

Economic Impact of Value Addition to Sri Lankan Rock Phosphate Deposit: A Non-renewable Phosphate Source

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Abstract- Worldwide rock phosphate deposits are a kind of non-renewable natural resources, which do not regenerate themselves over humanly meaningful time spans. Obtaining the right compensation as a resource-related wealth is a timely requirement. Current study discusses both the economic importance and impact of value addition to Sri Lankan Eppawala rock phosphate via innovative commercial products. Rock phosphate has been value-added into Hydroxyapatite bio ceramic chemically, their properties were analyzed under several characterization techniques, their composites were processed to obtain improved properties via incorporating with liquid monomers and costs analysis were performed to obtain economic validity. Results were compared and contrasted with raw materials, human hard tissues, and commercial products. Results show that novel products can be applied directly as bio ceramic materials due to their close chemical, structural similarity to human hard tissues than commercial products. Considering better performance, eco-friendliness, and novel composites can be introduced to global market with high value.

Index Terms- Sri Lankan Rock Phosphate, Eppawala, Natural Resources, Orthopedics, Dentistry, Biomedical applications

I. INTRODUCTION

A part of the real wealth of nation is natural resources including both renewable, non-renewable resources and ecosystem services. Contribution of this natural capital towards income, poverty reduction and fiscal revenue, led to buildup other forms of capital.^[1]

Worldwide rock phosphate deposits are those kinds of non-renewable natural resources, which do not regenerate themselves over humanly meaningful time spans. Therefore, we as humans should have a responsibility to manage those non-renewable natural resources in a fruitful manner sustainably. Researchers show that the worldwide poor natural resources management led less developed countries to loss of income.^[2,3,4]

Sri Lankan rock phosphate deposit situated at Eppawala within North Central province, also a that kind of non-renewable natural resource which contains nearly 34 - 40% P₂O₅. Eppawala phosphate deposit covers an area of around 6 km with containing around 60 million metric tons of phosphate, while only about 1.4 million metric tons out of the entire phosphate deposit has been utilized by Lanka Phosphate Ltd. (LPL) and Government institutions from 1976 to 2019 period of time. Also, International

Fertilizer Development Corporation has been stated that cadmium and arsenic contained generally in phosphate are present in insignificant levels in this deposit (cadmium composition at 0.0005%), which isn't in harmful condition to humans.^[5,6]

Currently, this natural resource use only as the raw material for fertilizer industry, while there are so many ways to manufacture value added phosphorus products in a sustainable way. Therefore, it is important to give consideration for invent and commercialize novel phosphorous findings from Eppawala rock phosphate deposit. As a result, current paper discusses both the economic importance and impact on value addition to Sri Lankan Eppawala Apatite, natural resource into innovative commercial products to get much better foreign income into the country and by doing, improve living standards in Sri Lankan Citizens.

Researchers perform several studies on value addition to Eppawala rock phosphate. Many of them have proven that Eppawala Chloroapatite can be converted directly into Hydroxyapatite ceramic by replacing its Chlorine positions with Hydroxyl groups as its structure under strain. Varying some physiological conditions including temperature, acidic and alcoholic environment (different PH conditions) can be used to increase reactivity of these reaction mechanisms.^{[7]-[17]}

Hydroxyapatite (HAp) is a bio ceramic which has a close chemical and structural similarity to mammalian hard tissues. It's having a hexagonal crystal structure and chemical formula can be written as Ca₁₀(PO₄)₆(OH)₂ with Ca/P ratio 1.67. As a bio ceramic, Hydroxyapatite can be applied into variety of biomedical applications including orthopedics and dentistry fields, considering its properties such as biocompatibility, bioactivity, osteoconductivity, non-toxicity, etc. It is widely using for bone and dental implants, implant coatings for metallic implants, bone tissue engineering, bone void fillers, maxillofacial and dental surgeries, restoration of periodontal defects, Edentulous ridge augmentation, Endodontic treatments, post teeth bleaching, toothpastes etc.

While there are so many synthesizing methods to convert apatite into hydroxyapatite solid-state sintering technique and sol-gel alcoholic and acidic routes have used to synthesize Eppawala Hydroxyapatite ceramic. Furthermore, its properties have improved by incorporating with two different liquid monomers which are used in the commercial products.

Mainly, this study aimed to brief out the economic impact of synthesizing and commercializing ceramic composite products

for biomedical applications using Eppawala rock phosphate as the raw material.

II. METHODOLOGY

I. Product synthesis and characterization

A. Product synthesis and characterization

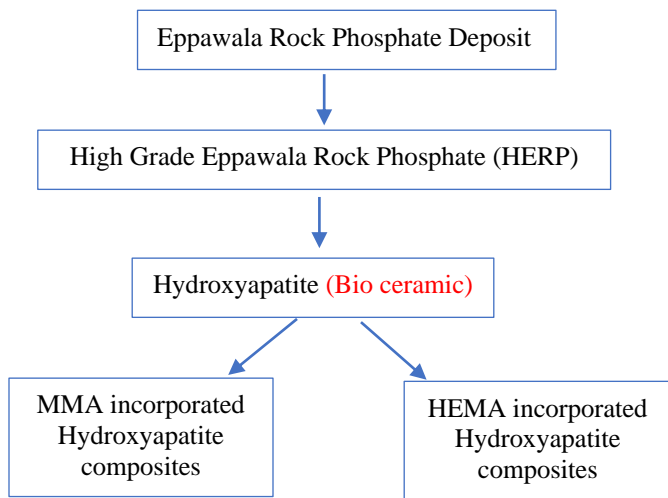


Figure 1. Processing Eppawala ceramic composites for orthopedic and dentistry applications

Eppawala Rock phosphate deposit produces two main types of apatite as High grade Eppawala Rock Phosphate (HERP) with 38% P_2O_5 and Eppawala Rock Phosphate (ERP) with 28% P_2O_5 . Among them, HERP was subjected to this study as the raw material considering high percentage of P_2O_5 .

As mentioned in the Figure 1 Eppawala High Grade Phosphate rocks (HERP rocks) were sort out from the deposit, after removing mud and drying under sun light, it was crushed into powder using a jaw crusher and a ball mill. Powdered and sieved apatite was heat treated and used for solid state sintering and sol gel processes. Preprocessed HERP powder was reacted with acid, alcohol and base under sol-gel technique acidified and alcoholic routes and solid-state sintering to obtain Hydroxyapatite ceramic. [7,8]

Next those synthesized products were characterized using X-ray fluorescence Spectroscopy (XRF), X-ray Powder Diffraction (XRD), Scanning Electron microscopy with Energy Dispersive spectroscopy (SEM with EDS), Thermogravimetric Analysis (TGA), Fourier-transform infrared spectroscopy (FTIR) etc. to find out chemical structural morphology of products and to confirm the Eppawala Hydroxyapatite formation from Eppawala rock phosphate.

Synthesized Eppawala Hydroxyapatite ceramic products were further incorporated with liquid monomers to obtain more properties as bio ceramic composites. Methyl methacrylate (MMA) monomer is widely used acrylic resin in a variety of medical, dental, and industrial applications. Selected commercial product for orthopedic applications (fast curing bone cement)

also majorly consists of zirconium dioxide as the ceramic and a liquid monomer methyl methacrylate (MMA). Therefore, in this study MMA was incorporated with synthesized Eppawala Hydroxyapatite ceramic products to obtain ceramic composites as a substitute for bone cements. [18,19]

Selected commercial product as a dental filling material, as Glass Ionomer Cement (GIC) majorly consists of fluoroaluminosilicate glass and 2-hydroxyethyl methacrylate monomer (HEMA). Therefore, dental composite materials were prepared using HEMA as the liquid monomer, widely used in dentistry applications [20,21]

As the next step, raw Eppawala High Grade Rock Phosphate (HERP), synthesized Eppawala Hydroxyapatite ceramic products, MMA incorporated Eppawala Hydroxyapatite ceramic composite and HEMA incorporated Eppawala Hydroxyapatite ceramic composite, human tooth, human bone and currently clinically using bone cements and dental filling materials were analyzed using several characterization techniques including X-ray fluorescence Spectroscopy (XRF), X-ray Powder Diffraction (XRD), Scanning Electron microscopy with Energy Dispersive spectroscopy (SEM with EDS), Thermogravimetric Analysis (TGA), Fourier-transform infrared spectroscopy (FTIR) etc. [9]-[17]

II. Cost analysis of value-added products

Next raw material costs, novel product manufacturing costs and commercial products market costs, income of currently producing fertilizer were analyzed and w.r.t. commercial products novel product manufacturing profit were calculated. Finally, results were compared and contrasted with each other.

III. RESULTS AND DISCUSSION

A. Resulted value added Eppawala Hydroxyapatite ceramic and its composite products

A.1. Synthesized Eppawala Hydroxyapatite ceramic products

As the first step, three types of Hexagonal, Hydroxyapatite bio ceramic products named Solid state sintered Eppawala Hydroxyapatite (SSHAp), Sol gel Acidified Hydroxyapatite (SGHAp1) and Sol gel alcoholic Hydroxyapatite (SGHAp2) were successfully invented using Eppawala High Grade Rock Phosphate (HERP).

XRF results for all three products has shown that Ca, P and O include in higher weight percentages. Fe, Al and Si present as the impurities. Solid state products contain more Ca than Sol gel products and that may occur due to the addition of Calcium hydroxide base in the Solid-state product synthesis.

XRD and FTIR results have confirmed formation of hexagonal hydroxyapatite in the synthesized products as well as in the human bone and tooth. XRD results carried all characteristic peaks related to the crystallographic phases 002, 210, 211, 112, 300, 202, 310, 222, 213 and 004 of hexagonal Hydroxyapatite and FTIR results interpret peaks at $(560-640) \text{ cm}^{-1}$, 963 cm^{-1} and $(1028-1110) \text{ cm}^{-1}$ for phosphate groups together with the characteristic peak for hydroxyl group in the hydroxyapatite at broad envelop between the 3200 cm^{-1} to 3700 cm^{-1} wave number

range. Absence of that characteristic peak at 3200 cm^{-1} to 3700 cm^{-1} in the raw apatite and presence of that peak in the synthesized products and human hard tissues confirm the formation of Hydroxyapatite under the three routes.

When comparing TGA results of human bone, human tooth and synthesized Hydroxyapatite products least amount of weight loss can be found in the synthesized HAp product samples than human hard tissues. As a result, it can be concluded that the synthesized products perform high thermal stability and good material stability in nature and application.^[8,9]

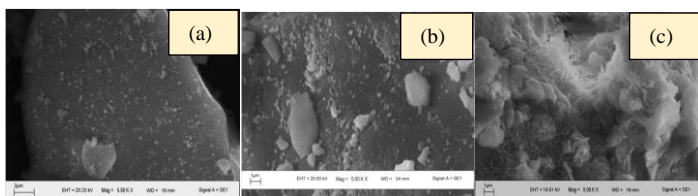


Figure 2. SEM images for Synthesized Hydroxyapatite products, 20 kV,5kX (a) SSHAp product (b) SGHAp1 product (c) SGHAp 2 product^[9]

Microstructural differences between synthesized products can be observed in the figure 2. SEM images. SSHAp and SGHAp1 consists of micro pores which may lead to improve osteoconductive property in the bio ceramics. SGHAp2 product consists of special cylindrical /needle shape structures. It describes SGHAp2 product is highly crystalline than synthesized other products.^[8,9]

A.2. Synthesized Eppawala Hydroxyapatite ceramic composites for orthopedics

XRF results have shown that human bone and all novel products including MMA incorporated Eppawala solid state sintered hydroxyapatite composite product (SSHAp-MMA) and MMA incorporated Eppawala sol gel acidified hydroxyapatite composite product (SGHAp-MMA) consists of Ca, P and O in higher weight percentages and Fe, Al and Si as negligible percentages as the impurities. Commercial bone cement product chemical composition is different from them those novel products and especially human hard tissues via consist of Zr and S in higher amounts and Hf in fewer amounts. Therefore, it can be concluded that novel products perform more composition similarity to human hard bone more than commercial products.

When consider XRD results; all novel composites products (SSHAp-MMA and SGHAp-MMA) and human bone consist of 002, 210, 211, 112, 300, 202, 310, 222, 213 and 004 peaks related to hexagonal hydroxyapatite apart from commercial product. Commercial product also interprets crystalline properties with 110, 111, 111, 002, 200, 102, 211, 022, 122, 300, 013, 302, 113 and 222 peaks related to the crystallographic phases of monoclinic zirconium dioxide. FTIR results has shown common peaks related to phosphate groups (560 cm^{-1} , 640 cm^{-1} , 963 cm^{-1} , 1028 cm^{-1} and 1110 cm^{-1} wave no range) and characteristic hydroxyapatite peak (3572 cm^{-1} wave no range) in the novel Eppawala Hydroxyapatite-MMA composites and human bone. Even though FTIR pattern for commercial product has shown a hydroxyl peak related to 3572 cm^{-1} wave no range it can't be identified as Hydroxyapatite peak as there is absence of

phosphate groups in the pattern. The Similar FTIR peaks can be found within SSHAp-MMA, SGHAp-MMA and commercial product curves nearly, 750 cm^{-1} - 2000 cm^{-1} and 3000 cm^{-1} wave no range related to the MMA. Therefore, it can be clearly stated, there is a structural similarity between human bone and synthesized novel Eppawala Hydroxyapatite-MMA composite products than commercial products.

TGA results have exhibited that; human bone and novel products including SSHAp-MMA product and SGHAp - MMA have shown the same pattern of weight loss, which was slightly different from commercial product mixture. Also, it indicates the presence of hydroxyapatite in products as well as in human bone. Those results confirm the composition similarity of human bone and synthesized composite mixtures, as they were containing hydroxyapatite. Considering least amount of weight loss in synthesized novel products than human bone and commercial products, it can be concluded that the synthesized products perform high thermal stability and good material stability in nature and application.^[11,12,13]

Apart from these results, several studies on hydroxyapatite in cooperated methyl methacrylate (MMA)/poly methyl methacrylate (PMMA) composites give good thermal stability as well as having improved mechanical properties such as tensile strength, impact strength, fracture toughness, wear resistance etc.^{[22]-[25]}.

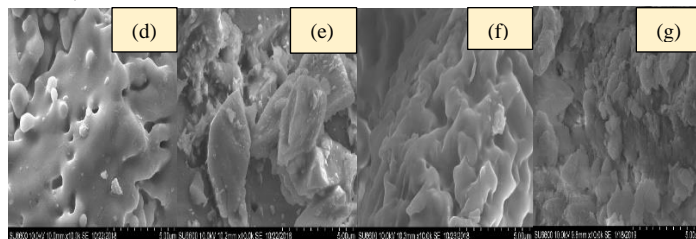


Figure 3. SEM images for Synthesized Hydroxyapatite ceramic composites for orthopedics applications,10 kV, 10kX (d) SSHAp-MMA product (e) SGHAp-MMA product (f) Commercial bone cement (g) human bone^[12]

As shown in the figure 3; SSHAp-HEMA composite product and commercial product consist of micro pores which lead to improve osteoconductive properties as a biomaterial which helpful for good blood circulation to tooth and tooth ingrowth. Both SSHAp-HEMA, SGHAp -HEMA composite products and human tooth are crystalline products. Among them, SGHAp-HEMA is highly crystalline which exhibits needle shape microstructures.^[14]

A.3. Synthesized Eppawala Hydroxyapatite ceramic composites for dentistry

XRF results have shown that human tooth and all novel products including HEMA incorporated Eppawala solid state sintered hydroxyapatite composite product (SSHAp-HEMA) and HEMA incorporated Eppawala sol gel acidified hydroxyapatite composite product (SGHAp-HEMA) consists of Ca, P and O in higher weight percentages and Fe, Al and Si as negligible percentages as the impurities. Commercial dental filling material (GIC product) chemical composition is different from them those

novel products and especially human hard tissues via consist of a Zirconium compound. Therefore, it can be concluded that novel products perform more composition similarity to human hard teeth more than commercial product.

When consider XRD results; all novel composites products (SSHAp-HEMA and SGHAp-HEMA) and human tooth consist of 002, 210, 211, 112, 300, 202, 310, 222, 213 and 004 peaks related to hexagonal hydroxyapatite apart from commercial product. Comparing those results with XRD pattern for commercial GIC product has carried out an amorphous structure without crystalline properties. FTIR results also interpreted common peaks related to phosphate groups (560 cm⁻¹, 640 cm⁻¹, 963 cm⁻¹, 1028 cm⁻¹ and 1110 cm⁻¹ wave no range) and characteristic hydroxyapatite peak (3572 cm⁻¹ wave no range) in the novel Eppawala Hydroxyapatite-HEMA composites and human bone apart from Commercial GIC product. Similar FTIR peaks can be found within SSHAp-HEMA, SGHAp-HEMA and commercial product curves nearly, 750 cm⁻¹- 2000 cm⁻¹ and 3000 cm⁻¹ wave no range related to the MMA. Therefore, it can be clearly stated, there is a structural similarity between human teeth and synthesized novel Eppawala Hydroxyapatite-HEMA composite products than commercial products.

TGA results have exhibited that; human teeth and novel products including SSHAp-HEMA product and SGHAp-HEMA have shown the same pattern of weight loss, which was slightly different from commercial product mixture. Also, it indicates the presence of hydroxyapatite in products as well as in human tooth. Those results confirm the composition similarity of human tooth and synthesized composite mixtures, as they were containing hydroxyapatite. Considering least amount of weight loss in synthesized novel products than human tooth and commercial products, it can be concluded that the synthesized products perform high thermal stability and good material stability in nature and application. [10,14,15]

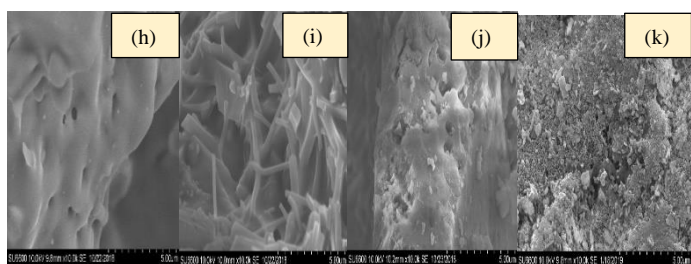


Figure 4. SEM images for Synthesized Hydroxyapatite ceramic composites for dentistry applications, 10 kV, 10kX (h) SSHAp-HEMA composite product (i) SGHAp-HEMA composite product (j) Commercial dental filling material (k) human tooth [14]

As shown in the figure 4; SSHAp-HEMA composite product and commercial product consist of micro pores which lead to improve osteoconductive properties as a biomaterial which helpful for good blood circulation to tooth and tooth ingrowth. Both SSHAp-HEMA, SGHAp -HEMA composite products and human tooth are crystalline products. Among them, SGHAp-HEMA is highly crystalline which exhibits needle shape microstructures. [14]

B. Economic impact of value added Eppawala Hydroxyapatite ceramic and its composite products

Solid state Hydroxyapatite product gives higher yield than Sol gel Hydroxyapatite products. Solid state product manufacturing cost is somewhat lower than Sol gel product manufacturing cost as mentioned in the Table 1 and the Figure 6. [7,8]

Table 1. Comparison between fertilizer cost, novel synthesized products costs and commercially available product costs [6]

Material/product	Market Price /Cost (Lkr.) per 1kg
Eppawala High Grade Rock Phosphate – HERP**#	125.00
Eppawala Rock Phosphate # (ERP)	100.00
Commercial Bone cement (incorporated MMA) **@^	392,500.00
Commercial dental filling material (GIC incorporated HEMA) **@^	2,294,000.00
Commercially available synthetic Hydroxyapatite^	1,037,874.00
Solid state sintered Eppawala Hydroxyapatite product (SSHAp product)	1700.00
Sol gel Alcoholic Eppawala Hydroxyapatite product (SGHAp1 product)	5325.00
Sol gel Acidified Eppawala Hydroxyapatite product (SGHAp2 product)	6850.00
MMA incorporated SSHAp ceramic composite product (novel bone cement product A)	2182.00
MMA incorporated SGHAP1 ceramic composite (novel bone cement product B)	5807.00
MMA incorporated SGHAp2 ceramic composite (novel bone cement product C)	7332.00
HEMA incorporated SSHAp ceramic composite (novel dental filling material 1)	1885.00
HEMA incorporated SGHAp1 ceramic composite (novel dental filling material 2)	5,510.00
HEMA incorporated SGHAp2 ceramic composite (novel dental filling material 3)	7,035.00

*Raw material, **Currently clinically used products in Sri Lanka, (1US dollar = Lkr.185, 1Euro= Lkr. 219), # Currently used as the fertilizer, @ synthetic products not having structural similarity to human hard tissues, ^shipping cost not included.

Table 2. Percentage of Economic profit from synthesized product

Material/product	Gross profit (%)
SSHAp product *	99.83
SGHAp1 product *	99.48
SGHAp2 product*	99.33
novel bone cement A **	99.44

novel bone cement B **	98.52
novel bone cement C **	98.13
novel dental filling material 1***	99.9
novel dental filling material 2 ***	99.75
novel dental filling material 3 ***	99.69

*Calculated w.r.t. commercially available synthetic Hydroxyapatite, **Calculated w.r.t. commercial bone cement, ***Calculated w.r.t. commercial dental filling material

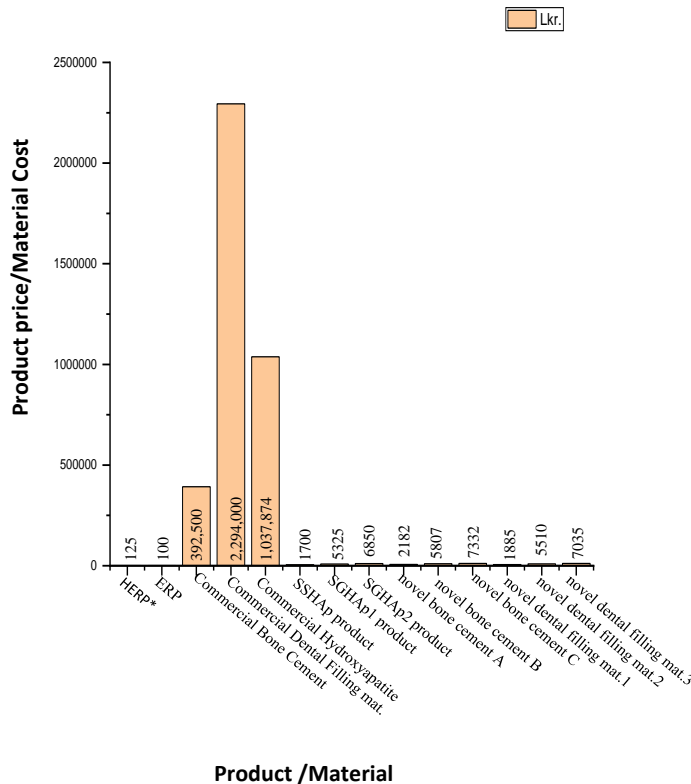


Figure 5. Cost variation of products

When consider ceramic composite synthesis; our recent studies exhibit previously synthesized Hydroxyapatite types successfully incorporated with the MMA and HEMA monomer liquids to obtain bio ceramic composites which are having similar properties to human hard tissues and better properties than commercial products in the market [9]-[17].

As mentioned in the Table 1 and the Figure 5; it has clearly described that the Eppawala fertilizers (both HERP and ERP) available at very cheap prices in the market. Manufacturing cost of novel Eppawala Hydroxyapatite types are very less than import commercial Hydroxyapatite ceramic for local biomedical industry. Manufacturing cost for novel bone cement and dental filling materials also low cost than purchasing commercial bone cement and commercial dental filling materials.

Substituting novel products for currently using each commercial product will give economic profit around 98-99% as mentioned in the Table 2. When compare and contrast material/product costs in the market and profit which gives after selling value added products as mentioned in the Table1, Table 2 and Figure 5 with each other, it has proven that introducing value added products will earn huge economic benefits for Sri Lankan

economy than selling Sri Lankan rock phosphorous into the market directly as phosphorous fertilizers (HERP and ERP).

When purchasing those commercial products from global market shipping costs also going to add for the total costs of product purchases. If we can export our products without importing those commercial products into Sri Lankan, we can increase our exports and save additional expenses. It'll be cost beneficial for our local biomedical industry as well.

Therefore, novel products economic and clinical performance is higher than commercial products.

IV. CONCLUSION

It has proven that introducing value added products will earn huge economic profit for Sri Lankan economy than selling Sri Lankan rock phosphorous into the market directly as phosphorous fertilizers (HERP and ERP). Most important fact is invented novel products have close similarity with human hard tissues and made out of natural ingredients than commercial products which are eco-friendly. Also, introducing these value-added products into Sri Lankan hospitals as a substitute for current clinically using commercial products (bone cements and dental filling materials) will reduce costs and service charges as well as healthier than previous used products due to improved bio ceramic properties. Exporting those novel value-added products in to global market will earn foreign income to Sri Lanka as well. Study concludes that; manufacturing value added products from Sri Lankan rock phosphate deposit may lead to increase its income as a natural resource in a fruitful manner sustainably. It'll lead to get much better foreign income into the country and by doing, improve living standards in Sri Lankan Citizens while providing positive impact for Sri Lankan economy.

V. ACKNOWLEDGEMENT

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