its size. Volume measurements were taken and the experiment was repeated again for each sample to ensure accurate results were obtained. Then the density was calculated from the relationship shown previously, so that the density values for each value are recorded in table (5) below:

Table 5: Density values of new composites.

Sample	Density	
	Trial 1	Trail 2
Ball milling 1	1.226	1.435
Ball milling 2	1.091	1.086
Ball milling 3	0.800	0.824
Ball milling 4	0.831	0.880
Porcelain	1.002	1.208

Ball milling 1 has a higher density than the rest of the samples in both experiments and compared to the density of porcelain, which is (2.4 – 2.9) (Rizkalla & Jones, 2004) it is pretty good.

Since the density is high, this ensures that there are fewer voids between its molecules, which constitutes greater cohesion.

6.3.2. Swelling test

Swelling occurs as a result of absorbing a large amount of water, causing harmful pressure within it, damaging the surrounding tooth material. That is why it is necessary to know the ability of the material to swell in order to determine the damage at this point.

0.5 g of each sample was weighed, and 15 ml of deionized water was prepared for each sample, then 0.5 of each sample was gradually added into the designated graduated cylinder for this sample. All samples were left in deionized water for 24 hours at room temperature (Deboucha et al., 2020).

After the end of the allotted 24 hours, there was no significant change in the level of any one of the samples inside the deionized water. There was no swelling, as is the case with the PEG-treated porcelain sample, and the other sample treated with nitric acid. This indicates that the samples are not affected by moisture, so will not pose any danger, as it is

very little and negligible. The following figure shows how the four samples looked after the specified 24 hours. Where the level of any of the samples in the deionized water did not change from the level it was in the beginning (McCabe & Rusby, 2004).

(Sample.4) (Sample.3) (Sample.2) (Sample.1)

Figure 12: swelling test results.

6.3.3. Hardness test

One of the available tests that we have the ability to conduct it, is the hardness test. 8 samples are tested, 4 samples are the 4 ball milling samples, and the rest of samples are the 4 ball milling samples with KBr at ratio (1:1) the disks made using KBr piston that use for FTIR analysis then the hardness test made using tablet hardness analyzer.

Table 6 below shows the results that we obtained from the hardness test, as they are much less than expected. according available information the hardness should range between 50-70 N. The reason for the low hardness could be due to the lack of exposure of the discs after squeezing to sufficient heat so that a preliminary examination was conducted for ball milling 1 before being placed in the oven for 4 hours, it showed a hardness of 3N.

Table 6: Hardness test results.

Pure samples		Samples with addition of KBr (1:1)	
Sample	Hardness value (N)	Sample	Hardness value (N)
Ball milling 1	13.08	Ball milling 1	13.13
Ball milling 2	11.78	Ball milling 2	13.13
Ball milling 3	12.50	Ball milling 3	13.08
Ball milling 4	10.27	Ball milling 4	13.11

7.CONCLUSION AND RECOMMENDATIONS

This study presents experiments for the manufacture of dental porcelain, so that we were directed to the use of solid waste as a source of the raw material, as a tendency to reduce the waste resulting from eggshells or damaged tiles.

1. The process of treatment both eggshells and porcelain were successful, as we obtained the desired compounds from eggshell. As for the porcelain, a powder was obtained after the treatment processes.
2. Eggshell produce 67.88% $CaCO_3$ of its weight after treatment.
3. As for the stages of synthesis the composites, the analyzes of FTIR and TGA showed that it was as desired and FTIR show that the physical mixing was enough.
4. Ball milling 1 give the best color, compared to other components that had a darker color.
5. As for the density, ball milling 1was somewhat close to the density value of porcelain.
6. According to swelling test the samples not effected by moisture because there was no significant change in the level of any one of the samples.
7. Hardness value for ball milling 1 = 13.08 N its less than expected.

Nevertheless, here we recommend the following for any future work on this project:

1. Conduct experiments by changing temperature when drying samples.
2. Conduct absorption test that need long time to achive-168 days-.
3. Make a control sample from commercial porcelain and compare the results got from the project with it.
4. ANOVA analysis to detect the perfect percent weight should be added to enhance porcelain.
5. Conducting more tests on sample number one so that it showed the best results in all respects.

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APPENDIX A

These figures show the apparatuses used in preparation and treatment methods.

Fig 12 shows the muffle furnace-(MS8-36 Laboratory burnout furnace (Electrotherm marketing-ShenPaz Technologies, Ramat Gabriel Industrial Park Migdal HaEmek) -that used for prepare PEG samples at high temperatures.

Figure 13: MS8-36 Laboratory burnout furnace.

Fig 13 show the drying oven that used in eggshell treatment, direct thermal process and porcelain treatment by nitric acid.

Figure 14: Drying oven.

Fig 14 shows the los Angeles machine that used to prepare the ball milling samples and grinding for tiles that use as a source of porcelain it used as substitute of the original ball milling machine.

Figure 15: Los Angeles machine.

The vacuum filtration machine use to wash porcelain treated with nitric acid by water.

Figure 16: Vacuum filtration machine.

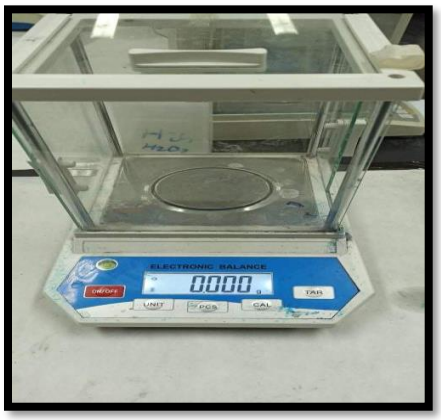

Figure 17: Analytical balance

The mixer in Fig 17 used in the preparation of direct-thermal samples, it used at 1300 rpm.

Figure 18: Mixer.

In direct thermal process it is important to know when the precipitate appear, so pH meter shown in Fig 18 is used to detect the appearance of CaO at pH = 11.2.

Figure 19: pH meter.

APPENDIX B

Eggshell:

Some assumptions were taken during the calculation:

Weight per egg = 50 g.

The number of restaurants that consume eggs =100

We took 6 days a month when the restaurant was not working or working less than other days so factor 0.2 is used.

The accounts are built on the basis of the highest and lowest consumption value.

$$weight\ of\ eggs\ in\ one\ cartoon\ = weight\ of\ one\ egg\ \times number\ off\ eggs$$

$$= 50\ \times 30$$

$$= 1500\ g = 1.5\ kg$$

$$weekly\ consumption$$
$$= weight\ of\ eggs\ in\ one\ cartoon$$
$$\times maximum\ number\ of\ egg\ cartoons\ used$$

$$= 1.5\ \times 15$$

$$= 22.5\ kg$$

$$monthly\ consumption = 22.5\ \times 30\ day$$

$$= 675\ kg$$

Take factor 0.2 from the monthly consumption

$$= 675\ \times 0.2 = 135\ kg$$

In all restaurants in the study

$$= 135\ \times 100 = 13500\ kg$$

For the six major governorates of Palestine

$$= 6 \times 13500 = 81\ ton$$

In one year

$$= 81\ \times 12 = 972\ ton$$

5 years accumulation

$$= 972\ \times 5 = 4869\ ton$$

The quantity of eggshell collected in one day from Hazem Restaurant = 279.5 g

Weight of egg shell after drying = 142 g

Amount of eggshell processed = 96.4 g

Approximately 67.88 % $CaCO_3$ from the original weight of waste eggshell

From this percent we can say that its economically viable to take this waste as a source of $CaCO_3$

These calculations are based on the consumption of eggs by restaurants, but the large quantities generated by bakeries, cake shops, sweets and homes cannot be neglected.