# Investigation Biosorption Potential of Copper and Lead from Industrial Waste-Water Using Orange and Lemon Peels

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## Abstract

Much attention has been made towards adsorbent materials to be used in heavy metal removal from polluted water and various techniques are applied such as chemical, physical and biological techniques. This study was designed for using less expensive and much frequently available materials (orange & lemon peels) to remove copper and lead from industrial waste-water. Three forms of these peels (fresh dried small pieces and powder) were used. Also other factors such as pH and temperature were examined for probable effects on biosorption. Current data show that both orange and lemon peels are capable of removing copper and lead ions at significant capacity. Furthermore, lemon peels had higher capability than orange peels and the form of peel powder of both orange and lemon showed higher capacity than fresh and dried pieces where lemon powder has shown biosorption capacity of 72.5% and 71.3% for lead and copper respectively while orange powder had bioremoval percentage of 56.7% of lead and 34.5% for copper. In case of fresh lemon peels, these figures were 70.9% for lead and 62.2% for copper but fresh orange peels gave much less percentage (48.7of lead and 29.6% of copper). Regarding dried peels which showed the lowest values, but again, lemon peels were significantly better than those of orange. These values of lemon were 58.0% for lead and 57.1% for copper but for orange peels, the biosorption percentages reached 37.2% and 23.7% for lead and copper respectively. However, biosorption capacity of both fruit peels at different forms were significantly affected by various levels of both pH and temperature. The optimum pH and temperature values for better bioremoval capacity for all treatment within this study were 5 and 40 C° for pH and temperature respectively. Based on above, current data found that lemon peels are more efficient than the orange peels as biosorbents materials.

Keywords: orange and lemon peels, biosorption, copper, lead, industrial wastewater.

## Introduction

The characteristics of industrial waste-water may differ considerably both within and among industries. The impact of industrial discharges would depend not only upon collective characteristics such as BOD and suspended soil, but also on their content of specific inorganic and organic substances. Heavy metal water pollution represents an important environmental problems due to the possible toxic effects of the metal to both human and environment. The main sources of water contamination with various heavy metals are industrial waste water [1].

Several techniques were applied to remove heavy metal ions from industrial waste water such as activated carbon adsorption [2]; chemical precipitation, reverse osmosis [3]; electrodialysis and ion exchange.

However, recently much attentions have been focused on possible biological methods for the removal of heavy metals from industrial waste water such as microbial biomass [4] and biological wastes [5]. These biosorbent materials are characterized being less expensive, high bio-removal efficiency, metal selective, non sludge generation, possible ion recovery and environmentally sound methodology [6].

The technique of plant residues heavy metal ions adsorption was world widely used for waste water treatment [7] such as peat and nut shells, coconut shells, rice husk, tea waste, peanut hulls, almond shells, peach stones, banana peels, and many others [8,9].

Peels of citrus plants contain up to 80% water and the remaining 20% are solid fractions consisting pectin, soluble sugars, cellulose, proteins, phenols. The most abundant represented class of biomolecules in citrus peels are polysaccharides [10] that offer with the presence of pectin a greatest potential for enzymatic or chemical conversion to create desired properties such as ion exchange capacity, galacturoriic acid (GA) the major sugar found in citrus pectin [11].

## Material and Methods

Industrial waste water samples were collected from pretreatment units of both pasting and charging sites of battery producing Babylon 2 factory (From each site, a sample of 500 ml waste water were collected in three random periods between 13th March to 4th April 2009. Each sample was divided into two subsamples, the first was examined for chemical & physical analysis and the second was employed for bioremoval of lead and copper ions.

## Chemical Analysis:

Temperature of industrial wastewater was measured *in situ* at approximately 15-20 cm depth using portable thermometer. Also, pH and EC were measured in the laboratory. Lead and copper concentrations of industrial wastewater were determined by using 100 ml of each sample and 5 ml concentrated nitric acid was added and placed on a hot plate with gradual heat increase to insure full digestion and the disappearance of any residual nitric acid and both lead and copper contents were measured by using flame atomic absorption spectrophotometer (FAAS).

## Biosorption capacity of citrus peels:

Orange and lemon peels were collected and washed thoroughly by DDW and used subsequently in the following examinations:

### a. Various citrus peel forms

Three citrus peel forms were used, the first was as fresh pieces, the second was as dried pieces and finally powdered peels that sieved through 4mm stainless steel sieve. All peel forms were examined for bioremoval of both copper and lead from aqueous synthetic solutions under various factors such as pH, temperature and contacting time.

Synthetic aqueous metal solution was prepared by taking 20 ml of metal solution (100 mg/l) of lead or copper ions and placed into 50 ml volumetric flasks and the pH was adjusted to 5. About 0.05 g citrus peels as fresh, dried and powder were added to each flask in three replicated experiment in addition to control (metal ion solution free from peels). All samples were left for almost one hour at 40º C. Afterwards, each sample was passed through 0.45µm filter paper and metal concentration was determined by using FAAS following [12].

### b. Factors affecting metal bioremoval

The test carried out above was reassessed for the examination of possible effects of different levels of pH, and temperature. For pH, the range of 1–5 and temperature range was from 10º to 60º C was applied for both metals.

## Bioremoval copper and lead from industrial wastewater

According to the results of all experiments applied above, this test was designed to examine the capacity of lemon peels for the bioremoval of both copper and lead ions from industrial wastewater after the determination of these metals in such wastewater.

In this experiment, 12.5 g powder of dried lemon peels, being much better metal bioremoval, were placed into plastic tank containing two and half liters of industrial wastewater collected from pretreatment of both pasting and charging units and left under laboratory conditions at pH 5 and 40º C for almost 1 hour. Biosorbed metal concentration (mg/l) and biosorption capacity (%) were calculated by using the following equations [13]:

**Biosorbed metal conc. (mg/l) = $C_i - C_f$**

**Biosorption capacity % = $C_i - C_f / C_i$ X 100**

Where

$C_i$ =initial metal concentration and $C_f$ = final metal concentration.

## Statistical Analysis

The data of all experiments were subjected to various statistical tests for the significant differences such as analysis of variance (F test), correlation test and least significant differences test LCD [14].

## Results and Discussion

All obtained data were subjected to various biometrical analysis such as analysis of variance and least significant difference.

## Chemical analysis

Table (1) shows temperature, pH, electrical conductivity (EC), lead and copper concentrations in industrial wastewater samples collected from pasting and charging unites of battery producing Babylon 2 factory, Baghdad, Iraq.

Mean temperature values didn't exceed 33.5º C varying from 28.0 to 33.5 in pasting samples and from 28.0 to 33.0 in charging samples. Mean pH values were less than 8 for all examined samples. Mean electrical conductivity data were almost similar ranging from 0.7 - 1.3 µS/cm. Furthermore, mean lead content of all tested samples were two times greater than those of copper where they varied from 3.88 mg/l to 5.8 mg/l and from 0.9 mg/l to 1.4 mg/l for lead and copper respectively.

***Table (1)***
***Mean value ± SD of temperature, pH, electrical conductivity, lead and copper concentrations in sampled industrial wastewater.***

| *Measurements* | *Mean ± SD (n = 3)* | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *Pasting unit* | | | | *Charging unit* | | | |
| | *Sampling time (week)* | | | | | | | |
| | *1st week* | *2nd week* | *3rd week* | *4th week* | *1st week* | *2nd week* | *3rd week* | *4th week* |
| Temp. º C | 30.0±0.1 | 28.0±0.2 | 30.0±0.5 | 33.5±0 .5 | 30.0±0.2 | 28.0±0.5 | 30.0±0.5 | 33.0±0 .5 |
| pH | 7.95±0.22 | 7.5± 0.37 | 7.48±0.61 | 7.6±0 .14 | 7.68±0.15 | 7.33±0.33 | 7.9±0.0 | 7.03±0 .17 |
| Ec (µS/cm) | 1.2±0.21 | 0.7±0.61 | 1.1±0.27 | 0.9±0 .41 | 0.8±0.16 | 1.0±0. 16 | 1.3±0.29 | 1.0±0 .14 |
| Lead (mg/l) | 3.9±0.71 | 3.88±0.81 | 4.55±0.79 | 5.7±0 .22 | 4.7±0.08 | 5.8±0.22 | 5.3±0.29 | 5.6±0 .29 |
| Copper (mg/l) | 1.3±0.098 | 0.9±0.21 | 1.1±0.12 | 1.4±0 .21 | 1.3±0.2 | 1.6±0.5 | 1.2±0.15 | 1.4±0 .23 |

**Biosorption capacity of citrus peels:**

**a. Various peel forms**

It is clear from Table (2) that both orange and lemon peels are capable of removing copper and lead ions capacity. However, different forms of orange peels had effective ability to biosorbed both metals (LSD=3.349%; P ≥ 0.05) and such ability was found to be significantly different from each form to other. Highest capacity was recorded in case of peel powder for both metals (56.7 ± 0.8 % of lead and 34.5 ± 1.05 % for copper) followed by fresh peels (48.7 ± 1.4 % of lead and 29.6 ± 1.0 % of copper) and finally the less capacity was in case of dried peels (37.2 ± 0.5 % and 23.7 ± 1.1 % for lead and copper respectively).

Lemon peel forms had similar pattern of ability but significantly higher than those of orange peel forms These values were 72.5 ± 1.0 % for lead and 71.3 ± 1.1 % for copper at powder form and 70.9±1.4 % and 62.2±1.0 % for lead copper respectively at fresh peels whilst recorded 58.0 ± 0.05% for lead and 57.1 ± 1.5 % for copper when dried peels were used (Table (2)).

***Table (2)***
***Mean biosorption capacity ± SD % of both orange and lemon peels at three different forms.***

| *Peel form* | *Mean biosorption capacity ± SD %* | | | |
|---|---|---|---|---|
| | *Orange peel* | | *Lemon peel* | |
| | *lead* | *Copper* | *Lead* | *Copper* |
| **Dried pieces** | 37.2 ± 0.5% | 23.7 ± 1.1% | 58.0 ± 0.05% | 57.1 ± 1 .5% |
| **Fresh pieces** | 48.7 ± 1.4% | 29.6 ± 1.0% | 70.9 ± 1.4% | 62.2 ± 1.0% |
| **Powder (0.075 mm)** | 56.7 ± 0.8% | 35.4 ± 1.1% | 72.5 ± 1.0% | 71.3 ± 1.1% |
| **P≤0.05** | LSD= 3.349 | | LSD= 3.349 | |

Analysis of variance (Table (3)) reveals significant differences, firstly between both citrus peels and secondly between different peel forms ($P \leq 0.001$). Also significant differences were found between both biosorbed lead and copper ($P \leq 0.001$). Furthermore lead LSD at $P \leq 0.05$ was 2.483% and copper LSD at same probability was 4.366%.

***Table (3)***
***Analysis of variance of different citrus peel forms bioremoved lead and copper ions.***

| *S. of Variance* | *d.f* | *Lead LSD=2.483* | | | *Copper LSD=4.366* | | |
|---|---|---|---|---|---|---|---|
| | | *SS* | *MS* | *P* | *SS* | *MS* | *P* |
| **Reps** | 1 | 5.337 | 5.337 | | 0.084 | 0.084 | |
| **Treatment** | 5 | 2106.7 | 421.334 | 0.001 | 5154 | 1030.88 | 0.001 |
| **Fruit (F)** | 1 | 1452.003 | 1452.003 | 0.001 | 4840.083 | 4840.083 | 0.001 |
| **Forms (F)** | 2 | 630.17 | 315.085 | 0.001 | 268.167 | 134.084 | 0.001 |
| **F X F** | 2 | 24.492 | 12.249 | 0.001 | 46.167 | 23.084 | 0.001 |
| **Error** | 5 | 4.663 | 0.9326 | | 14.416 | 2.883 | |
| **Total** | 11 | | | | | | |

**a. pH & temperature affecting bioremoval capacity**

The effects of pH on the adsorption capacity of both citrus peel were found to be significant ($P \leq 0.001$) where adsorbed levels of both lead and copper were increased once pH increased (Fig.(1)).

In case of orange peels, maximum adsorption level of 64.1 ± 2.7% and 52.8 ± 1.2% for lead and copper respectively. But with lemon peels, these values were significantly higher where they have been found to be 83.5 ± 0.6% for lead and 79.7 ± 0.9% for copper. However, highest levels in both situations were at pH 5 whilst lowest values were at pH 1.

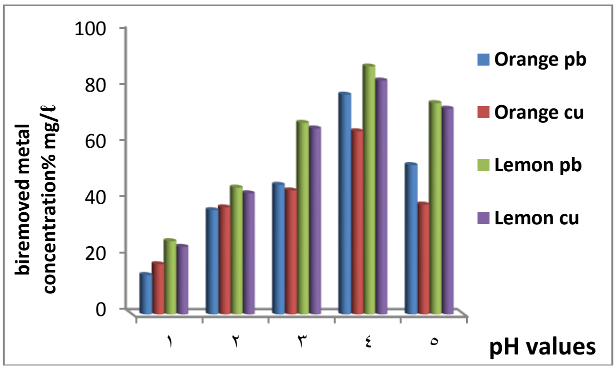


***Fig.(1) The effect of increased pH on bioremoval capacity of both orange and lemon peels.***

The least significant differences between all adsorption levels for orange peels was 2.589% for lead and 2.765% for copper. The analysis of differences between both orange and lemon peels and between different pH levels were at $P \leq 0.001$.

Various studies have examined the possible impact of pH upon heavy metal biosorption of different biosorbent materials and reported similar findings. Highest copper bioremoved by orange peel was achieved at pH range of 4.5 – 5.5. Cd ions bioremoved by corn, durian, pummel and banana was found to be high at pH 5 [12]. Optimum pH value for lead biosorption by okra wastes was within a range of 4 – 6 [15]. A study [16] had shown that highest lead bioremoved by maize leaf occurred at pH 3 and reported that 97% copper bioremoval found at pH 5 with using carrot residues.

The pH of aqueous solution plays a significant role in the biosorption process. This is partially due to the fact that $H^+$ ions are strongly competing adsorbents. The pH affects the specification of metal ions and the ionization of surface functional groups [17].

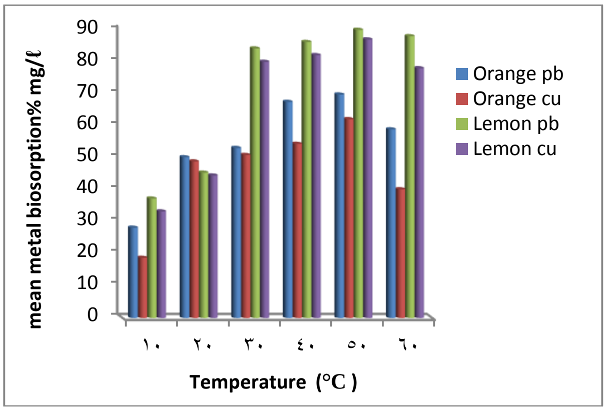


***Fig.(2) The effect of increased temperature on bioremoval capacity of both orange and lemon peels.***

Regarding the temperature influences upon Pb and Cu biosorption, the current study has found that the bioremoval capacity of both orange and lemon peels were affected significantly by temperature (Fig.(2)).

It very clear from the Fig.(2) that the temperature had significant effects on the biosorption of both Pb and Cu by orange peels (LSD at P$\leq$ 0.05 = 2.75% ) and similar impacts on both metals bioremoved by lemon (LSD at P$\geq$ 0.05 = 5.048 % ). However, the highest levels of lead and copper biosorbed by orange and lemon peels occurred at temperature of 50° C (Fig.(2)).

In case of orange peels, the highest bioremoved levels of both lead (66.4± 4.0%) and copper (58.1 ± 1.4%). These values were significantly lower in case of lemon peels reached 87.3 ± 0.2% for lead and 80.9 ± 1.0% for copper (Fig.(2)).

Recent study [18] has reported that highest Cr bioremoved by Maize tassel powder was at 45° C while for Cd bioremoval, was at 25° C. These contracting values may be related to several variables such as biosorbent substances, quantity, and other environmental factors.

However, the adsorbed species might have enough energy from temperature of the system and subsequently be desorbed at even a faster rate than adsorption rate, or may be due to linkage of cells in both higher and lower temperature extremes which may reduce the availability surface area of contact [19].

**Bioremoval of copper and lead from industrial wastewater**

It seems that the capacity of lemon peels for copper bioremoval, was much higher than that for lead bioremoval. Also such capacity was significantly (P $\leq$ 0.05) greater in case of charging wastewater unit than that of pasting unit (Fig. (3)).

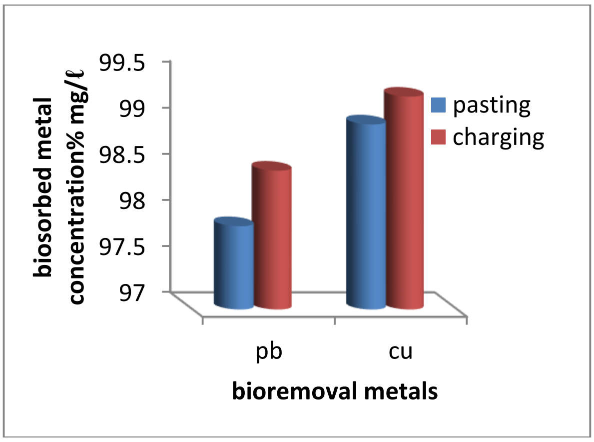


***Fig.(3) Biosorption capacity of lemon peels for removal both lead and copper ions from pasting and charging wastewater units.***

Mean capacity of lemon peels for lead bioremoval was 97.3 ± 0.01 % and for copper was 99.0 ± 0.05 % in case of pasting wastewater unit while these data regarding charging wastewater unit, where 98.5 ± 0.01 % and 99.3 ± 0.01 % for lead and copper respectively (Fig.(3)).

The current work indicate the ability of both orange and lemon peels for the removal of heavy metal ions from industrial wastewater as it had been reported for various biosorbent plant materials [8,17, 19, 20, 21] and would successfully be applied for various heavy metals from industrial wastewater since it seems environmentally sound.

**References**

[1] Richman, M.I. Water pollution. Wastewater, 5(2):24-29. 1997.

[2] Singh, C.K.; Sahu, J.N.; Mahalik, K.K. Mohanty, C.R.; Mohan, B.R. and Meikap, B.C. Studies on the removal of Pb (II) from wastewater by activated carbon developed from *Tamarind wood* activated

with sulphuric acid. J. Hazard. Mater.153; 221-228, 2008.

[3] Rengaraj, S.; Kyeong-Ho, M. and Seung, H. Removal of chromium from water and wastewater by ion-exchange resins. J. Hazard. Mater, 87; 273-28. 2001.

[4] Gadd, G.M. and White, C. Microbial treatment of metal pollution- a working biotechnology, Trends Biotechnol. J. 11 ; 353-359. 1993.

[5] Reddad, Z.; Gerente, C.; Andres, Y. and Pierre, L.C. Adsorption of several metal ions onto a low cost biosorbent: Kinetic and Equilibrium studies. Environ. Sc. Technol., 36(9):2067-2073. 2002.

[6] Deans, J.R. and Dixon, B.G. Uptake of $Pb^{+2}$ & $Cu^{+2}$ by noval biopolymers. Water Research, 26(4); 469-472. 1992.

[7] Mohan, D. and Singh, K.P. Single- and multi- component adsorption of chromium and zinc using activated carbon derived from bagasse-an agricultural waste. Wat.Res.36, 2304-2318. 2002.

[8] Khan, N.A., Ibrahim, S. and Subramanian, P. Elimination of heavy metals from wastewater using agricultural wastes as adsorbents. Malaysian J. Sci., 23,43-51. 2004.

[9] Doyurum, S. and Celik, A. Pb (II) and Cd (II) removal from aqueous solution by olive cake. J. Hazard. Mater, 138 (1):22-28. 2006.

[10] Grohmann, K.; Cameron, R.G. and Buslig, B.S. Fractionation and pretreatment of orange peel by dilute acid hydrolysis. Biores. Technol. 54(2): 129-141. 1995.

[11] Saikaew, W. and Kaewsarn, P. Pomelo peel: Agricultural waste for biosorption of cadmium ions from aqueous solution. World Academy of Sci. Eng. Technol.56. 2009.

[12] Hashem, M. Adsorption of lead from aqueous solution by okra wastes. Int. J. Phys. Sci, 2(7), 178-184. 2007.

[13] Fahad, H. G.. A study of efficiency of different microorganisms in thorium sorption from aqueous solutions. M.Sc. thesis. College of Science, Baghdad University, Iraq. 1994.

[14] Bernard, R. Fundamental of Biostatistics. 5th ed., Duxbury Publication, 527-532. 2000.

[15] Babarinde, N.A.A. ; Babalola , J.O. and Sanni, R.A. Biosorption of lead from aqueous solution by maize leaf. Int. J. Phys. Sci, I (1), 23-26. 2006.

[16] Eslamzadeh, T. ; Nasernejad, B. and Pour, B.B. Removal of heavy metals from aqueous solution by carrot residues. Iranian J.Sci. & Technol. Transaction A.28(A):16-19. 2004.

[17] Scheiwer, S. and Patil, S.B. Pectin-rich fruit wastes as biosorbents for heavy metal removal: Equilibrium and Kinetics. Biores. Technol.99; 1896-1903. 2008.

[18] Zvinowwanda,C.M.; Okonko, J.O. ; Agyei, N.M. and Shabalala, P.N. Physiochemical characterization of maize tassel adsorbent: Part I .Surface texture, microstructure and thermal stability. J. Applied Poly. Sci. 1923-193. 2009.

[19] Vijayaraaghavan, K.J. and Yun, Y.S. Bacterial biosorbents and biosorption. Biotechnol. Adv.26; 266-291. 2008.

[20] Annaduria, G. Juang, R.S. and Lee, D.L. Adsorption of heavy metals from water using banana and orange peels. Water Sci. Technol, 47 (1): 185-190. 2002.

[21] Saikaew, W. and Kaewsarn, P. Cadmium ion removal using biosorbents derived from fruit peel wastes. Songklanakarin J. Sci. Technol. 31 (5); 547-554. 2009.

**الخلاصة**

تم توجيهه الكثير من الاهتمام إلى الأنواع المختلفة من ألمازات لاستخدامها في امتزاز العناصر الثقيلة من مياه الفضلة الصناعية من خلال استخدام المتوفر من التقنيات الكيميائية و الفيزيائية و الإحيائية، صممت الدراسة الحالية لاستخدام مازات اقل تكلفة واكثر وفرة (قشور البرتقال والليمون) لازالة النحاس والرصاص من مياه الفضلة الصناعية وقد استعملت ثلاث صور من قشور كلا النباتين وهي قشور طرية، قشور جافة ومسحوق القشور. كذلك تم دراسة بعض العوامل المؤثر في عملية الامتزاز مثل الدالة الحامضية ودرجة الحرارة، اظهرت نتائج الدراسة الحالية بان قشور كل من البرتقال والليمون لها القابلية على امتزاز ايونات

النحاس والرصاص. في ذات الوقت؛ اظهرت الدراسة ان قشور الليمون كانت افضل من قشور البرتقال ولجميع صور القشور وبشكل عام يلاحظ في كلا الحالتين أن مسحوق القشور كان الاكثر كفاءة حيث بلغت نسبة امتزاز الرصاص ٧٢,٥% ونسبة امتزاز النحاس كانت ٧١,٣% في حالة قشور الليمون بينما في حالة قشور البرتقال كانت هذه القيم أقل حيث كانت ٥٦,٧% و ٣٤,٥% للرصاص والنحاس على التوالي. أما القشور الطرية فقد اظهرت قدرة امتزاز افضل من القشور الجافة لكلا النباتين حيث سجلت قشور الليمون معدل امتزاز للرصاص بلغ ٧٠,٩% و ٦٢,٢% لعنصر النحاس في حين اظهرت قشور البرتقال الطرية كفاءة اقل لتسجل معدلات امتزاز ٤٨,٧ و ٢٩,٦% لعنصري الرصاص والنحاس على التوالي. أما كفاءة القشور الجافة، فقد اظهرت أقل معدلات امتزاز لكلا النباتين في حالة قشور الليمون، كانت المعدلات ٥٨,٠% للرصاص و ٥٧,١% للنحاس بينما قشور البرتقال الجافة امتزت معدل رصاص بلغ ٣٧,٢% ومعدل نحاس وصل الى ٢٣,٧%. كذلك اظهرت الدراسة ان عملية امتزاز كلا العنصرين بقشور كلا النباتين تأثرت معنويا بالدالة الحامضية ودرجات الحرارة حيث تبين ان افضل قيمة للدالة الحامضية لتعطي اعلى معدل امتزاز هي ٥ وكذلك

الحال بالنسبة لدرجة الحرارة حيث تبين ان أنسب درجة هي ٤٠° م، ويستنتج من الدراسة الحالية أن قشور الليمون هي أكثر كفاءة من قشور البرتقال كمازات حيوية.