

Recycling of Waste Oyster Shells for the Treatment of Acidified Water toward Stabilization of Aquaculture Environment

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Oyster shells are one of the most abundant seafood wastes in Vietnam which have not been deposited efficiently, causing many negative effects on the ecosystem and the quality of human life. In this study, the recycling of waste oyster shells was investigated to provide a calcium carbonate-rich material for improving and stabilizing the pH value of acidified water. Characterization of the recycled shells using various techniques proved that the thermal treatments at temperatures from 120 to 220 °C led to no significant changes in the chemical composition and calcite-based layer structure of oyster shells. Testing the performance of the recycled oyster shells in the adjustment of the aqueous pH value was conducted in a solution containing NH₄Cl (0.5 g/L) as a simulation of the acidified aquaculture phase. As expected, using 1 g of the 220 °C -calcinated oyster shell for 2 L of the simulated solution, the solution pH rapidly increased from 6.3 to 7.7 in the first 2 h, reached the extreme value (~ 7.8) after 24 h and slowly decreased to the stabilized pH range of ~ 7.2 after 5-6 d. It was proved out that the oyster shell amount significantly affected the solution pH value. Importantly, the elemental analysis showed that the content of toxic transition metals including Cd, Pb, As, and Cr in the oyster shell was below the detection limit of each other, implying great potential for the application in the real aquaculture environment in Vietnam.

1. Introduction

Aquaculture has been a pivotal contributor to socio-economic development in Vietnam thanks to the advantage of abundantly-dense river network and long coastlines with rich biodiversity. Many stringent regulations on water quality parameters have been enacted and strictly monitored during farming to ensure the robust health and sustainable growth of aquaculture animals for high-quality productivity. pH value is employed as an important indicator in water quality control owing to its impact on most chemical and biological processes in aquatic ecosystem (Inga-Rengifo et al., 2023), which leads to the alternation of chemical state and toxicity of many pollutants, namely, ammonia. Different species thrive in their exclusive pH ranges with common range of 7 to 7.5. In recent decades, many both long-term and short-term environmental stresses comprising of increasing anthropogenic carbon dioxide, respiratory activities of living organisms or additional nutrients, etc. have been attributed to the water acidification to pH value of 6.5 that immensely inhibited the healthy survival and productivity of cultured animals. Acidification adjustment was performed via utilization of basic chemicals such as Ca(OH)₂, NaHCO₃, Na₂CO₃, Ca(HCO₃)₂, CaCO₃, dolomite. The prolonged applications of those could be against the cost-effectiveness of the treatment. Notably, the abrupt decline in pH value of chemical regulation treatment could lead to undesirable stress and mortality of water organisms.

The farming of oyster has offered not only a valuable food source but also great opportunities for employments and financial benefits to coastal harvesting regions (Popović et al., 2023). According to the Food and Agriculture Organization of the United Nations (FAO), the average global production of oyster shell waste in 2019 was 3.08 million t (Lu et al., 2022). Shells are thus a major by-product, which should not be deemed as waste, but rather a new material to be used to the best of its potential. These statistics also prompt the need for disposal of these

residues properly, and to assess the feasibility of reuse and their introduction to new recycling processes. In fact, many attempts have been undertaken to constructively contribute to tackling this issue in diverse fields such as construction material, pharmaceutical, food and agricultural industries (Sadeghi et al., 2019). On the other hand, oyster shell exhibits the promising remedy for acidified water due to its high content of CaCO_3 . It was previously shown that the oyster shell could act as a medium consisting of many bioreactors on its surface (Chen et al., 2012). Inspired by this potential, the present study was to discover the plausibility of recycling oyster shell as a basic material toward the treatment of acidified aquaculture environment. This is a considerable example of a circular economy for the sustainable development, and it would be expected to reduce the utilization of mineral sources to enhance pH of the acidified aquacultural medium.

2. Experimental Section

Ammonium chloride (NH_4Cl) was purchased from Xilong Scientific. Raw oyster shells (Figure 1a) were provided by Hung Anh Company (Vietnam) as waste products of manufacturing packed frozen oysters.

2.1 Treatment and characterization of waste oyster shells

Raw oyster shells were washed and intensively brushed with a 1 % Javel solution and water to remove moss and mud on the surface (Figure 1b). After sterilization upon ultraviolet (UV) irradiation for 30 min, the shells were dried at room temperature for 7 d (Figure 1c). In the thermal treatment step, the shells were placed in an oven and heated to a predetermined temperature ($5\text{ }^\circ\text{C}/\text{min}$) which was subsequently kept for 5 h (Figure 1d), yielding the recycled oyster shells (Figure 1e). Depending on the recycling steps included, the corresponding sample was denoted as W-C-T in which W included the washing, sterilization and drying steps, C was the calcination step and T was the calcination temperature. For instance, the W-C-220 sample was washed, sterilized, dried and calcined at $200\text{ }^\circ\text{C}$ while the W sample was obtained via only washing, sterilization and drying steps.

Thermogravimetric analysis (TGA) was conducted on a Thermal Gravimetric Analyzer (TA Instrumentals SDT Q600). Morphology images were obtained via using a scanning electron microscope (SEM, Hitachi TM 4000) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector (Bruker). Powder X-ray diffraction (XRD) analysis was performed on a diffractometer instrument (Bruker AKS D8 Advanced) with Cu-K α radiation.

2.2 Studies on improvement and stabilization of acidified water using waste oyster shells

An acidified aquacultural medium was simulated with a solution of NH_4Cl (0.5 g/L , $\text{pH} = 6.35$). A predetermined amount of the recycled oyster shell in the pristine form or fragmented in large pieces was added to 2 L of the NH_4Cl solution at $30\text{ }^\circ\text{C}$ under slight stirring (200 rpm). An aliquot of the solution was withdrawn at different time intervals for the measurement of pH which was performed by using a pH meter (Horiba LAQUA 1100-S).

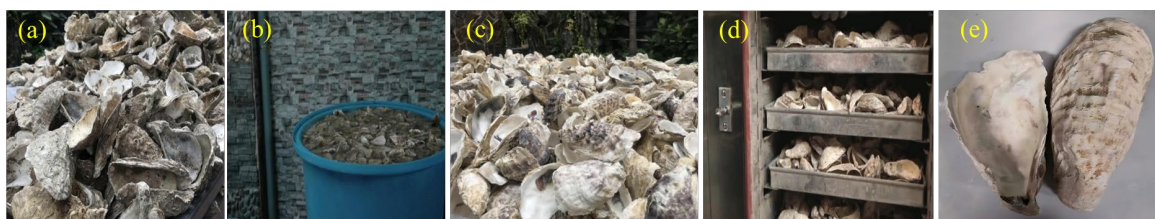


Figure 1: (a) Fresh oyster shells, (b) washed oyster shells, (c) air-drying oyster shells, (d) calcinating oyster shells in an oven, (e) obtained oyster shells after calcination

3. Results and Discussions

3.1 Characterization of recycled oyster shells

The crystalline structure in the oyster shells obtained under varied conditions was discovered by the XRD analysis. As shown in Figure 2a, the diffraction result for the raw oyster shell involved the signature peak of the calcite phase of CaCO_3 (Maia et al., 2015). A low-intensity peak assigned to the minor dolomite phase ($\text{CaMg}(\text{CO}_3)_2$) at $2\theta \sim 31.5^\circ$ was observed, indicating the presence of Mg species in the oyster shell (Kaczmarek et al., 2017). Notably, treatments of the oyster shells including washing, UV irradiation, and calcination at the elevated temperatures from 120 to $220\text{ }^\circ\text{C}$ led to no considerable changes on the crystalline structure of the material with the similar XRD patterns recorded. To gain more insight into the thermal stability of the material, the TGA profiles of the washed oyster shell was collected (Figure 2b), which showed that the oyster shell was stable up to $600\text{ }^\circ\text{C}$. The only mass loss observed from 600 to $800\text{ }^\circ\text{C}$ was assigned to the production of CO_2 based on the thermal decomposition of CaCO_3 . It was previously reported that CaCO_3 in the form of calcite could undergo the degradation into CaO and CO_2 in the same temperature range (Al Omari et al., 2016).

Notably, the shell calcined at 220 °C showed a similar thermal behavior in the TGA profile consistent with the XRD results, suggesting that the thermal treatment applied for the oyster shells in this study did not significantly affect their chemical composition and crystallinity. The purpose of thermal treatment was to completely remove contaminants on the shell surface and water in the shell, enhancing the contact with the aqueous phase.

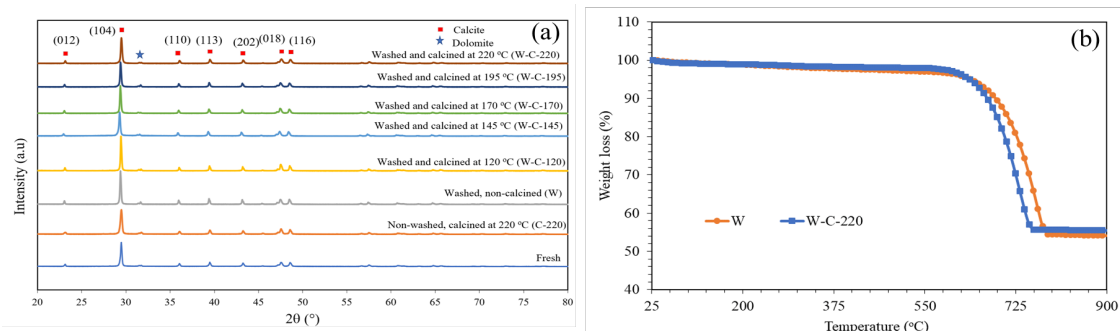


Figure 2: (a) XRD patterns of untreated oyster shell and oyster shells under various recycling conditions; (b) The TGA profiles of non-calcined (W) and 220 °C-calcined oyster shell samples (W-C-220)

The SEM analysis provided important data on the morphology at the different positions of the oyster shell (Figure 3a). The outer layer of the shell was generally smooth; the inner part consisted of the thin flakes which was highly ordered, forming a large number of cavities in the shell. These morphologies remained unchanged when the shell was calcined at the elevated temperatures. In respect to the chemical composition of the oyster shell, the EDX analysis presented the homogenous presence of the main elements involved in calcite including Ca, C, and O (Figure 3b). Other elements such as Mg, P, S were found with uniform distribution throughout the shell. It also showed that these elements were distributed evenly on the surface of the shells. These results were similar to the previous work on the presence of chemical element of oyster shell in the previous study (Aguila et al., 2021). A precise quantitative assessment for the metal elements was employed via ICP-OES analysis. As described above, the oyster shell contained principally calcium carbonate; calcium accounted for more than 33 wt.% similar to an earlier result (Hamester et al., 2012). Magnesium was the second common metal species in the shell with a content of 0.2 wt.%. As expected, the content of toxic heavy metals, namely, Cd, Pb, As, and Cr was lower than the detection limitation of the ICP-OES method, satisfying the chemical standards of materials applicable to the aquaculture.

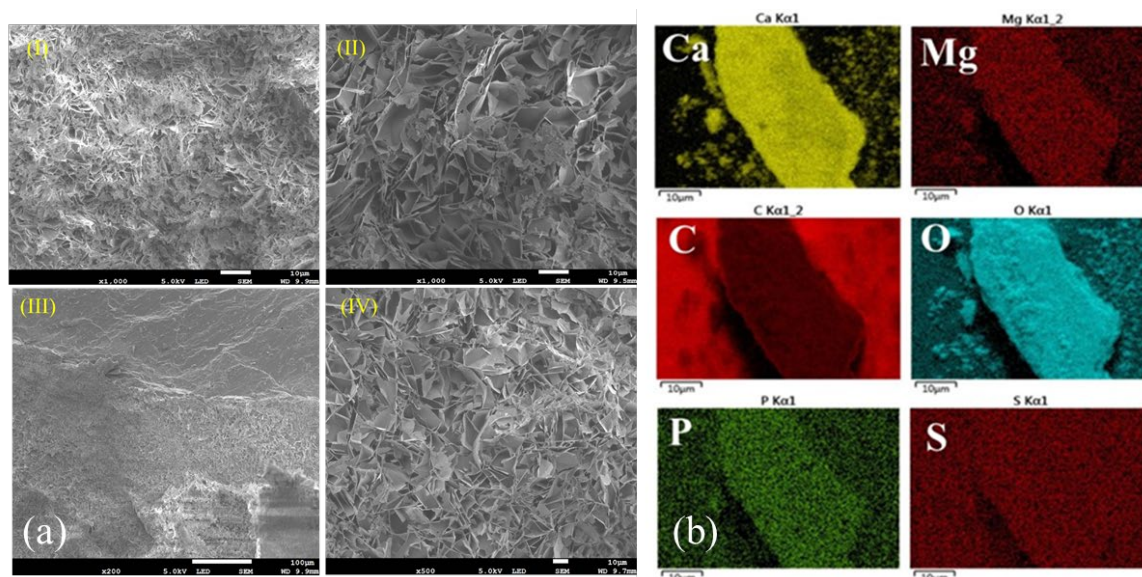


Figure 3: (a) (I, II) SEM images of the W, and (III, IV) W-C-220 oyster shells; (b) EDX mapping of Ca, C, O, Mg, P, S species for W-C-220 sample

3.2 Oyster shell-mediated improvement and stabilization of acidified water

As mentioned above, pH of the aquaculture milieu is one of the most crucial parameters to be monitored during farming aquatic animals. A pH reduction might impede the growth and development and even cause uncontrollable fatality of aquatic animals. The pH limit of the acidified aqueous environment which needs to be instantly improved is usually in the range of 6.0 to 6.5. The simulated aqueous solution of NH_4Cl (0.5 g/L) with pH of 6.3 was prepared to investigate the performance of the recycled oyster shell in the enhancement and stabilization of the aquaculture milieu. The initial studies were addressed to the effect of the shell amount on the pH change of the simulated phase. In detail, the recycled shells calcined at 220 °C were added with the amount varied from 1 to 10 g and the time-dependent pH values were shown in Figure 4a. It was observed that as the recycled oyster shell in a fine-powder form or in small pieces (0.2-0.5 cm) was applied, the reactivity of CaCO_3 cannot be controlled and the time-dependent pH results were unreproducible. Its large pieces or even an entire shell was applied to all of the experiments to avoid these disadvantages. The optimal ratio of oyster shell/solution ratio was chosen to be 0.5 g/L. Upon the application of oyster shells to the acidified medium, pH rapidly increased within the first four h. In the NH_4Cl solution, the principal constituent of shells, namely CaCO_3 , slowly reacted with the acidic ammonium cation (NH_4^+) (Reaction 1); the NH_4^+ concentration gradually declines, leading to a pH rise. The same mechanism could be applied for the case of other acidic species formed in water which are reactive to CaCO_3 such as proton (H^+), hydronium (H_3O^+), carboxylic acids.

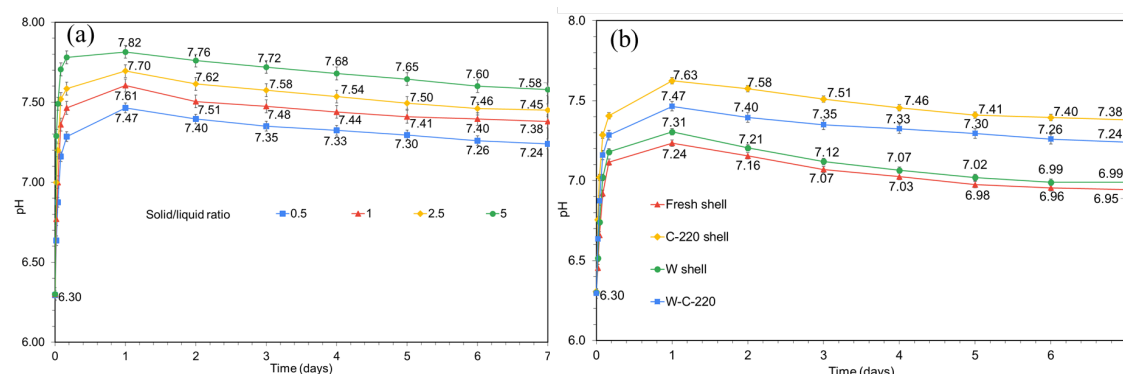


Figure 4: Effect of (a) oyster shell/solution ratio on the pH improvement in 2 L of the simulated environment within 7 d; (b) washing and calcination of the oyster shell on pH improvement capacity

In the second h, the pH improvement slowed down and the extreme pH value higher than 7.0 was obtained after 24 h. The result can be explained based on the formation of NH_3 in Reaction 1. It should be noted that the bicarbonate anion (HCO_3^-) produced from Reaction 1 is amphoteric, not only further donating H^+ to water (Reaction 2) but also disassociating into hydroxide ion (OH^-) (Reaction 3). The latter reaction was more dominant due to a higher equilibrium constant (K_3). As a result, the solution was more basic with a pH value in the range of 7.5 – 8.0 (Rahman et al., 2013). It was observed that an increase in the shell weight applied resulted in the corresponding acceleration in the rate of the pH elevation as well as the higher basicity of the solution. The maximum pH values recorded in the experiments using 2 g and more of the oyster shell were out of the 7.0-7.5 criterion range which was set for the aquaculture. To meet this criterion, 1 g of the oyster shell should be applied for the experiment involving 2 L of NH_4Cl . The shell weight/solution volume ratio of 1 g / 2 L, was used in the next studies. After the pH peak was reached for a day, it was suggested that the Ca^{2+} concentration was sufficient for its reaction with HCO_3^- and OH^- (Reaction 4), resulting in a pH reduction observed in all of the experiments. Such OH^- consumption proceeded in a very slow rate ($K_4 \ll 1$). In general, an almost stabilized state was attained on the fifth and sixth day of the experiment due to negligible pH drops ($\Delta\text{pH} = 0.00\text{-}0.02$ per day). Using the calcite-based oyster shell in the solution could lead to evident increases in the concentration of HCO_3^- and CO_3^{2-} ions, and CO_2 in the solution. Notably, the aqueous phase was open to atmosphere and a liquid-gas equilibrium state of CO_2 could be obtained, controlling the CO_2 content in water and reducing its negative impact on the growth and development of aquatic animals. On the other hand, the introduction of Ca and Mg species to the solution should be intensively considered. After a 7-day experiment, the Ca and Mg contents in the solution were found to be 160.3 and 4.8 ppm, which generally satisfied the total hardness standard (150 - 300 ppm) in aquaculture (Rajkumar et al., 2018). Obviously, the influence of these components during the process should be further investigated toward the long-term application.





Different approaches for recycling the waste shells were carried out in this study, yielding the corresponding products which were applied to the simulated acidic phase. As shown in Figure 4b, the pH enhancement of the recycled shells was impacted by the treatment procedure. The product washed and subsequently dried at room temperature exhibited a higher reaction rate than the fresh shells. It can be suggested that the removal of the outer impurities can improve the interaction of the CaCO_3 layer with the liquid phase. This improvement was insignificant as the pH value was lower than 7.0 after 5-7 d for both cases. Further treatment at 220 °C revealed a better 7-day experiment in which all of the pH values recorded were in the range of 7.0-7.5. It was proposed that the calcination at 220 °C might more efficiently eliminate residues on the surface, improving the heterogeneous interaction of the CaCO_3 sites with the solution. The formation of cracks on the shell surface upon the thermal treatment could reveal the more reactive internal calcite framework. Such cracks were not observed in the SEM images of the 220 °C -calcinated sample probably due to their nano-scale width. Notably, calcinating the raw shell without washing produced the more active sample which could increase the pH value to 7.63 under the identical conditions. More basic compounds formed from the thermal decomposition of the surface impurities could lead to this exceptional result. It can be proved that both washing and calcinating the raw shells at 220 °C were essential to yield the most efficient material which can improve and control the pH value of the solution in the required range.

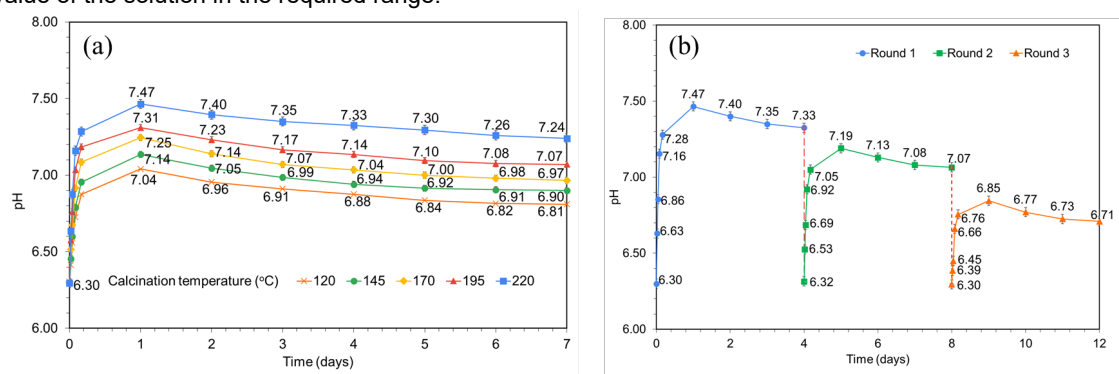


Figure 5: (a) Effect of calcination temperature on pH improvement; (b) pH improvement efficacy assessment

Finally, the effect of the calcination temperature on the activity of the recycled oyster shells was discovered. The shell samples calcinated at different temperatures from 120 to 220 °C. As can be seen in Figure 5a, the efficiency of the shell in the consumption of the acidic species in the solution increased with the calcination temperature. This tendency could be assigned to a cleaner shell surface and more surface cracks obtained at the elevated temperatures. To strengthen the proposal, the nitrogen isothermal sorption measurements were performed for non-calcined and 220 °C-calcined washed shell. The calcinated sample at 220 °C revealed enhanced a specific surface area of 1.7 m^2/g possibly due to obtained cracks after the thermal treatment, compared to 0.006 m^2/g for the non-calcined one. Notably, the pH data recorded during in the experiments using the samples treated at 195 and 220 °C were observed to be in the favourable pH range while the other samples were not efficient enough to maintain the neutralization for 7 d. It was proposed that the thermal treatment of the oyster shell could produce cracks on the shell surface, revealing the more reactive internal calcite framework. The most appropriate pH range was obtained within 7 d using the shells calcinated at 220 °C. The highest pH value was recorded at 7.47 under these conditions. Applying a higher calcination temperature for the oyster shell could boost the solution pH out of the expected range. On the other hand, the cost for investment and operation of the harsh-conditions procedure could be raised unnecessarily. These economic and safety issues should be intensively considered for scaling up the procedure.

An abrupt decline in pH of the aquaculture environment which is usually caused by acid rain or considerable aquatic changes could seriously affect the aquatic animals. An attempt on investigating the use duration of oyster shells was performed when the solution was re-acidified to pH ~ 6.3 by adding a certain amount of NH_4Cl after each 4 d. The obtained results exhibited the decreasing trend in the efficiency of the recycled oyster shell in the enhancement and stabilization of pH in the next runs (Figure 5b). In detail, the first round underwent a

rapid pH rise from 6.30 to 7.16 within the first 2 h and the maximum pH value was recorded at 7.47. As shown in Figure 5b, a longer time, namely approximately 4 h, was required to obtain a pH value in the desired range (7.0 – 7.5) in the second round. And this experiment exhibited the highest pH value of 7.19 much lower than that of the first run. It is noteworthy that the pH values observed in the third loop could not reach the desired range. Such activity declines could be explained based on the decrease in the active CaCO₃ amount after the repeated pH adjustments. As mentioned above, establishing and maintaining the pH value in the range of 7.0-7.5 is crucial because the growth and development of the aquatic animals are limited in the environment with pH below 7.0. In other words, the recycled shell should be added to the solution after the second adjustment round to ensure the appropriate pH condition when the shell/solution ratio of 0.5 g/L was applied. It should be noted that this conclusion was based on the acidification to approximately 6.3 for each test. The practical use duration could be prolonged more than 7 d without such sudden pH decreases.

4. Conclusions

In summary, the present study demonstrated that the waste oyster shell could be recycled to be a useful material for the remediation of acidified water. Washing and thermal treatment introduced to the material resulted in the significant improvement in the interaction between aqueous environment and shell surface, thereby promoting the pH elevation capacity. This study represents an innovative and practical solution in recycling a waste product of the aquaculture into a low-cost and green material for the aquaculture. It is expected to significantly contribute to valorization of the waste oyster shells and improvement of the environment quality.

Acknowledgements

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