

## Environmental Effect of the Coffee Waste and Anti-Microbial Property of Oyster Shell Waste Treatment

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### Abstract

Coffee is one of the most popular and consumed beverages in the world, which leads to a high contents of solid residue known as spent coffee grounds (SCG). As is known, coffee beans contain several classes of health related chemicals, including phenolic compounds, melanoidins, diterpenes, xanthines and carotenoids. The waste water coming out of coffee industries has high concentration of organic pollutants and is very harmful for surrounding water bodies, human health and aquatic life if discharged directly into the surface waters. Hence it is essential to treat and manage the coffee waste. Oyster shells are a waste product from mariculture that creates a major disposal problem in coastal regions of southeast Korea. In the study, the oyster shell waste was used to treat the coffee waste and its effluents. Oyster shells are calcined at 1000°C for 2 h, and allowed to test the calcined CaO powder ability to inhibit the growth of bacteria in different aging coffee wastes. Calcined oyster shell powder showed anti-bacterial effect that inhibited cell growth of *Escherichia coli* and other bacterial forms. The antimicrobial activity of calcium oxide from oyster shell waste for biological treatment and utilization as a fertilizers with economic ecofriendly in nature.

**Key words** : Calcium oxide, Oyster Shell Waste, Coffee Waste, Bacteria.

### 1. Introduction

Coffee is one of the most important agricultural commodities in the world. It belongs to the family *Rubiaceae* and it has many species. *Coffea arabica* and *Coffea robusta* are the two principal varieties of the genus cultivated all over the world for commercial purpose<sup>1-3</sup>. Nowadays coffee produced a large number of countries throughout the world. However, the ten largest coffee producing countries are responsible for approximately 80% of the world production. Of this percentage, South America participates with

around 43%, Asia with 24%, Central America 18%, and Africa with 16%. Brazil, Vietnam, Colombia, and Indonesia are respectively the first, second, and third largest world producers, responsible for more than half of the world supply of coffee, according to the International Coffee Organization<sup>4</sup>, in 2009 Brazil produced approximately 40 million bags of coffee as shown in Table .1.

The spent coffee waste contains large amounts of organic com-pounds like fatty acids, lignin, cellulose, hemicellulose, and other polysaccharides that justify its valorization, the wet processing of coffee cherries is an alternative, however generates a large amount of coffee processing wastewater (CPW), rich in suspended organic matter, organic and inorganic

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**Table 1.** Annual worldwide coffee production (million bags of 60 kg).<sup>4)</sup>

Countries	Production					
	2004	2005	2006	2007	2008	2009
Brazil	39.272	32.944	42.512	36.070	45.992	39.470
Vietnam	14.370	13.842	19.340	16.467	18.500	18.000
Colombia	11.573	12.564	12.541	12.504	8.664	9.500
Indonesia	7.536	9.159	7.483	7.777	9.350	9.500
Ethiopia	4.568	4.003	4.636	4.906	4.350	4.850
India	4.592	4.396	5.159	4.460	4.372	4.827
Mexico	3.867	4.225	4.200	4.150	4.651	4.500
Guatemala	3.703	3.676	3.950	4.100	3.785	4.100
Peru	3.425	2.489	4.319	3.063	3.872	4.000
Honduras	2.575	3.204	3.461	3.842	3.450	3.750
Côte d'Ivoire	2.301	1.962	2.847	2.598	2.353	1.850
Nicaragua	1.130	1.718	1.300	1.700	1.615	1.700
El Salvador	1.437	1.502	1.371	1.621	1.547	1.500
Other countries	15.713	15.779	16.019	16.138	15.680	15.455
Total	116.062	111.463	129.138	119.396	128.181	123.002

compounds in solution, with high polluting potential<sup>4</sup>, which must be necessarily treated before its release into the environment.

Environmental pollution because of improper waste management is an alarming challenge for developing countries to meet the millennium development goals. Several studies reported<sup>5-7</sup> that untreated waste from traditional and modern industries is threatening surface waters worldwide, and it is severe in developing countries<sup>8</sup>. Water pollution is the gloomy setback for the development in coffee producing countries<sup>9-10</sup>, and this also appears to be the case in Ethiopia<sup>11-12</sup>.

The International coffee organization estimates that, 6,985,680 tons of coffee beans were produced worldwide in 2004<sup>13</sup>. Coffee processing is vilified for the

production of byproducts such as parchment husks, coffee pulp and coffee husks all of which contribute to environmental pollution unless treated or recycled<sup>14</sup>. Developing countries are facing a serious problem in properly disposing of the waste produced by production of coffee. It is estimated that more than two million tons of coffee waste is generated yearly<sup>15</sup>. Mexico produced 232,020 tons of Arabica coffee beans and was the 7<sup>th</sup> leading producer of coffee in 2004. As a result, Mexico faces the challenge of economically treating coffee waste to avoid soil and water pollution while staying competitive in the global coffee market. In fact all coffee producing countries face this challenge, however generates a large amount of coffee processing wastewater (CPW), rich in suspended organic matter, organic and inorga-

**Table 2.** Oyster culture production (with shell, tons) by country.<sup>31)</sup> FAO yearbook, Fishery statistics, Aquaculture production, Vol.100/2 (2005)

Species	Country	Production of Shell (Tons)	
		Year-2000	Year-2005
Pacific cupped oyster ( <i>Crassostrea gigas</i> )	China	3,291,929	3,826,363
	Japan	221,252	218,896
	Korea Rep	177,079	251,706
	France	133,500	118,120
	USA	38,418	21,323
	Taiwan	19,972	28,430
	Australia	4,693	7,295
	Canada	5,500	7,638
	Chile	5,641	2,226
	Ireland	5,031	5,811
	New Zealand	3,500	2,800
	Other	3,722	6,477
Thai oyster ( <i>Crassostrea spp.</i> )	Thailand	13,556	27,680
American oyster ( <i>Crassostrea virginica</i> )	USA	38,255	55,188
	Canada	4,124	4,946
Slipper oyster ( <i>Crassostrea iredalei</i> )	Philippines	14,222	16,495
European flat oyster ( <i>Ostrea edulis</i> )	Spain	3,383	2,980
	France	2,000	1,280
	Other	656	909
Sydney oyster ( <i>Saccostrea commercialis</i> )	Australia	4,961	4,456
	Other	6,836	4,144
Grand Total		3,998,513	4,615,400

nic compounds in solution, with high polluting potential<sup>5</sup>, the waste water from coffee industries has high concentration of organic pollutants<sup>16</sup>, and is very harmful for surrounding water bodies, human health and aquatic life if discharged directly into the surface waters<sup>17</sup>. This effluent is being directly discharged to the nearby water bodies and thus causing

many severe health problems like spinning sensation, eye, ear and skin irritation, stomach pain, nausea and breathing problem among the residents of nearby areas.

Besides these characteristics, the coffee processing wastewater has phenolic compounds<sup>18</sup>, organic, acidic acids and the fermentation of sugars in the mu-

cilage make the wastewater very acid (pH down to 3.8). Under these acid conditions, higher plants and animals will hardly survive and after the first fermentation of sugars in the waste water took place, the organic substances diluted in the waste water break down only very slowly by microbiological processes using up oxygen from the water. This process causes problems as the demand for oxygen to break down organic material in the waste water exceeds the supply, dissolved in the water, thus creating anaerobic conditions.

### 1.1 Environmental problems caused by oyster shells

In the southern coast of Korea, a lot of oyster shells are dumped as a by-product of marine aquaculture industry<sup>19</sup>. A large amount of oyster shells is a general waste fishermen should take care of but it seems difficult to handle it effectively due to the problems of securing of landfill sites and collection/transportation of oyster shells<sup>20</sup>. This waste piles up at coastal areas and causes many environmental problems including pollution of coastal fisheries, management problem of public water surface, dam-

age of natural landscape, and health/sanitation problem. Table 2. Shows as Oyster culture production (with shell, tons) by country<sup>21</sup>.

In Japan, 200,000 tons of oysters were produced in 2007<sup>22</sup>, and Korea has a lot of oyster shells production as shown in Table-3 from 1997 to 2006. On the basis of these data, generation of oyster shells is estimated on the average at 270,000 tons/year, and more than 50~70% of which was dumped into public waters and reclaimed lands, which cause an unpleasant fishy smell as a consequence of the decomposition of fresh remnant attached to oysters<sup>23</sup>.

Environmental problems caused by waste oyster shells were as follows, i) increase of waste, ii) pollution of marine eco-system due to illegal landfill, iii) increase of bad smell due to negligence, iv) a huge amount of treatment expense, and v) weak demand on recycled materials (fertilizer, etc.) from oyster shells. Environmental engineering research on recycling of oyster shells has been somewhat conducted in China and Japan, but most of the research has focused on the purpose of water purification in a limited scope. In case oyster shell is used as a soil conditioner, it has higher adsorption and desorption

**Table. 3.** Oyster production and estimated generation of oyster shells in Korea

Year	Oyster Production (Ton)	Estimated Generation of Oyster Shells (Ton)
1997	17210	258150
1998	9905	148575
1999	11690	175350
2000	15939	239085
2001	10056	150840
2002	7950	119250
2003	20201	303015
2004	25690	385350
2005	27320	409800
2006	31016	465240

of heavy metals than general soil, and so it may bring in stable and economical effects.

The oyster shell can neutralize acidic waste water from mines very fast and remove 99% of heavy metals, and so it is judged to be a useful material to replace limestone. Oyster shells have been utilized effectively as fertilizers, soil conditioners, natural medicines rich in calcium, waterworks filter mediums, etc. dried oyster shells had an effective bacteriostasis. In addition, the fact that burned and finely powdered oyster shells, as compared with oysters shells dried at room temperature, showed a stronger bacteriostasis. In various kinds of tests by using limestone powder or pure calcium carbonate ( $\text{CaCO}_3$ ) to determine if the bacteriostasis of oyster shells was caused by  $\text{CaCO}_3$ <sup>48</sup>. Oyster shells are not fishery waste material but valuable source material for a new industry, it shows such a strong bactericidal activity that it kills one of the most virulent pathogens, *Escherichia coli* O-157:H7 effectively.

## 1.2 Calcium Carbonate synthesis from Oyster Shell Waste

Lime stone with a purity of more than 90 wt%  $\text{CaCO}_3$  is usually used in waste water treatment, similarly Oyster shell are comprised of 90 to 95 wt percent  $\text{CaCO}_3$ , making this material an excellent potential alkalinity source for treatment of coffee waste water. The structure of the shells is comprised of three layers: an inner layer consisting both aragonite and calcite interbedded with protein molecules, and an outer layer made of chitin. The aver-

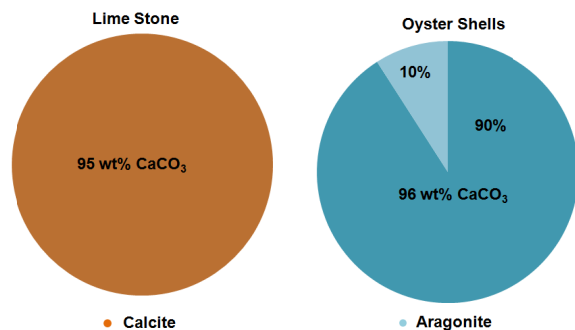


Figure. 1. Mineralogical composition of oyster shell

age composition of minerals in the shell is approximately 90% Calcite and 10% Aragonite<sup>24</sup>, as shown in Fig.1. Mineralogical composition of limestone and oyster shells showing the total content of  $\text{CaCO}_3$  and the relative abundance of calcite and aragonite.

Calcium carbonate synthesis from Oyster shell waste by calcinations and hydration process as used to mix with coffee waste water for many application like anti-microbial activity, control the acidity of coffee waste for reducing toxic effect to the environment and utilized as a fertilizer with economic eco-friendly in nature. In recent study suggested that alkalinity generation rates between 60 to 113% higher obtained with oyster shells used instead of limestone.

The main objective of this work is the oyster shell recycling for utilizing as an anti-microbial agent to control the bacterial content present in coffee waste. Oyster shell are comprised of 90 to 95 wt% of  $\text{CaCO}_3$ , making this material an excellent potential alkalinity source for treatment of coffee waste and it is to be very helpful in preventing the damage of natural landscape and solving coffee waste health problem. Therefore, new applications utilizing these wasted oyster shells are expected to contribute towards recycling consciousness within the society.

## 2. EXPERIMENTAL PROCEDURE

### Materials and Methods

The starting materials were Coffee waste material (Deete espresso Coffee shop, Daejeon, South Korea), oyster shell waste (Namhae, South Korea), 3M Petri films and sodium chloride (Junsei Company, Japan).

Fresh coffee waste collected from Deete espresso coffee shop and stored at room temperature with different aging periods. The coffee waste samples are divided into four different groups based on their aging times like fresh coffee waste, Three days after coffee waste, Five days after coffee waste and one week after coffee waste was used to analysis the total and E-coli bacterial counting.

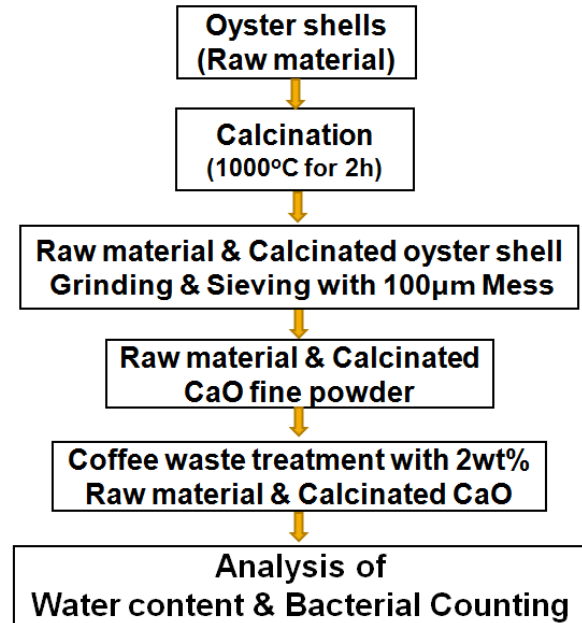
Oyster shell waste collected from waterfront areas

in Namhae, South Korea, and cleaned with alcohol and water to remove impurities attached to the surfaces. This cleaned oyster shells was calcined in an electric furnace at a constant three different temperatures from 900 to 1200 °C for 2 h, which was increased to this point at a rate of 10 °C/min. The calcined raw materials were mechanically grinded for 1 h until the particle size was less than 100µm. This fine powder hydraulic activity was measured and also used as a antimicrobial agent to treat different aging coffee waste samples.

In hydraulic activity measuring process, 30g of quick lime sample was placed in the heat measuring apparatus for agitation. After 20 minutes of running the agitator, time and temperature shall be recorded to 0.01 °C using the Beckmann thermometer. The change in temperature within the heat measuring apparatus during agitation shall be 25 °C. Distilled water shall be added to the reactor at a constant rate through the funnel. The amount of distilled water shall be 120 mL, and have a temperature of 25 °C ± 2 °C. The temperature inside the calorimeter shall be measured at 5-second intervals upon addition of the distilled water. Heat produced from hydration reactions of quicklime from oyster shells shall be measured for 2 h after reactions begin.

The fine oyster powder (2 wt%) was used to treat with different aging coffee waste samples. Fig. 2, shows the flow sheet of coffee waste treatment with oyster shell waste. After treatment measured water content and bacterial counting was measured by Aerobic Colony Count (ACC) method, in these process to estimates the number of viable aerobic bacteria per gram or mL of product. A portion of the product is mixed with a specified agar medium and incubated under specific conditions of time and temperature. It is assumed that each viable aerobic bacterium will multiply under these conditions and give rise to a visible colony which can be counted.

In these bacterial colony counting process, the 5g or 5ml of samples was transfer to 45 ml of 0.85% NaCl diluents (or 1 g/1ml to 9 ml). The density of the product must be known if the transfer is based



**Figure. 2.** Coffee waste treatment with oyster shell waste.

on weight. Homogenize the dilutions and spread 100 µl of dilutions in duplicate on the surface of the agar coated 3M Petri film. Use the  $10^{-1}$ ,  $10^{-2}$  and  $10^{-3}$  dilutions for the bacterial challenges. For subsequent sampling select the dilutions to be analyzed on the basis of the results.

In these experiment we measured different aging coffee wastes and treated with oyster shells powder (before and after calcination), to analyzed the water content (wt%) present in the sample and total number of bacteria also E-Coli bacterial counting present in the samples.

### 3. Results and Discussion

During this experimental process, we are measuring the chemical composition of oyster shells and activity. After calcinated oyster shell CaO was used as an antimicrobial agent for coffee wastes treatment.

#### 3.1 Oyster shells chemical composition.

Oyster shells major composition is  $\text{CaCO}_3$  (98.2 %) are present, remaining other impurities, X-ray Fluorescence spectroscopic (XRF) results shows in Table

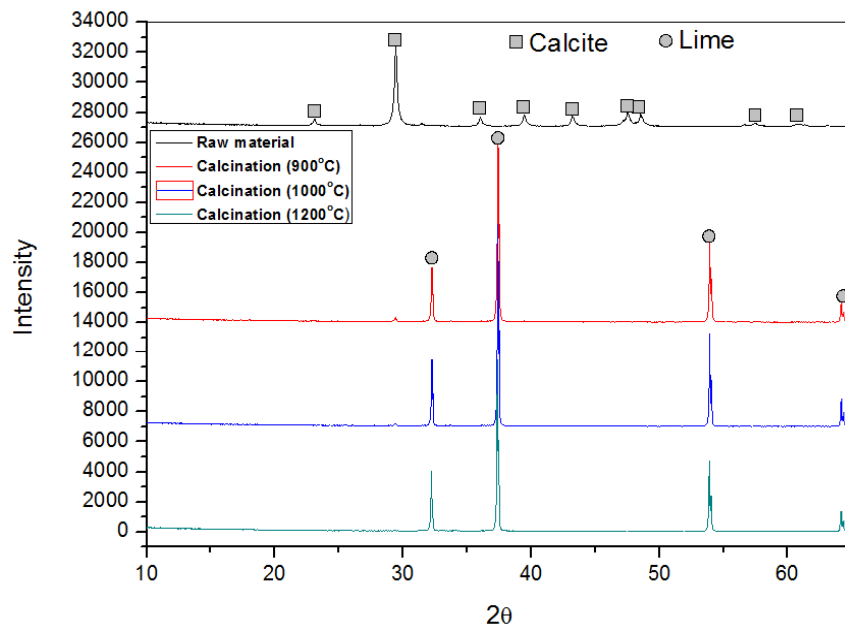
4, presents the chemical composition analysis, it was found that oyster shells consists of mostly CaO (53.66 %) and the Ignition loss (44.56 %) from the decomposition of  $\text{CaCO}_3$  to release  $\text{CO}_2$  gas, which

**Table. 4.** Chemical composition of oyster shells.

Oxides	Oyster (%)
CaO	53.66
$\text{SiO}_2$	0.45
$\text{Al}_2\text{O}_3$	0.12
$\text{Fe}_2\text{O}_3$	0.06
MgO	0.26
$\text{K}_2\text{O}$	0.06
$\text{Na}_2\text{O}$	0.55
$\text{P}_2\text{O}_5$	0.16
Ig Loss	44.56

is comparable to that of commercial Jungsun limestone and was in good agreement with the results of Yoon et al. (2003) reporting the CaO content of oyster-shells was about 53.7 wt.%, and also some of other impurities such as  $\text{SiO}_2$  (0.45%),  $\text{Al}_2\text{O}_3$  (0.12%),  $\text{Fe}_2\text{O}_3$  (0.06%) MgO (0.26%),  $\text{K}_2\text{O}$  (0.06%),  $\text{Na}_2\text{O}$  (0.55%),  $\text{P}_2\text{O}_5$  (0.16%) are present.

X-ray diffraction (XRD) patterns of waste oyster shells raw material and calcined waste oyster shells are shown in Fig. 3. The results of XRD analyses of the waste oyster shells with and without calcination. The patterns for waste oyster shells raw material diffraction peaks of  $\text{CaCO}_3$  as major phases (98.2 %) are identified and the patterns for calcined at different temperatures, at 900 °C calcination the oyster shells waste were exhibited peaks characteristics of lime (CaO) (93.46%), at 1000 °C calcination the oyster shells waste were exhibited 98.13 % of CaO, and the calcination at 1200 °C the oyster shells waste were exhibited 98.27% of CaO. These results indicated that the intensity of these peak increases with increasing the calcination temperature indicating CaO phase has been formed enough after calcination.



**Figure. 3.** XRD analysis of oyster shells waste without calcination and with calcination at different temperatures.

### 3.2. Oyster shells calcination characteristics.

We examine the calcination characteristics and hydraulic activity of oyster shell waste. The shells were calcinated at different temperatures (900-1200°C) as shown in Fig 4. These calcined oyster shells brightness was gradually increase with increasing temperature, and these calcined shells were mechanically grinded for 1 h until the particle size was less than 100µm.

These fine powder (<100µm) of oysters was used to measure the hydraulic activity for heat generated by hydration reactions in relation to hydration reaction time for quicklime (CaO) from calcined oysters at different temperatures. Fig. 5, shows the hy-

draulic activity of calcined oyster shells at different temperatures (900-1200 °C).

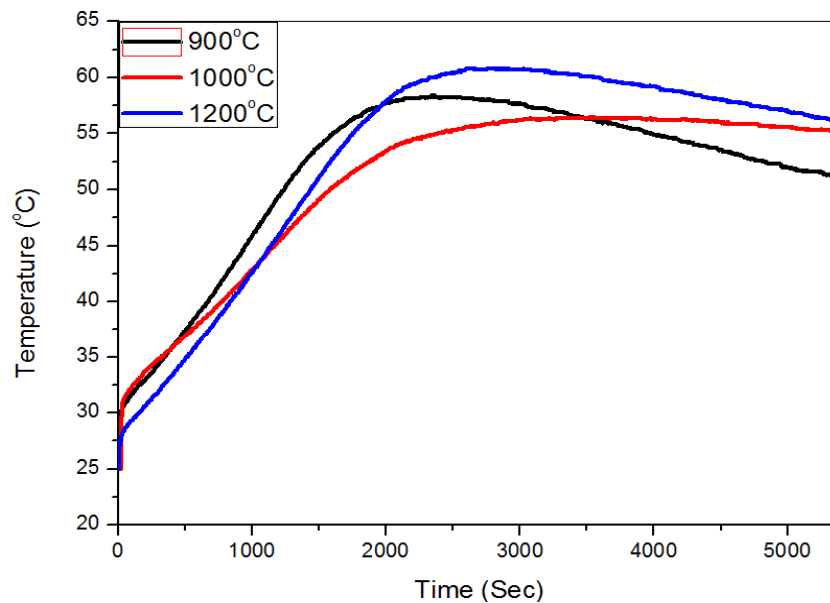
### 4. Antimicrobial property of oyster shell treatment with coffee waste.

Coffee waste treated with Oyster shell powder and utilizes as a safety fertilizer

Coffee waste is produced at high temperatures (70°C), the pH is near 4 and, due to the roasting process, and a number of phenol heterocyclic compounds may appear. The anaerobic digestion of coffee waste has been reported at mesophilic



**Fig. 4.** Oyster shell waste calcination at different temperatures (a) Before calcination, (b) Calcination at 900 oC, (c) Calcination at 1000 oC and (d) Calcination at 1200 oC.



**Fig. 5.** Calcinated oyster shells CaO hydraulic activity at different temperatures (900, 1000 and 1200 oC).



temperatures. Fresh coffee pulp contains a vast microbial population of bacteria, fungi and yeast. During composting of pulp, an increase of mesophilic and actinomycete populations has been observed. Fungi play an important role in the initial steps of composting because of their saprophytic activity and the attack of lignin and cellulose transforming them into simple carbohydrates, by the adding oyster shell waste to neutralize the pH and reduced the toxic effluents and micro organisms and utilized as a fertilizer has gained attention due to the great potential in both the availability of used coffee grounds and its beneficial properties in compost.

While there have been few studies conducted on used coffee grounds, multiple studies have discovered the benefits of coffee waste, or pulp. The pulp, the fruit part of the coffee berry, is attributed to greater soil and compost quality. When the pulp is placed in the soil, its rich nutrient levels, along with the relatively high alkalinity of soil humus, contributes to reductions in soil acidity with oyster shell waste and increased retention of water, and increased levels and retention of nutrients. The organic matter of coffee waste also provides more nitrogen and potassium than common fertilizers, making it a valuable organic fertilizer. Nutrient value enhancement with the presence of coffee pulp provides soil fertility richness along with nutrients for both plants and the soil microorganisms. Based off of these known positive effects of coffee pulp on soil nutrients and organisms, we look to extrapolate from these known benefits to investigate the effect of coffee wastes adding with oyster shell powder.

In North America, almost two million metric tons of spent coffee grounds are generated annually and are either put into landfills or processed at waste facilities with other organic wastes. If coffee drinkers began to compost their used grounds instead of throwing them away, they could create a significant reduction in their environmental impact. Because of the widespread availability of coffee grounds, along with its known ability to improve soil composition, coffee grounds were chosen as the experimental

compost with oyster shell waste to be further investigated.

## 5. Conclusions

Overall, these studies revealed that the extracted calcium carbonate from oyster shell waste has highly beneficial. This oyster shell wastes are highly rich mineral sources of calcium carbonate and alternative to limestone. The present study has demonstrated that a waste product of oyster shells can be transformed into an effective treatment for coffee wastewaters. This treatment process is simple, economic ecofriendly a novel method for recycling waste oyster material to provide a beneficial product and promises to greatly reduce problems caused by mariculture in coastal regions. Preliminary economic evaluation indicates that the product is competitive with other wastewater treatment chemicals. Further research is needed to optimize the conditions under which activated oyster shells are produced and to understand the conversion process from calcium carbonate to calcium oxide in the oyster shell matrix. This extracted calcium carbonate used as an advanced functional filler to waste water treatment, fertilizer, pathogens removal, coffee waste treatment, water content and simultaneously can used for light-weight plastics.

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## References

1. International Coffee Organization (ICO), <http://www.ico.org/proddoc.htm>, 1998.
2. P.S. Rodriguez, S.R.M. Perez, B.M. Fernandez,

- Studies of anaerobic biodegradability of the wastewater of the humid benefit the coffee, *J. Inter-ciencia.*, 25, 2000, 386-90.
3. Food and Agricultural Organization (FAO). Production yearbook, Vol. 50. FAO Statistics Series No.135. Rome, Italy. 172, 1997.
  4. ICO, International Coffee Organization. Available at: <http://www.ico.org/>. Accessed (05 March 2010), 2010.
  5. A.T. Matos, R.F. Fia, F.A.R. Luiz, Características rastreáveis dos sistemas de tratamento de águas residuárias geradas no processamento de frutos do cafeeiro. In: ZAMBOLIM, L. (Org.). Rastreabilidade para a cadeia produtiva do café, Visconde do Rio Branco: Suprema Gráfica e Editora., 2007, 321-77.
  6. R. Fia, A.T. Matos, F.A.R. Luiz, P.A. Pereira, Coeficientes de degradação da matéria orgânica de água residuária da lavagem e descascamento dos frutos do cafeeiro em condições anóxica e aeróbia, *Engenharia na Agricultura.*, 15, 2007, 45-54.
  7. N. Fernandez, C.F. Forster, A study of the operation of mesophilic and thermophilic anaerobic filters treating a synthetic coffee waste, *Biore-source Technology.*, 45(3), 1993, 223-27.
  8. A. Beyene, Y. Kassahun, T. Addis, F. Assefa, A. Amsalu, W. Legesse, H. Kloos and L. Triest, "The impacts of traditional coffee processing on river water quality in Ethiopia and the urgency of adopting sound environmental practices. *J Environ Monit Assess.*, 184, 2011, 7053-7063.
  9. P.K. Mwaura, J.K. Mburu, Effect of wet processing of coffee on river water quality. *Kenya Coffee.*, 63, 1998, 2779-2787.
  10. K. Varunprasath, N.A. Daniel, Physico-chemical parameters of river Bhavani in three stations, Tamilnadu, India, *Iranica J Energy Environ.*, 1, 2010, 321 - 25.
  11. A. Haddis, R. Devi, Effect of effluent generated from coffee processing plant on the water bodies and human health in its vicinity, *J Hazard Mater.*, 152, 2008, 259-262.
  12. A. Beyene, Development and validation of ecological water quality monitoring tools for river systems of Ethiopia, VUB Press, Brussels., 2010.
  13. International coffee organization. Trade statistics. Available at: [http://www.ico.org/trade\\_statistics.asp](http://www.ico.org/trade_statistics.asp). Accessed January 17, 2006.
  14. J.K. Mburu, P.K. Mwaura, Environmentally sound management of coffee processing by-products: a review, *Kenya Coffee.*, 61, 1996, 2237-2244.
  15. A. Pandey, C.R. Soccol, P. Nigam, D. Brand, R. Mohan, S. Roussos, Biotechnological potential of coffee pulp and coffee husk for bioprocesses, *Biochem. Eng. J.*, 6, 2000, 153-162.
  16. C. Chapman, Water quality assessments, A guide to the use of biota, sediments and water in environmental monitoring, Chapman and Hill, London, United Kingdom, 1996.
  17. J.C. Enden, K.C. Calvert, Limit environmental damage by basic knowledge of coffee waste waters, GTZ-PPP Project-improvement of coffee quality and sustainability of coffee production in Vietnam, 2002.
  18. F.R.L. Fia, A.T. Matos, A.C. Borges, D.A. Moreira, R. Fia, V. Eustaquio Junior, "Remoção, "decompostos fenólicos em reatores anaeróbios de leito fixo com diferentes materiais suporte. *Revista Brasileira de Engenharia Agrícola e Ambiental.*, 14(10), 2010, 1079-1086.
  19. B. Monoj Kumar, Savitha U Ulavi, H.S. Ramesh, G. Asha, R. Pallavi, Pretreatment of coffee pulping waste water by Fenton's reagent, *Ind. j. of Chem. Tech.*, 19, 2012, 213-217.
  20. J.H. Jung, Reuse of waste oyster-shells as a SO<sub>2</sub>/NO<sub>x</sub> removal absorbent, *Jour. of Indus. and Eng. Chem.*, 13(4), 2007, 512-517.
  21. FAO, FAO yearbook, Fishery statistics, Vol. 100/2 (2005), Food and Agriculture Organization of the United Nations, Rome. 2007.
  22. S. Asaoka, Removal of hydrogen sulfide using crushed oyster shell from pore water to remediate organically enriched coastal marine sediments, *Bio resource Tech.*, 100, 2009, 4127-4132.
  23. H.S. Kim, The study of application of discarded oyster shell powder as an architectural material,

Dong-A University, Master thesis, Korea, 2007.

24. J. Hutchinson, A.D. O'Sullivan, Scanning electron microscopy of substrates from bioengineered treatment reactors, elucidating the blank box. Department of Civil and Natural Resources Engineering. University of Canterbury. 2008.