Efficient Management of Egg Shell and Conch Shell Wastes by Utilization as Bio-Fillers in Eco-Friendly Gypsum Mortar

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Abstract: The efficient waste management and recovery of waste materials are the most important goals of sustainable environmental development. The egg shells and conch shells are solid wastes being deposited in enormous amount which creates large disposal problem. In order to examine the possibility of utilizing these wastes for use in building materials the egg shell and conch shell powders were used as partial replacement for the manufacture of eco-friendly bio mortars. The mechanical characterization of the bio mortar produced by substituting finely ground egg shell and conch shell powder at various percentages were quantitatively investigated. The present research work was executed in two groups—the first group of bio mortar consists of raw egg shell and conch shell powder and the second group consists of thermally treated egg shell and conch shell powder as a partial substitute for binder. The results showed that the untreated egg shell and conch shell powder did not cause much improvement in the strength parameters of bio mortar whereas the thermally treated egg shell and conch shell substituted mortar exhibited a significant improvement in the mortar strength. The scanning electron microscopy images also reveal the denser and compact structure of mortar which supports the filling effect caused by these wastes. This improvement in strength was due to the calcite present in the egg shell and conch shell powder. The calcite traces were further confirmed by the FTIR and XRD studies. Thus the usage of these waste materials as binder reduces the manufacture of cement which minimizes the environmental pollution by mitigating the CO$_2$ emissions.

Keywords : egg shell powder; conch shell powder; thermal treatment; calcite; bio-mortar; pollution abatement.

I. INTRODUCTION

The eggshells are the most common aviculture by-product that seriously contributes to the environmental pollution as they promote microbial action [1]. The disposal of egg shells are usually a very complex problem that contaminates the environment and also dumping of these wastes leads to the inefficient utilization of the space used as disposal site [2,3]. Nearly millions of tons of egg shell wastes are being generated manually from several industries [4]. Though the egg wastes are non-toxic and non-hazardous the direct disposal of these wastes into the environment undergoing microbial degradation thereby attracting worms leading to potential health hazards [5]. The egg shells possess good strength characteristics and the addition increases the strength of the concrete [6-9]. The use of egg shells also increases the durability of concrete to a greater extent [10-13]. The ever-growing increase in the shell wastes from the aquaculture industries demands the need for finding alternative ways to efficiently incorporate these shell wastes for commercial usage [14, 15]. Hence the use of these shell wastes as a building material can be an economical solution to solve the problem of disposal [16]. The conch shells are one of the commonest sea shells mainly found in coastal region [17] and their disposals also causes serious environmental problems [18]. Several previous works have yielded significant results by using waster shell powders as a substitute for cement [19-20] and aggregate.

The manufacture of cement increases the release of carbon-di-oxide which is the major green house gas. Hence there is a growing interest to reduce the CO$_2$ emission by using alternative construction material as binder instead of cement. The gypsum mortar is an efficient substitute for cement to be used in internal plastering and several other structural applications. Gypsum based mortars contributes significantly towards the society and hence are generally known as ‘green cements’ [21]. The construction industry are in thrive search for low cost building material which can reduce the construction budget without compromising the strength and stability of construction industry.

The calcium carbonate is the most widely used filler material in bio mortars. The higher cost of fine grade of calcium carbonate is considered to be a drawback to be used as building material in higher ways of producing magnitude. Hence the cheaper ways of producing calcium carbonate to reduce the cost as well as to modify the strength parameters of the bio mortars are under progress. The eggshell and conch shell are the commonest source of calcium carbonate commonly known as calcite. This mineral of calcium carbonate is highly stable at room temperature and can be used as an alternative construction material. The objective of this work is to evaluate the mechanical behaviour of egg shell and conch shell powder used as replacement for binders in bio mortar at various percentage levels. Initially the strength parameters of the bio mortar manufactured using egg shell and conch shell powder without subjected to any treatment were investigated.

Secondly the performance of thermally treated eggshell and conch shell powder...
incorporated powder bio mortar were evaluated. X-ray diffraction studies, Fourier transform Infra Red spectroscopy and SEM imaging was done to investigate the chemical composition and surface morphology of the eco-friendly bio mortar manufactured with eggshell and conch shell as bio filler.

II. MATERIALS

The commercially available hemi hydrate plaster obtained from the local manufacturer is used as a binder for the production of mortar. The technical data sheet provided by the manufacturer indicated that the plaster mainly consists of (CaSO₄ ½ H₂O) calcium sulphate hemi hydrate. The raw eggshells were collected from the local food processing industry and the conch shells were collected from the nearby coastal regions. The shells were rinsed thoroughly with distilled water to remove the dirt and other residual matters attached to the shell. These shells were then dried under hot sun for about 24 hours to remove the moisture content. The dried shells were then hammered to form coarsely crushed shells. They were then finely ground using ball mill for about six hours. These shell powders were then made to pass through 750 micron sieves. The particle size distribution of the shell powder has obtained from particle size analyzer is shown in fig 1. These finely powdered shells are referred as raw egg shell and conch shell powder. The raw egg shell and conch shell powder were thermally treated at 300°C for 2 hours and this treated egg shell and conch shell powder is referred as treated egg shell and conch shell powders respectively.

Fig. 1. Particle size distribution of egg shell powder and conch shell powder

III. MATERIAL CHARACTERIZATION

A. Thermo Gravimetric Analysis (TGA)

Simultaneous thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) experiments were performed on powdered egg shell and conch shell powders to evaluate the weight change and monitor their purity levels and thermal decomposition behavior. The instrument was a Perkin thermal analyzer. The temperature ranged from room temperature to 900°C, using a heating rate of 10°C/min under a nitrogen atmosphere. The sample loading was approximately 100 g of each powder loaded in an alumina crucible.

The thermo gravimetric analysis was done for evaluating the thermal stability of the raw egg shell and conch shell powders. The weight loss of the samples as a function of temperature range from 100 - 900°C is shown in fig 2. It can be clearly observed that the weight loss decrease slowly at the temperature of range 100 – 600°C where as the quick loss of the weight was observed at the temperature range of 600-800°C. The initial loss weight may be due to the presence of water molecule and molecules like CO and CO₂ in organic protein materials. The rapid loss of weight at the temperature range of 600 – 800°C may be due to the release of carbon dioxide from the carbonates present in the shell. The thermo gravimetric curve showed the continuous annealing of the shell powders at a temperature from 100 – 900°C which transforms carbonates to oxides and hence no loss of weight is observed above 850°C. Thus the thermo gravimetric curves obtained by heating the egg shell and conch shell powders were almost similar to commercial calcium carbonate which further confirms the presence of calcium carbonate by the phase transformation of calcium carbonate to calcium oxide.

Fig. 2. TG - DTA curves of raw egg shell powder and raw conch shell powder

IV. METHODOLOGY
A. Mix Proportion
The proportions for the bio-mortar mix are obtained by varying the percentage of raw and thermally treated egg shell and conch shell powder as partial substitutes for gypsum binder in the mortar. The egg and conch shell powder is replaced as 5, 10, 15 and 20% of the total binder content. A total of 5 samples were casted for each proportion of egg and conch shell powder replaced mortar and the average value of the five specimens were taken as result. The specimen designation for different proportion of egg and conch shell is shown in Table II.

Table-I: Composition of raw materials (Oxide %)

<table>
<thead>
<tr>
<th>Oxides (%)</th>
<th>Gypsum Hemihydrate</th>
<th>ESP</th>
<th>CSP</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>2.746</td>
<td>5.772</td>
<td>4.591</td>
</tr>
<tr>
<td>CaO</td>
<td>37.068</td>
<td>92.818</td>
<td>95.020</td>
</tr>
<tr>
<td>SO₃</td>
<td>60.185</td>
<td>1.257</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>0.152</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-</td>
<td>0.388</td>
<td>-</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>2.57</td>
<td>48.1</td>
<td>48.9</td>
</tr>
</tbody>
</table>

The curing of the produced plaster specimens were done at 70°C moisture. The SEM images were obtained about 7 days and then dried in oven at 40°C for 2 hours to attain a maximum homogeneity.

Table-II: Specimen Designation and Mix Proportion

<table>
<thead>
<tr>
<th>Raw Egg Shell (RES)</th>
<th>Raw Conch Shell (RCS)</th>
<th>Burnt Egg Shell (TES)</th>
<th>Burnt Conch Shell (BCS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>10%</td>
<td>10%</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>15%</td>
<td>15%</td>
<td>15%</td>
<td>15%</td>
</tr>
<tr>
<td>20%</td>
<td>20%</td>
<td>20%</td>
<td>20%</td>
</tr>
</tbody>
</table>

The repair mortar was manufactured by substitution of the main binder by ESP and CSP.

B. Mixing Methods
The coating of shell powders by the gypsum binder is an essential parameter that determines the strength of gypsum plaster. The shell powders should also be uniformly distributed in the gypsum matrix and must be well compact in nature to achieve a compact gypsum plaster mix the shell powders and the gypsum binder were initially hand mixed in dry state to attain a maximum homogeneity.

C. Casting of Specimens
To determine compressive strength of the bio mortar, 50x50x50 mm cubes specimens were tested. The specimens used in flexural process were prismatic of size 160x40x40 mm. The size of cylindrical sample used in the split tensile is 100 mm length with 50 mm diameter.

D. Curing conditions
The curing of the produced plaster specimens were done at room temperature for about 7 days and then dried in oven at 40°C ± 2°C for 2 hours to remove the external moisture.

V. EXPERIMENTAL TECHNIQUES
A. Compressive Strength Test
The compressive strength test was performed on the 50x50x50 mm cubical mortar specimens. The load is applied at a uniform rate of 1 KN/min until the test piece was broken. The breaking load was noted and the crushing strength was calculated from the formula as per the Indian standard [33]:

\[
\sigma = \frac{W}{A}
\]

Where, \( \sigma \) = compressive strength in MPa
\( W \) = total load in N at which the specimen failed
\( A \) = average of the gross areas in mm of the top and bottom side surface of the specimen subjected to load.

B. Three Point Flexural Test
The flexural testing was done on the specimens of size 160 x 40 x 40 mm under three point loading condition. The maximum load F reported by testing machine was noted and the flexural strength of the specimen was evaluated, using the relation stated in the Indian standard [33]:

\[
f = \frac{3Fl}{bd^2}
\]

Where, \( l \) = distance of the loading point
\( b \) = width of specimen
\( d \) = thickness of specimen

C. Split Tensile Test
The split tensile tests were conducted on the cylindrical specimens of size 100 mm length with 50 mm diameter. The test was carried out by placing the cylindrical specimens horizontally between the loading surfaces of a compression testing machine and the load was applied until failure of the cylinder along the vertical diameter. The following equation is used to find the split tensile strength:

\[
\text{Split tensile strength} = \frac{2P}{\pi DL}
\]

where \( P \) = split tensile load
\( D \) = diameter of the cylinder

D. X-Ray Diffraction studies
XRD analysis of thermally treated eggshell and conch shell replaced bio mortar samples was identified using the X-ray Diffractometer which operated at a voltage of 45 kV. The patterns were recorded at 20 intervals ranging from 10° to 70° using Cu-Kα radiation. The crystalline composition of the produced plaster mixes were identified using XRD patterns.

E. FTIR Spectroscopy
The functional groups and the chemical bonds present in the plaster mixes were characterized using FTIR spectroscopic analysis. The spectral curves obtained from FTIR analysis of the thermally treated egg shell and conch shell powder containing samples were analyzed using Shimadzu IR tracer to detect the presence of carbonates.

F. Scanning Electron Microscopy
SEM images helps to analyze the grain structure and distribution of shell powders. The SEM images were obtained by scanning the specimens using SEM Zeiss EVO, Japan.

VI. RESULTS AND DISCUSSIONS
The egg shell and conch shell powders rich in calcium carbonate is used as partial replacement of gypsum based bio mortar exhibited the following test results.

A. Bulk Density
The bulk densities of...
gypsum based bio mortar manufactured by using raw and thermally treated egg shell and conch shell powder are shown in fig 3.

It can be observed that the egg shell powder replaced bio mortar exhibited higher density values but the conch shell powder replaced mortar specimens exhibited decreasing density values than the reference mortar. This may be attributed to the fact that the conch shell powder has a lower density compared to the egg shell powder. The decrease in density of the bio-mortar may be the consequence of replacing the higher density gypsum plaster with the lower density shell powder. It is also clearly shown that the raw egg shell and conch shell powder substituted bio mortar showed comparatively higher density which may be due the presence of moisture and biological residue in the untreated shells.

Fig. 3. Bulk density of egg shell and conch shell powder containing bio-mortar

B. Compressive strength

Fig 4 shows the compressive strength of the bio-mortar using egg shell and conch shell powders as partial substitutes for binders. The compressive strength of the bio-mortar which was obtained without the replacement of gypsum by egg shell and conch shell powders is taken as reference. The raw egg shell powder and conch shell powder without any treatment caused a negative influence on the compressive strength of gypsum based bio mortar. The initial replacement level of 5% has a little positive impact on the compressive strength whereas the further replacement levels of gypsum by egg shell and conch shell powders caused a negative impact causing a wide decrease in the compressive strength of the bio mortar. The compressive strength decrease of the raw egg shell and conch shell substituted bio mortars may be due to the fact that the natural layers of the egg shell and conch shell were not completely removed since they were not subjected to any treatments. This may cause the inability of the egg and conch shell powder to react with the bio mortar thus maintaining its inert nature. When the gypsum in the bio mortar was substituted by the egg shell and conch shell powder which were thermally treated to a temperature of about 300ºC caused a positive influence on the compressive strength of the bio mortar. This temperature for thermal treatment of the raw egg and conch shell powder was done as per the previous established research works which stated that the fine grade calcite can be obtained by heating the egg shells to a temperature of 300ºC [3]. This shows that the increase in compressive strength of the gypsum based bio mortar due to the pure calcite obtained from egg and conch shell powder after subjected to heat treatments. Moreover it can also be explained that the removal of the external biological layers of egg and conch shell powders after subjected to thermal treatments made these powders become chemically active for the efficient participation in the mechanical strength enhancement.

Fig. 4. Compressive strength of egg shell and conch shell powder containing bio-mortar

C. Flexural strength

Fig 5 shows that flexural strength of the bio-mortar using egg shell and conch shell powder as a partial substitute for binder. It can be observed that the flexural strength increase steadily with the increasing content of thermally treated egg shell and conch shell powder whereas the bio-mortar with raw egg shell and conch shell powder were found to exhibit lower flexural strength due to the non removal of their inert biological layer. The significant increase in the flexural strength of the bio-mortar can be attributed to the filler effect of the treated egg shell and conch shell powder. Moreover the dominating calcium carbonate content in the filler leads to the formation of strong interfacial bond between the binder and filler thus leading to an effective stress transfer from the binder to the filler.

Fig. 5. Flexural strength of egg shell and conch shell powder containing bio-mortar

D. Split Tensile strength

Fig 6 shows the variation of splitting tensile strength of the bio-mortar with varying contents of egg shell and conch shell powders. It can be observed that the presence of egg shell and conch shell powders has no significant role to play in the improvement of splitting tensile strength of mortar. The strength variation was observed
to be minimal due to the treated egg shell and conch shell powders while the raw shell powder substitution led to decrease in the splitting tensile strength of bio–mortar.

![Fig. 6. Splitting tensile strength of egg shell and conch shell powder containing bio-mortar](image)

**E. FTIR**

The FTIR Spectra graph for the gypsum bio mortar by substituting 15 % (weight of binder) thermally treated egg shell and conch shell powder is shown in fig 7. The dominating band of carbonate was observed in the spectrum and shows that the bio–mortar contains a higher amount of calcium carbonate and therefore seems to dominate the structure of the mortar. The absorption bands of carbonate at their corresponding wave numbers as indicated in the fig 7 have features similar to the carbonate ions present in calcium carbonate [34, 35]. This agrees well with the above stated results by confirming the presence of calcite in the bio mortar. Moreover the large OH stretching band appears around 3400 cm\(^{-1}\) shows the presence of water present in the dihydrate crystal indicating the well formed gypsum by the hydration process.

![Fig. 7. FTIR spectra of Thermally treated egg shell powder and conch shell powder substituted bio-mortar](image)

**F. XRD**

The X – ray diffraction patterns of the bio – mortar manufactured using 15% (weight of binder) thermally treated egg shell and conch shell powder are shown in fig 8. From the graph it can be observed that the characteristic peak of calcite appears as prominent peak. The dominating peaks representing the presence of calcite are indicated in the fig 8 which shows that the analyzed bio – mortar contains a greater amount of calcite. This is in line with the above experimental results which stated that the increase in strength of the bio – mortar was due to the presence of calcite.

![Fig. 8. XRD patterns of Thermally treated egg shell powder and conch shell powder substituted bio-mortar](image)

**G. SEM**

Fig 9 shows the morphology of the 15% (weight of binder) substituted thermally treated egg shell and conch shell powder bio – mortar. The SEM images show the presence of cube like calcite crystals spread over the needle like gypsum matrix. The images also reveal the dense and compact structure of the bio – mortar due to the effect of egg shell and conch shell powders that filled the interspatial pores which substantially led to the increase in the strength of the mortar.

![Fig. 9. SEM images of Thermally treated egg shell powder and conch shell powder substituted bio-mortar](image)

**H. Regression Analysis**

In order to analyze the relationship between various strength parameters of the mortar the regression analysis was performed on the results obtained from various experimental procedures.

Fig 10 shows the relationship between the compressive strength and the flexural strength of the bio – mortar. The relationship between the compressive strength and the bulk density of the bio – mortar.
is shown in fig 11. From the experimental results the relationship between each strength parameter with the predicted model and the obtained regression coefficient are shown in table III and IV. The higher values of correlation coefficients were obtained which shows that the experimental data best fits the proposed model.

**Table- III: Relationship between compressive and flexural strength of bio – mortar**

<table>
<thead>
<tr>
<th>Mix</th>
<th>Predicted Equation</th>
<th>Regression coefficient ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RES</td>
<td>$y= 1.406x-4.721$</td>
<td>0.984</td>
</tr>
<tr>
<td>RCS</td>
<td>$y= 1.765x-7.656$</td>
<td>0.913</td>
</tr>
<tr>
<td>TES</td>
<td>$y= 1.106x-2.340$</td>
<td>0.925</td>
</tr>
<tr>
<td>TCS</td>
<td>$y= 0.886x-0.196$</td>
<td>0.942</td>
</tr>
</tbody>
</table>

**Table- IV: Relationship between compressive strength and bulk density of bio – mortar**

<table>
<thead>
<tr>
<th>Mix</th>
<th>Predicted Equation</th>
<th>Regression coefficient ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RES</td>
<td>$y= -8.523x+20.40$</td>
<td>0.922</td>
</tr>
<tr>
<td>RCS</td>
<td>$y= 10.17x-4.691$</td>
<td>0.733</td>
</tr>
<tr>
<td>TES</td>
<td>$y= -24.65x+41.78$</td>
<td>0.982</td>
</tr>
<tr>
<td>TCS</td>
<td>$y= -17.37x+31.71$</td>
<td>0.737</td>
</tr>
</tbody>
</table>

**Fig. 10.** Relationship between compressive and flexural strength of Raw egg shell and conch shell powder substituted bio- mortar and Thermally treated egg shell and conch shell powder substituted bio- mortar

**Fig. 11.** Relationship between bulk density and compressive strength of Raw egg shell and conch shell powder substituted bio- mortar and Thermally treated egg shell and conch shell powder substituted bio- mortar

**VII. CONCLUSIONS**

Nowadays there is a growing concern for the search of locally available waste materials as a substitute for conventional building materials due to the negative impacts caused by the cement and cementitious materials on the environment. With this view this experimental study was conducted on the potentials of using waste egg shell and conch shell powders which are causing environmental nuisance as valuable filler in the manufacture of bio- mortar. From the experimental results obtained it can be concluded that the shell powders when thermally treated to a temperature of about 300°C can be used as a perfect substitute for binder materials in the production of bio mortar. The addition of these thermally treated shell powders also promoted the strength of the mortar due the calcite present in the egg shell and conch shell powders which were confirmed by the XRD and FTIR patterns. The use of the thermal treated egg shell and conch shell powders also drastically reduced the density of the mortar thus proves to be advantageous for use in light weight construction and manufacture of less dense building products. Thus it can be concluded that the bio- mortar manufactured by the use of thermally treated egg shell and conch shell powders which does not require complex processing technique proves to be an ideal and economic replacement for gypsum mortar meeting the design requirements as well as reducing the environmental pollution.

**REFERENCES**

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