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Derleme Makalesi- Review Article

Research in Applications of Eggshell in Different Industries

Yumurta Kabuğunun Farklı Endüstrilerdeki Uygulamalarına Yönelik Araştırmalar

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ABSTRACT

In addition to using eggs as a food source, eggshells are also used in various applications in different fields. While eggshells are considered a byproduct of the food industry, they have been the subject of extensive research in recent years due to their unique properties and versatile use potential. This study aims to examine the various uses of eggshell and highlight its potential advantages. Eggshells have a structure consisting mainly of calcium carbonate (CaCO₃) and organic substances. While this structure ensures the mechanical durability of the shells, it also allows properties such as porous structure and surface area to change. These properties make eggshells an ideal candidate for many applications. In this study, the areas where eggshell is used are examined. According to this, Its potential in areas such as agriculture, calcium supplementation in food, medical applications, ceramic raw material, adsorption applications, construction and nanocomposite applications is explained. The aim of this study is to evaluate the broad use potential of eggshells and their effects in different industrial sectors. Understanding the role of eggshells in various applications could be an important step towards sustainability, environmental protection, and industrial innovation. This initiative is intended to provide a perspective on the evaluation of eggshells and lay the foundation for future research.

Keywords- Eggshell, Biowaste, Biomaterial, Industrial usage, Recycled materials

ÖΖ

Yumurtanın besin kaynağı olarak kullanılmasının yanı sıra yumurta kabukları farklı alanlardaki çeşitli uygulamalarda da kullanılmaktadır. Yumurta kabukları gıda endüstrisinin bir yan ürünü olarak kabul edilirken, benzersiz özellikleri ve çok yönlü kullanım potansiyeli nedeniyle son yıllarda kapsamlı araştırmalara konu olmuştur. Bu çalışma, yumurta kabuğunun çeşitli kullanımlarını incelemeyi ve potansiyel avantajlarını vurgulamayı amaçlamaktadır. Yumurta kabukları ağırlıklı olarak kalsiyum karbonat (CaCO₃) ve organik maddelerden oluşan bir yapıya sahiptir. Bu yapı kabukların mekanik dayanıklılığını sağlarken aynı zamanda gözenekli yapı ve yüzey alanı gibi özelliklerin değişmesine de olanak sağlar. Bu özellikler yumurta kabuklarını

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birçok uygulama için ideal bir aday haline getirir. Bu çalışmada yumurta kabuğunun kullanıldığı alanlar incelenmiştir. Buna göre; tarım, gıda endüstrisinde kalsiyum takviyesi, tıbbi uygulamalar, seramik hammaddesi, adsorpsiyon uygulamaları, inşaat ve nanokompozit uygulamaları gibi alanlardaki potansiyeli gibi konulara değinilmiştir. Bu çalışmanın amacı yumurta kabuğunun geniş kullanım potansiyelini ve farklı endüstriyel sektörlerdeki etkilerini değerlendirmektir. Yumurta kabuklarının çeşitli uygulamalardaki rolünü anlamak sürdürülebilirlik, çevre koruma ve endüstriyel inovasyona yönelik önemli bir adım olabilir. Bu çalışma sayesinde yumurta kabuklarının değerlendirilmesine yönelik bir bakış açısı sunması ve gelecekteki araştırmalara temel oluşturması amaçlanıyor.

Anahtar Kelimeler- Yumurta kabukları, Biyoatık, Biyomalzeme, Endüstriyel kullanım, Geri dönüştürülmüş malzeme

I. INTRODUCTION

It is noteworthy that many scientific studies have been conducted on eggshells. As a result of the search made with the keyword eggshell in the Web of Science database, 10886 pieces of literature were found. These literature studies are primarily classified according to scientific fields. The second stage of the screening was done using the filtering method and the keywords eggshell/quail, eggshell/partridge, eggshell/goose, eggshell/ostrich, and eggshell/chicken. All scanning data are summarized in Figure 1 with their percentage and numerical values.

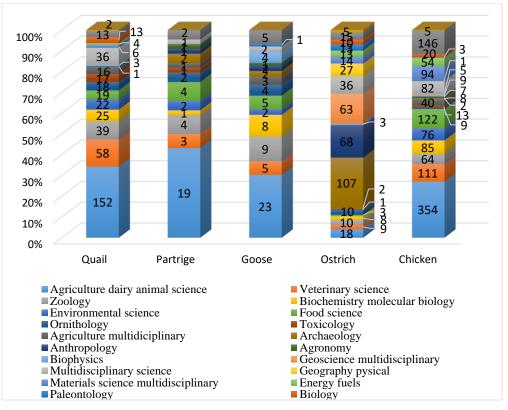


Figure 1. All Articles on Eggshell Species According to the WOS Database

It is seen that the preferred eggshells vary according to the study areas. When the Figure 1 is examined, it can be seen that research on ostrich eggshells focuses on archaeology, anthropology, and physical geography, while quail eggshells are more preferred in studies conducted in the fields of veterinary science, molecular biology, and food science. In studies on environmental science and toxicology, classical chicken eggshells and quail eggshells were generally preferred, but ostrich eggshells were not preferred. Partridge and goose eggshells were primarily preferred in studies agriculture and dairy animal science. In addition, detailed information about the usage areas of eggshells is given below in the form of sectoral headings.

A. Agricultural Applications

It is inexpensive and environmentally friendly to use eggshells as fertilizer due to their calcium content. When eggshells were added to fertilizers as a supplement, it was observed that soil calcium levels increased [1]. Calcium supplementation is therefore an easy way to treat infected plants. Eggshells are an inexpensive and environmentally friendly supplement for fertilizer preparation [2]. The mixture made from eggshells can be used as a soil rehabilitation and improvement product [3]. To enrich soil with nutrients, eggshell powder can be added as fertilizer. To provide nutrients to plants, eggshell powder can also be mixed with fertilizers. This supplement increases the nutritional value of the plants. It is 90% easier for eggshells or eggshell powder to absorb calcium than some others [1]. At the same time, plants grow better when the soil's pH is increased or neutralized by calcium in eggshells [2].

On the other hand, calcium affects the pH level in soil [4]. It was seen that using eggshells to fertilize red clover plants resulted in larger growth (10 mm) than that of non-fertilized plants. Gaonkar and Chakraborty also used eggshells as a source of plant fertilizer [1]. Deficient calcium in the soil causes tomatoes to grow more inefficiently. To develop the soil's calcium content, calcium was extracted from eggshells and added to it. Using eggshell as a fertilizer enriched soil with calcium and maintained its pH level, according to the results. Berry plants can also be treated with these eggshells for blossom end root disease. As a fertilizer, eggshell powder has been found to be effective in improving all the features in potato and pea plants according to Wazir, Gul, and Hussain (2018) [5]. In addition to improving the mean height of the plant, eggshell powder also improved the size of several nodes, leaves, leaf areas, branches, and tubers.

B. Calcium Supplement in Food

Considering the studies examined as a calcium supplement, animals and humans can use calcium from eggshells to treat calcium deficiency [6]. It was investigated that the powdered eggshell has antirachitic effects in rats and stimulates cartilage cell growth in chick embryos [7]. Additionally, eggshell powder can reduce pain and increase bone density. Proteins found in eggshells act as calcium binders and are involved in mineralization [8]. Calcium-binding properties have been reported for eggshell extracts that are insoluble or soluble [9].

Milk tablets are solid products composed of powdered milk base and at least one binding agent. There is less water content in them, and they taste decent, and they are easier to chew and more bioavailable than many other types of supplements. Milk tablets contain powdered milk, sugars, and calcium; calcium is necessary for humans. Nanotechnological research increases the bioavailability of calcium in food products compared to others. It means the human body can absorb a great amount of nutrient and store it. Additionally, it has been revealed in a study [10] that there is no significant difference between nano-sized calcium powder and milk tablets.

For individuals with lactose intolerance, Fina, Brun, and Rigalli prepared lactose-free milk using eggshell powder and kefir [11]. By fermenting milk with lactic acid and carbon dioxide, kefir milk can be produced. This type of milk does not cause lactose intolerance, demineralization is prevented, and heart health is improved. Three samples were prepared and compared with a control (milk). A calcium source was added to one test sample by adding eggshell powder, a kefir grain source was added to the second sample, and a calcium source was added to the third sample by adding 200 grams of eggshell powder. As a result of this study, it was stated that people with lactose intolerance can consume calcium-treated milk, as the lactose content is reduced, and the calcium content is higher.

Moreover, many calcium salts are commonly found in calcium supplements; however, they are not always effective. There are certain calcium supplements made from oyster shells that are sold in stores. Since oyster shells are scarce, calcium extraction from them is not only time-consuming but also expensive. Therefore, eggshells appear to be a promising alternative source to include in calcium supplements because they are easy to gather, calcium extraction from them is much simpler than from other natural shells, and they have excellent solubility. In addition, eggshell powder is acidic, has a high calcium concentration, and is simple to ionize.

C. Medical Applications

It has been seen in the literature study that eggshell is used for medicine and medical applications, especially in dentistry. In the literature, some prominent factors in the preference for eggshells in medical applications can be listed as biocompatibility, disease-freeness, easy accessibility, ease of application, and ease of bone regeneration.

Onwubu et al. obtained clinically acceptable polished dental prosthesis surfaces by reducing the surface roughness of the dental prosthesis [12]. In another study, Onwubu et al. synthesized an acid-resistant nano-sized dental material using eggshell and titanium. They determined the characterization of this material and performed its in-vitro evaluation [13]. Mony et al. evaluated chicken eggshell solutions at different pHs and determined that high pH solutions have the potential to store the minerals lost from the tooth surface during the tooth decay process [14]. Kongpaopon et al. prepared bio-cellular glass-ceramic composite materials containing calcium phosphate from eggshells as a biomaterial source. They suggested that the biomaterials they prepared could be used as an alternative in medicine and dentistry applications and could support the strength and thermal stability of teeth and bones [15]. Durmuş et al. investigated whether varnish-containing bioactive glass, eggshell, eggshell membrane proteins and eggshell and eggshell membrane protein treated with STMP has a remineralizing effect similar to

varnish containing furur on demineralized enamel. It has been emphasized that combining biological or bioactive components into dental polishes instead of fluoride can reduce cytotoxicity [16]. Feroz et al. carried out an in vitro study on artificially induced tooth erosion to determine the protective effect of chicken eggshell powder solution and determined that the surface roughness of all treated tooth samples decreased and had a protective effect against erosive enamel loss [17].

Muhammed synthesized membranes from eggshells at different rates (1%, 3%, 5%, and 7%) and determined the mechanical parameters of these membranes and determined the possibilities of using them as membranes in tooth production [18].

Than et al. investigated eggshell powder as a pharmaceutical supplement in tablet dosage form. In their study, they prepared four different eggshell powders by using paracetamol as a model drug. As a result of their research, they recommended eggshell powder to the pharmaceutical industry as an excipient to increase the release [19]. A very similar study was done by Habib et al. In their study, they examined the release of aceclofenac in tablets prepared using eggshell powder [20].

Li et al. emphasized that the product they created by synthesizing nanoscale calcium citrate layers using eggshells supports new bone formation [21].

Verma et al. developed an eggshell-derived apatite drug delivery system. They explained that this drug delivery system will prevent post-cancer inflammation, contribute to bone repair and regeneration, and is very suitable for curing osteosarcoma [22].

D. Raw Material in Ceramics

Eggshell is a calcium phosphate-based bio-ceramic reproduced from natural biowastes such as fish and bovine bone. The reason why calcium phosphates (CaP) are a preferred biomaterial is their non-toxicity and high bioactivity [23].

Kazami et al. synthesized nanostructured diopside bioceramics using eggshell in their study and observed that the diopside samples they obtained were thermally stable [24]. Ho et al. In their study titled "Calcium phosphate bioceramics synthesized from eggshell powders via solid state reaction", they proposed eggshells as a potential material that could be used in future waste management, ecology, as well as calcium phosphate synthesis [25].

In the literature research, it has been seen that the use of eggshells is given importance in the production of glass-ceramic foam in order to increase energy efficiency and provide thermal insulation in buildings [26,27]. A similar study was done by Noor et al. In their study, they synthesized wollastonite glass ceramics in different compositions using eggshell and waste glass and performed characterization analyses [28].

Freire and Holland conducted a characterization study targeting the use of bird eggshell waste in ceramic wall tile paste and indicated that powdered eggshell solid waste can be taken into account as a recent raw material for the production of single-fired ceramic wall tile materials. [29]. Vilarinho et al. aimed to improve an eco-ceramic wall tile containing bio-calcium carbonate from eggshell waste as a raw material. In their studies, the paste was prepared by using eggshell waste instead of limestone, which is a natural raw material, and they proved that limestone could be completely replaced with eggshell waste [30].

Adeogun et al. developed nano-sized calcium hydroxyapatite-based ceramics by preparing pure hydroxyapatite from uncalcined eggshells. They focused on synthesis and characterization methods in their studies. In addition to the eggshell, the eggshell membrane has also been the subject of research in the production of ceramic raw materials. It is known that perovskite ceramics have a highly crystalline structure [31]. Dong et al. synthesized crystalline perovskite ceramics using a bio-template eggshell membrane via strong metal-protein bonding. As a result of their research, they produced a mixed oxide ceramic material that preserves the interwoven fibrous structure of the material at 1000°C [32]. In the literature, some studies on the applicability of glass-ceramic materials in the medical field have been found. Ayawanna et al. synthesized a permanent implant to support ocular tissues in eye diseases by using eggshell waste [33].

E. Adsorption Applications

1) Elements And Ions Adsorption:

Some scientific studies have explored the potential of eggshells for elements or ion adsorption, which involves the removal of elements or ion contaminants from wastewater or soil. It has been suggested that the phosphorus element can be removed from wastewater by using eggshells and calcined eggshells, as it may contribute to the deterioration of the organism balance in nature by mixing with water and to the reduction of oxygen in the water [34-36]. Heavy metals have harmful effects on the environment and human health. Cu(II) [37], Pb(II) and Zn(II) ions, which cause severe problems by polluting nature, were removed from aqueous

solutions using eggshells [38]. The very small amount of Cd (II) ion in the environment also causes serious problems for living organisms. Therefore, studies have been carried out to remove it from wastewater [39-41]. When the adsorption of Cd(II) ion by eggshell was compared with the adsorbing of Ag(I) and Zn(II) ions, it was revealed that there was a correlation in the form of Ag(I) > Cd(II) > Zn(II) [40]. In another study, the ability of eggshell waste to adsorb Co(III), Zn(II), Hg(II), and Pb(II) heavy metal ions was compared and Co(III) ion was the ion most adsorbed by eggshells [42]. Cr(VI), Cd(II), and Eu(III) heavy metal ions are also well adsorbed by eggshells, just like the metal ions listed above [43,44]. Polat and Aslan, in their study of adsorption of Cu ion using eggshells, explained that this reaction is endothermic [45]. Eggshells and calcined eggshells were used to remove Ni(II) ions from the synthetic solution, and it was revealed that calcined eggshells adsorbed Ni(II) ions 60 times more [46]. Abbas et al. conducted a study of removing Bi(III) from aqueous solution using eggshells, and suggested that adsorption took place using SEM-EDS and FTIR analyses [47]. As an adsorbent, eggshells were used to remove Studies [48].

Eggshells calcined at 800° C were highly effective for the adsorption of F⁻ ions [49]. Oke et al. mentioned the importance of the size of the eggshell particles in removing As ions from the aqueous solution using eggshells. They stated that with the decrease in particle size, the percentage of adsorption would also increase [50].

These studies collectively demonstrate that eggshells, with their high calcium carbonate content, offer potential as a highly cheap and environmentally friendly adsorbent for elements and ions harmful to the ecosystem to removal. The adsorption mechanisms involve both physical and chemical interactions between the heavy metal ions and the surface of eggshells, including ion exchange, surface complexation, and chemical reactions. Eggshells can be used as a valuable bioresource for heavy metal adsorption applications in water treatment and wastewater management.

2) Molecules Adsorption:

Phenol compounds have a toxic effect when mixed with drinking water. It also gives a bad taste to drinking water. Therefore, removal processes are required as these compounds are priority pollutants [44,51]. It has been shown by Kuśmierek et al, that Pentachlorophenol can be effectively extracted from aqueous solution using eggshell [52]. There is a study showing that H_2S , which is harmful to human health and the environment in many respects, can be adsorbed by calcined eggshells [53]. In another study, it was shown that Cypermethrin, Deltamethrin, and Indoxacarb compounds used as pesticides were adsorbed by various types of eggshells [54]. Especially in the swine industry, p-cresol, which is formed when animal wastes come together with other organic pollutants, can cause harmful effects in terms of human health. Therefore, eggshells were used to remove this unwanted molecule from the p-cresol solution [55]. Due to the CO₂ generated during the calcination process of the eggshells for phosphate ions increases when CO₂ is removed using N₂ [56]. Dyes, which can also be considered molecules, can cause negative effects in terms of the environment and human health. There are also various studies using eggshells to remove these dyes (for example, triphenylmethane, methylene blue, crystal violet dye, direct blue, Reactive Black 5, Acid Violet 90, Acid Yellow 194) [57-60].

These studies demonstrate the potential of eggshells as adsorbents for the removal of various molecules. Eggshells offer a promising option for the development of cost-effective and sustainable adsorbents in water treatment applications for the removal of different contaminants and molecules [61-68].

3) Modified eggshell's

In some studies, eggshells were modified to form a stronger adsorbent for metal or molecule adsorption [61-68].

These studies highlight the importance of modifying eggshells to improve their properties and expand their application. Modified eggshells exhibit improved adsorption capacities, increased surface area, improved stability, antibacterial properties, and broader functionality, making them valuable in various environmental, biomedical and materials science applications.

F. Construction Applications

There are also studies showing that eggshells can be used as construction materials. In these studies, it has been suggested that it is promising for applications such as Concrete, Cement, and Aggregate [69-79], Soil Stabilization and asphalt [80-88], Building Insulation [89-91].

It's important to note that while there have been promising findings in these areas, the utilization of eggshells as a construction material is still an active area of research. Further studies are needed to explore the optimization of eggshell incorporation, assess long-term performance, and evaluate the economic feasibility of implementing eggshell-based solutions in construction applications.

G. Nanocomposite Applications

In the study of eggshell nanocomposites containing silver nanoparticles [92], low-cost cleaning powder for household items, as well as antibacterial properties of silver-doped nanocomposites obtained from eggshells were revealed. In another similar study [93], nanocomposites were formed with eggshells after silver nanoparticles were obtained from plant extract by the green synthesis method. In this study, which is bifunctional, Ag/Eggshell nanocomposites have both eliminated the damages of 4 nitrophenols in water and disinfected water with their antibacterial properties.

In another study, eggshell nanocomposite formed with silver additive was used for heavy metal adsorption, removal of toxic dyes, and microbial pollutants from water [94]. The silver additive was made with biologically synthesized silver nanoparticles.

In a review study [95], the use of eggshell as a filling material, the use of eggshell in metal-composites or polymer composites, as well as the use of matrix material, as bio-composite and hybrid composites were also mentioned.

It has been stated that nano eggshells can be used as an effective additive to improve the mechanical properties and better workability in mixtures of cement composites containing nano eggshells [96].

Üllen et al. developed a low alloy steel foam coated with eggshell-based kappa-carrageenan-polyvinyl alcohol nano biocomposite [97].

Nano eggshell is a potential for construction applications indicating that it is a nanostructure candidate. For this reason, new composite forms of eggshell have been used in cement content in the studies, and their advantages have been indicated in these studies [96,98].

The use of eggshell as a filling material [99] is another area that attracts attention as much as the studies investigating the antimicrobial effects [100,101] of nanocomposites formed by various processes of eggshell.

Studies showing the antibacterial activity of nanocomposites of waste eggshells can be found in the literature [102,103].

While the eggshell is a suitable material for adsorption with its porous structure, studies have taken place in the literature that it is a suitable candidate for curcumin [104] and formaldehyde [105] adsorption by processing it into nanocomposite.

II. CONCLUSION

It has been observed that eggshells are used in agricultural and agriculture-related applications such as healing infected plants, increasing soil fertility as a fertilizer, enriching the soil in terms of calcium, and balancing the pH level.

Eggshells appear to be a promising alternative source for inclusion in calcium supplements; because they are easy to obtain, the extraction of calcium from them is much simpler than from other natural shells, and they have excellent solubility. In addition, eggshell powder is acidic, has a high calcium concentration and is easy to ionize. Due to these properties, it can be considered a promising candidate as a calcium supplement, by adding it to milk tablets, and in individuals with lactose intolerance.

The prominent factors why eggshell is preferred in medical applications are; These can be listed as biocompatibility, easy accessibility, ease of application and its effect on bone regeneration. There are studies on how more durable materials that can be used in dentistry can be produced with various additives made to eggshells.

It is seen that ceramics provide energy efficiency and increase durability thanks to the eggshell added as an additive to the ceramic raw material. Additionally, it is understood that eggshell ceramics can be used in construction and healthcare fields in terms of their usage areas.

Studies have shown that adsorption on eggshells is an effective method in preventing environmental pollution and removing pollutants such as ions, heavy metals and toxic molecules from wastewater or soil. Additionally, modified eggshells appear to make the adsorption process more effective.

It is suggested that eggshells are promising for applications such as Concrete, Cement, Aggregate, Asphalt and building insulation in the construction industry.

Nanocomposite materials created from eggshells; Due to its antibacterial properties, it has been used as a disinfectant and filling material in various sectors. It was appropriated to reveal the potential under the following headings together with the literature comparison.

A. Agricultural Applications

No studies have been found in the literature that distinguish eggshells based on type. It is thought that considering species-dependent diversity, especially in terms of calcium content, can enable soil fertility to be adjusted at an optimum level.

B. Calcium Supplement in Food

In this field, there are studies conducted with eggshells of CCJ [106], SC [107], and duck [90]. Ali and Badawy suggested that there is no significant difference between species in terms of calcium supplementation of eggshells [106]. Safety in food packaging can ensure that all eggshells are treated indiscriminately as waste for reinforcement purposes.

C. Medical Applications

Irokanulo and colleagues suggested that the antimicrobial properties of CCJ eggshells could be used [108]. Syafaat and Yusuf emphasized that the calcium level of CCJ eggshells is higher than that of hen and duck eggshells and preferred CCJ as the main material in the Hydroxyapatite synthesis application [109].

Durmuş et al. have demonstrated the possible beneficial effects of external and internal ostrich eggshell membranes alone and in combination with shell powder on bone regeneration in rabbit cranial defects using radiological, clinical, and histological methods [16].

Boldaji and Sheishi presented in their study that ostrich eggshell pulverized by ultrasound is more beneficial for bone healing compared to natural bone healing [110].

Dupoirieux et al. used ground eggshells of different sizes and implanted them into the bone. As a result, they suggested that eggshell could be a resorbable implant, but its degradation kinetics depended on size [111].

D. Raw Material in Ceramics

A study shows that CCJ eggshells can be used in ceramic production [69].

Sangmala et al. synthesized chicken eggshell waste as hydroxyapatite for flux replacement in ceramic production and showed that ceramic samples with various hydroxyapatite contents affected the improvement of physical and mechanical properties after heat treatment in the temperature range of 1000-1200°C [112].

The issue of using waste instead of natural raw materials in the ceramic industry has brought about different studies. In the literature, it is seen that eggshells are preferred instead of glass waste and polished tile waste in ceramic production [113]. In addition to the use of eggshells in the construction industry, there are studies showing that they are also used in the field of bioceramics as a bone repair material [114].

E. Adsorption Applications Elements, Ions, And Molecules Adsorptions

It has been demonstrated that eggshells, with their high calcium carbonate content, offer potential as a cost-effective, sustainable, and environmentally friendly adsorbent for elements, ions, and molecules harmful to the ecosystem to removal. Studies with CCJ [69,114], AC, DH [114,115], AA [115], and SC [117] have also been found to support this result.

1) Modified Eggshells:

Modified eggshells exhibit improved adsorption capacities, increased surface area, improved stability, antibacterial properties, and broader functionality, making them valuable in various environmental, biomedical and materials science applications. Studies in the field of modified eggshells are generally carried out with eggshells of unspecified type. In most of the studies, waste eggshells consumed in daily life were preferred.

The different pore diameters of different eggshell types provide selectivity in the adsorption process and allow a prediction to be made between the pore diameter in the eggshell and the molecule size of the eggshell to be adsorbed [116,117].

F. Construction Applications

It's important to note that while there have been promising findings in these areas, the utilization of eggshells as a construction material is still an active area of research. Further studies are needed to explore the optimization of eggshell incorporation, assess long-term performance, and evaluate the economic feasibility of implementing eggshell-based solutions in construction applications. In the studies proving that eggshells can be used as construction material, no studies were found based on the species differences of eggshells. The reason for this is that large amounts of eggshells will be needed in the construction industry and building materials, and thus

far, studies in this field are limited. It can be said that the field of ceramics, where less material is needed to reveal the potential differences between species, will be preferred over the construction sector.

G. Nanocomposite Applications

CCJ eggshells have been used to increase the strength in bio composite production [119] while SC has been used for bio-composite film production [120]. In such studies, it is seen that eggshell is used as a CaCO₃ support both to increase the strength and to reduce the moisture content in the bio composite. In our experimental results, it was determined that the highest calcium rate belonged to SC, DH, and AA eggshells with 98%. For this reason, using other eggshells instead of CCJ will provide the desired properties in bio composites.

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