USE OF AGRICULTURAL WASTE ASHES AS ADDITIVES MATERIAL IN BIOACTIVE GLASS PRODUCTION

Murat ÖZOCAK *

* Department of Biosystem Engineering, Faculty of Agricultre, University of Namik Kemal, TURKEY, PhD. Candidate, e-mail: murat.ozocak@outlook.com
ORCID ID: https://orcid.org/0000-0002-3997-9290

ABSTRACT

Demand for renewable energy sources is increasing day by day. The rapidly increasing population and energy needs on a global scale have increased the number of studies on renewable energy sources. In addition to energy needs, the search for disposal and storage of wastes harmful to the natural environment is of great importance. Disposal and storage requires high costs and labor. The need for energy and the necessity of protecting the natural environment provided the solution to convert wastes into energy or value added products without damaging the environment. The wastes of the crops produced as a result of agricultural production can be converted into energy or value added products. Some of the plant wastes meet the energy needs and some of them can be used in the production of value-added biomaterials. Biomaterials are materials which are used in the field of health and show bioactivity with parts such as organs and tissues. Bioactive glasses, which are one of these materials, are used in the health sector especially in dental filling, prosthesis and composite applications. The most important feature of raw materials to be used in the production of bioactive glasses is SiO2 (silica). Plants receive silica from soil during development and this silica is also present in plant waste. In this study, a wide literature review was conducted and the percentage of mass ash after burning of rice stalks, corn stalks, hazelnut shells, corn stalks which were firstly burned for heating and energy purposes were determined. Then, the composition of the ash obtained SiO2 (silica) and other substances were determined and all the results obtained in the light of this information was compiled to provide information about the possibilities of use in bioactive glass production.

Keywords: Agricultural waste ashes, Biomaterial, Bioactive glass, Agricultural wastes, Ash.
1. INTRODUCTION

Leaves, straw, stalks, fertilizers that occur in all stages of production, processing and post-harvest of agricultural production are defined as agricultural waste (Palabıyık and Altunbaş 2004). The basis of plant and living organisms is called biomass. Plants collect organic matter in their bodies as a result of photosynthesis using solar energy. Biomass formed by plant wastes has become an important energy source as it is among renewable energy sources (TÜGİAD, 2004).

Biomass sources vary widely. Resources such as agricultural, vegetable, animal wastes, forest products wastes, aquatic plant wastes constitute biomass. In terms of agricultural activity, there are approximately 26 million hectares of land in our country. The results of one study there are approximately 60 million tons of agricultural waste in Turkey. The highest share among the wastes constituting this amount is caused by vegetable wastes after corn, cotton and wheat cultivation (Başçetinçelik et al, 2004). Annual potential amounts of biomass species in Turkey are given in the table below (Demirbaş, 2008).

| Biomass type                        | Annual potential (million tons) |
|-------------------------------------|---------------------------------|
| Annual plant                        | 6,30                            |
| Multiple year plant                 | 6,14                            |
| Forest waste                        | 4,46                            |
| Agricultural industry wastes        | 7,12                            |
| Tree industry wastes                | 3,57                            |
| Animal products wastes atıkları     | 1,5                             |
| Other                               | 1,3                             |
| Total                               | 32                              |

Agricultural wastes are less hazardous than other solid wastes and have more rapid recycling. Leaving agricultural wastes in the environment should be avoided and used as raw materials. Re-evaluation and conversion to value-added products should be prepared by experts in certain technical stages and carried out in accordance with the legislation. Environmental pollution will be reduced with the utilization of agricultural wastes, economic recovery and the variety of raw materials will be increased. The ways of evaluating agricultural wastes differ according to their types like other wastes (Akırmak 2010).

Agricultural wastes are divided into 3 groups. These are plant production and subsequent wastes, animal production and subsequent wastes and agricultural products production and subsequent wastes (Akırmak 2010).

When the agricultural waste potential is compared as product in our country, the most waste is wheat, barley, corn and sunflower stalks. The potential of some green vegetable waste products in Turkey is given in the table below (Saracoglu, 2010).
Table 2. Annual waste production of some products grown in Turkey (Saraçoğlu, 2010)

| Agricultural waste       | Annual production (million tons) |
|--------------------------|----------------------------------|
| Wheat stalk              | 26.4                             |
| Barley stalk             | 13.5                             |
| Corn stalk               | 4.2                              |
| Cotton stalk             | 2.9                              |
| Sunflower stalk          | 2.7                              |
| Sugar beet stalk         | 2.3                              |
| Nut shell                | 0.8                              |
| Rice stalk               | 0.4                              |

All kinds of materials created for use in a wide range of medical applications are called biomedical materials (biomaterials). Biomaterials are materials that replace natural or artificial based organs, tissues, or any other region in the body of non-drug substances. In particular, the concept of biocompatibility is a term that determines the biological performance of biomaterials. Biocompatible materials are used as biomaterials and the ability of the material to respond appropriately to the body system ensures compliance (Hulbert. et al. 1987; TÜBİTAK, 2008).

Biomaterials; metals, polymers, composites and ceramics. Ceramics used to replace parts of the body that lose their function are defined as bioceramics. Bioceramics can be formed as polycrystalline ceramics, bioactive glass, bioactive glass ceramics and bioactive composites (MEDİCİNECUBE, 2008).

Bioglass is silicate based glass and consists of sodium, calcium and phosphate. Bioactive glasses and bioactive hydroxyapatite ceramics are generally used in dental and middle ear treatments. Bioactive glass ceramics are used in overloaded basins and backbone areas (Kükürtçü, 2008).

These are biomaterials in which chemical bonding occurs between tissue and implants as a result of the displacement of silica groups in bioactive glasses with calcium and phosphorus (Er, 2005). The main constituents of many bioactive glasses were determined as SiO₂, Na₂O, CaO, P₂O₅. The best bioactive glass composition is 45S5. According to the composition opening, 45% by weight SiO₂ and CaO / P₂O₅ should be 5: 1. Bone binding as a biomaterial is not possible in bioactive glasses with a CaO / P₂O₅ ratio lower than this ratio (Hench, 1998).

Silica (SiO₂) is a raw material that can be used in the production of electronics, ceramics, polymer materials and bioactive glass. It is possible to produce silica with initiators such as tetraethylorthosilicate - TEOS under laboratory conditions and it is not economical because of high cost (Konukoğlu, 2013). During the growth process, plants pick up various minerals and silicas from the soil (Mo et al., 2016). Since silica production with tetraethylorthosilicate - TEOS is not economical, the use of agricultural wastes containing SiO₂ has become an alternative (Konukoğlu, 2013).
2. MATERIAL AND METHOD

The material of this study is to determine the mass percentages and mineralogical contents of the agricultural waste ashes according to the results obtained in the domestic and international researches. The percentages of masses of agricultural wastes after incineration were determined and the highest and lowest ash amount were explained by graphs. Then, it was tried to determine which waste is more suitable than the basic mineralogical composition sought in the additives that can be used in the production of bioactive glass. In the light of the data obtained, it was tried to put forth the ratio of agricultural wastes to meet the composition of bioactive glass and the possibilities of converting them to value added products by preventing the damages to the environment of ashes which are waste of plant wastes.

Figure 1. Agricultural wastes of used in research

3. RESULT AND DISCUSSION

3.1. Determination of Ash Amount by Mass of Plant Wastes

Agricultural waste ash determined in the research is burned in houses, greenhouse and animal husbandry enterprises or kilns for heating and energy purposes and the resulting ashes are left directly to the environment. The associated ashes are left to the environment as waste at no cost to the environment. The highest amount of ash was obtained from corn stalk and the lowest was obtained from hazelnut shell (Er and Özdemir, 2018). The mass percentages of agricultural waste ashes are given in Figure 2.

Figure 2. Amount of ash by mass of plant wastes
3.2. Chemical Composition of Bioactive Glass

According to the studies, the highest substance in the chemical composition of bioglass is SiO₂ followed by CaO, Na₂O and P2O5 (Hench, 1982). Available in bioactive glasses containing Al₂O₃ and MgO. The amount of bioactive glass components in the plant wastes determined in the study was determined.

**Table 3.** Chemical composition of bioactive glass (Hench, 1982)

| Component | SiO₂ | CaO | Na₂O | P2O5 |
|-----------|------|-----|------|-------|
| Percent (%) | 45.0 | 24.5| 24.5 | 6.0  |

3.3. Determination of Chemical Contents of Plant Wastes

While determining the chemical composition of plant wastes, the most important SiO₂ contents of the bioactive glass components were determined. In terms of SiO₂ contents, the best ratio was found in paddy stem and rice husk and hazelnut husk showed similar values (Er and Özdemir, 2018). SiO₂ contents of all waste ash are given as follows.

**Figure 3.** SiO₂ contents of plant wastes

![SiO₂ contents of plant wastes](image)

The second component sought in bioactive glasses is the CaO content. As a result of the analysis, the best CaO value is the wood waste ash (Er and Özdemir, 2018). The value of this waste is followed by hazelnut shell ash. Other wastes are less valuable and very close to each other. The CaO contents of the plant wastes are given as follows.
Figure 4. CaO contents of plant wastes

When the Na₂O values, which should be close to the CaO content in the bioactive glass composition, are considered, it is observed that the corn stalk ash gives the best result even if there is a small difference that all the wastes take close values (Er and Özdemir, 2018). When compared in terms of Na₂O content, it can be said that all plant wastes in the study have almost the same characteristics. Na₂O contents of plant wastes are given as follows.

Figure 5. Na₂O contents of plant wastes

The P₂O₅ contents of plant wastes were close to each other and hazelnut husks and corn stalk ash gave the best results (Er and Özdemir, 2018). In terms of bioactive glasses, all wastes showed usable quality results. P₂O₅ contents of plant wastes are given as follows.
Another substance used in the production of bioactive glass is $\text{Al}_2\text{O}_3$. When the $\text{Al}_2\text{O}_3$ contents of the plant waste ashes were compared, the best results were found in wood shavings ash and the best values were found in hazelnut shells and corn stalk ashes (Er and Özdemir, 2018). $\text{Al}_2\text{O}_3$ contents of plant wastes are given as follows.

**Figure 7.** $\text{Al}_2\text{O}_3$ contents of plant wastes

MgO is the last substance determined in plant wastes. As a result of the analysis, all wastes were taken close values and the best value was found in hazelnut shell ash. MgO contents of plant wastes are given as follows (Er and Özdemir, 2018).
4. RESULTS

SiO$_2$, which has the highest share in bioactive glass content, was found to be the highest in the paddy stalk and rice husk ash of the plant wastes studied and hazelnut shell ash gave the best result after these wastes. It is possible to say that corn stalk and wood shavings ashes come after other wastes but there is not much difference between them as a percentage of SiO$_2$. It has been observed that other chemical compositions of bioactive glass are present in varying proportions in all of the plant wastes within the scope of the research and can be used in making bioactive glass.

As a result of the chemical contents of the plant wastes determined within the scope of the research, it was concluded that there are substances in the composition of bioactive glass. The plant wastes in the study have no economic value since they are the waste material of the plant wastes burned for heating and energy purposes. Since these wastes are seen in the group of materials that are harmful to the environment, the assessment of these wastes will also prevent the damages to nature caused by plant waste. In this way, it can be mentioned that the production of bioactive glasses which can be used in high value added health field can be realized.

As a result, in this article, where national and international studies are compiled, it is seen that it is possible to use ashes of environmentally harmful agricultural wastes as biomaterials. It is recommended that researches in this area be increased and supported in terms of the availability of value-added bioactive glass production as well as prevention of environmental damage. In this way, besides contributing to the economy, agricultural wastes will be removed from being a problem.
REFERENCES

AKIRMAK, E., (2010). “Tarımsal Atık şeker Pancarı Küşpesi ile Sürekli Çalışan Dolgulu Kolonda Tekli ve İkili Boyarmadde Ve Metal Gideriminin İncelenmesi” Hacettepe Üniversitesi, Fen Bilimleri Enstitüsü, Kimya Mühendisliği Anabilim Dalı, Yüksek Lisans Tezi.

BAŞÇETİNÇELİK, A., ÖZTÜRK, H.H., KARACA, C., KACIRA, M., EKİNCİ, K., KAYA, D., BABAN, A., 2004, First Progress Report of Exploitation of Agricultural Residues in Turkey. LIFE 03 TCY/TR/000061.

DEMİRBAŞ, A. 2008. Importance Of Biomass Energy Sources For Turkey. Energy Policy, 834-842.

ER, M. A., Mayıs 2005. SiO2-CaO-Na2O-P2O5 Biyoaktif Camlarının Kontrollü Kristalizasyonu, Lisans Tezi, T.Ü. Fen Bilimleri Enstitüsü, İstanbul.

ER, A., ÖZDEMİR, S. 2018. Tavuk gübresi ve tarımsal atıkların biyoyakıt karakterlerinin incelenmesi, Sakarya Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 22(2), 489-494, 2018.

HENCH L.L. and ETHRIDGE E.C., 1982. Biomaterials – An Interfacial Approach. New York: Academic Press, http://www22.aname.net/~tandlak1/files/science/Greenspan_8_1999.pdf (2008).

HENCH, L.L., 1998. Bioceramics, J. Am. Cer. Soc., 81, 1705-1728 (Edindildiği Kaynak: Dubok, V.A., 2000, Bioceramics-Yesterday, Today, Tomorrow, Powder Metallurgy and Metal Ceramics, 39; 381-394.).

HULBERT, S.F., BOKROS, J.C., HENCH, L.L., WILSON, J. and HEIMKE, G., 1987. Ceramics in Clinical Applications – Past, Present and Future, Ceramics in Clinical Applications, Vincenzini, P., Elsevier, New York, 3-27 (Edindildiği Kaynak: Er, M.A., Mayıs 2005, SiO2 CaONa2O- P2O5 Biyoaktif Camlarının Kontrollü Kristalizasyonu, Lisans Tezi, T.Ü.).

KONUKOĞLU, Z.A., 2013. Pirinç Kabuğu Kökenli Bazlı Silika İçerikli MgO, SrO ve Al203 İlaveli 45S5 Biyoaktif Cam Üretimi Karakterizasyonu, Yüksek Lisans Tezi, Yıldız Teknik Üniversitesi Fen Bilimleri Enstitüsü, İstanbul

KÜKÜRTÇÜ, 2008. Biyoaktif Cam ve Cam- Seramik Malzemelerin Üretimi ve Yapay Vücut Sıvısı İçerisindeki Davranlıkların İncelenmesi. Yüksek Lisans Tezi. İstanbul Teknik Üniversitesi Fen Bilimleri Enstitüsü, İstanbul.

MO, K. H., ALENGARAM, U. J., JUMAAT, M. Z., YAP, S. P., LEE, S. C., (2016). Green concrete partially comprised of farming waste residues: a review, Journal of Cleaner Production ,117, 122-138.

PALABİYIK, H., ALTUNBAŞ, D., (2004). "Kentsel Katı Atıklar ve Yönetimi", Çevre Sorunlarına Çağdaş Yaklaşımlar: Ekolojik, Ekonomik, Politik ve Yönetisel Perspektifler, 103-124. Beta, İstanbul.

SARACOĞLU, N., (2010). “Küresel İklim Değişimi, Biyoenerji ve Enerji Ormancılığı”. Ankara: Efil Yayınevi.

TÜĞİAD, 2004 Türkiye’nin Enerji Sorunları ve Çözüm Önerileri, Ajans-Türk Basin ve Basım A.Ş, Batıkent, Ankara.
http://www.biltek.tubitak.gov.tr/bdergi/yeniufuk/icerik/biyomalzemeler.pdf (2008)
http://www.medicinecube.com/content/view/108/64/ (2008).