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Converting Waste into Value-added Materials: Preparation and Application of a Low-Cost Adsorbent Derived from Clam Shells for Removal of Hardness

Dao Nguyen Song Oanh, Chau Khanh Bang, Ho Minh Tu, Dang My Thanh and Quynh Thi Phuong Tran*

Faculty of Environment and Labour Safety, Ton Duc Thang University, Ho Chi Minh City, Vietnam
*Correspondence: tranthiphuongquynh@tdtu.edu.vn; Tel.: +84 962 467 722

Abstract: This study investigates the potential use of clam shells, which are discarded in large quantities due to the promotion of clam farming in Vietnam's coastal regions, as a low-cost adsorbent material for removing water hardness in a filter column model. The study considers various parameters, including pH, temperature, and TSS, and examines the effects of modifications (using NaOH and KMnO4) to im- prove the effectiveness of the clam shell as an adsorbent material. The surface morphology characteris- tics of the materials were analyzed, which included SEM-EDS and XRD techniques. The results show that the modified clam shell soaked in KMnO4 and calcined at 300°C had the highest hardness removal efficiency of 73.7% in batch condition and 96.7% in column condition. Additionally, the study discovered that the materials, KMnO4-modified clam shell adsorbents, can cause alterations in pH and TSS. That is the weakness that needs to be addressed. Overall, the study suggests that clam shell is a promising low- cost adsorbent material for domestic water processing.

Keywords: waste clam shell; low-cost adsorbent; hardness removal; sustainability

1. Introduction

The white clam, Meretrix lyrata, is a bivalve mollusk commonly farmed in coastal prov- inces in Vietnam, also known as Ben Tre clam. In Vietnam, clam farming has increased signif- icantly, with an estimated area of 32.96 hectares and a production of 430,700 tons in 2020 [1]. While this industry generates income and job opportunities and contributes to seafood expor- tation, it also results in the accumulation of a significant amount of clam shells. The weight ratio of clam and shell is 1:0.7, and bivalve shells can persist for a long time and generate unpleasant odors as a result of decomposition, leading to the release of gases such as NH3, H2S, and amines. Thus, seafood processing companies must spend considerable resources to dispose of accumulated clam shells [1].

The global utilization of bivalve shells for diverse purposes, such as low-cost adsorbents, land reclamation, and construction materials, indicates a promising avenue for recycling clam shells [2]. This study aims to investigate whether clam shells can be repurposed to treat the issue of hard water in Vietnam. Hard water, characterized by high levels of minerals such as calcium and magnesium, is prevalent in both urban and rural areas. Its prolonged consump- tion can lead to harm to human health, scale formation, and the clogging of pipelines and other equipment that requires water.

Current research projects on bivalve shells have focused primarily on their ability to treat heavy metals, phosphates, and arsenic [3-14]. However, the usage of clam shells for water hardness treatment has not been adequately explored. Therefore, this project aims to synthe- size an adsorbent material from clam shells (CSPs adsorbent), design and test a filtering model on a laboratory scale at Ton Duc Thang University, and ensure that the post-treatment water quality complies with QCVN 01-1:2018/BYT National Technical Regulation on Clean Drink- ing Water Quality for Domestic Purposes, with a limit of 300 mg/L or less (as $CaCO3$). The findings of this study will serve as a foundation for promoting sustainable development and environmental protection.

2. Materials and Methods

Figure 1 illustrates the procedure for preparing calcium carbonate-based adsorbents from clam shells, procured locally from Ben Tre Province in Vietnam. The shells were initially scrubbed and soaked overnight in tap water to ensure the removal of salts, biomass, and re- sidual materials present on the surface. The washed shells were then rinsed with deionized (DI) water and subsequently dried at a temperature of 105°C for a duration of 3 hours. The dried shells were then thoroughly ground using a commercial grinder and passed through a 150 μm - 250 μm stainless steel sieve (Advantech Standard Sieve, USA series) to obtain natural clam shell particles (CSPs).

The CSPs were then impregnated with NaOH to obtain NaOH-CSPs. Following this, NaOH-CSPs were rinsed with DI water and then dried at a temperature of 105°C for a dura- tion of 5 hours. The resulting NaOH-CSPs were then continuously impregnated with $KMnO_4$ and calcined at temperatures ranging between 250°C and 450°C for a period of 30 minutes to collect MnO_2-CSPs ($2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$). The synthesized materials were char- acterized using surface morphology analysis techniques, including SEM-EDS (Scanning elec- tron microscopy with energy dispersive spectroscopy) and XRD (X-ray diffraction analysis) methods.

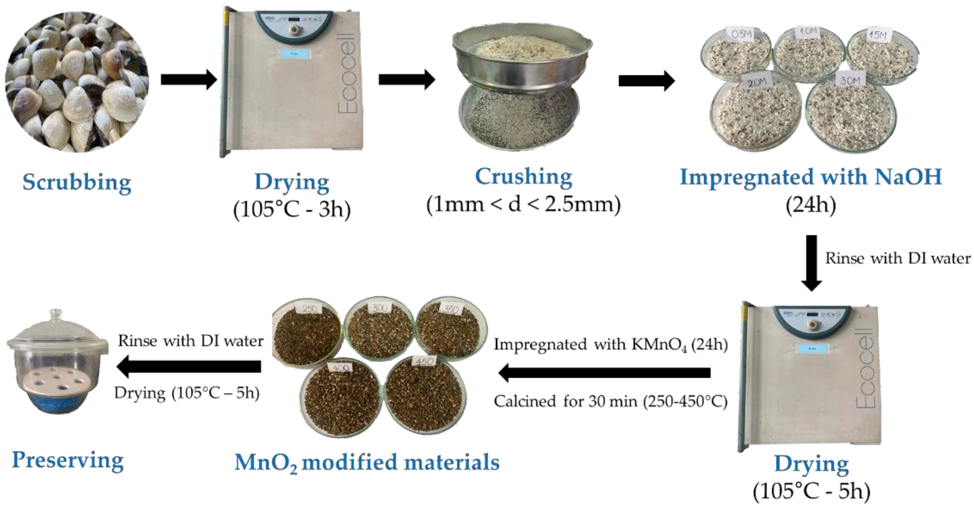

Figure 1. Process for preparing calcium carbonate-based adsorbents from clam shells

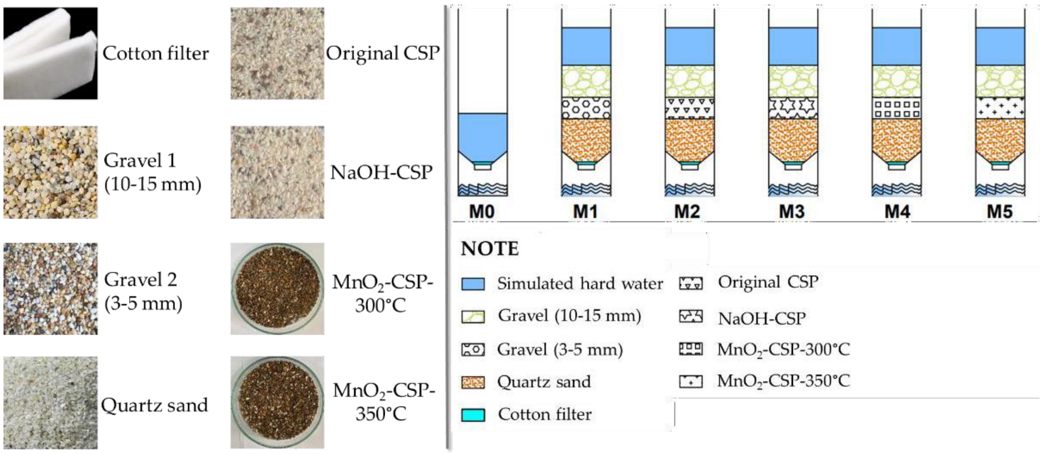

Figure 2. Experimental operating model of column filtration

Synthetic artificial hard water was prepared with primary ions mixed into an appro- pri- ate amount of fresh water according to Min Ahn et al. (2018) [15]. The laboratory testing and operation process encompassed six experiments pertaining to 6 test models, with a hard water treatment model engineered in the form of a plastic filter column. The design specifications for this model are encapsulated in Table 1 and Figure 2.

Table 1. Design parameters of hard water treatment column

Materials	Diameter (mm)	Quantity						Unit
		M0	M1	M2	M3	M4	M5	
Empty PVC bottle, 1.5L	250	1	1	1	1	1	1	Bottle
Cotton filter	–	–	–	–	–	–	–	–
Gravel 1	10 – 15	–	300	300	300	300	300	g
Gravel 2	3 – 5	–	300	–	–	–	–	g
Quartz sand	–	–	300	300	300	300	300	g
CSP (original)	1 – 2.5	–	–	300	–	–	–	g
NaOH-CSP	–	–	–	–	300	–	–	g
MnO_2-CSP-300°C	–	–	–	–	–	300	–	g
MnO_2-CSP-350°C	–	–	–	–	–	–	300	g

3. Results and Discussion

The morphological structure of the obtained adsorbent materials was analyzed by scan- ning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDS) to determine the elemental components of the clam shell prior to and following modi- fication. The study revealed that the surface structure of the clam shell exhibited a higher degree of porosity and contained more pores subsequent to the modification process with $KMnO_4$ solution and heating at 300°C. The EDS spectrum was also employed to determine the elemental components of the adsorbent materials, indicating the presence of manganese during the process of applying MnO_2 onto the surface of the clam shell.

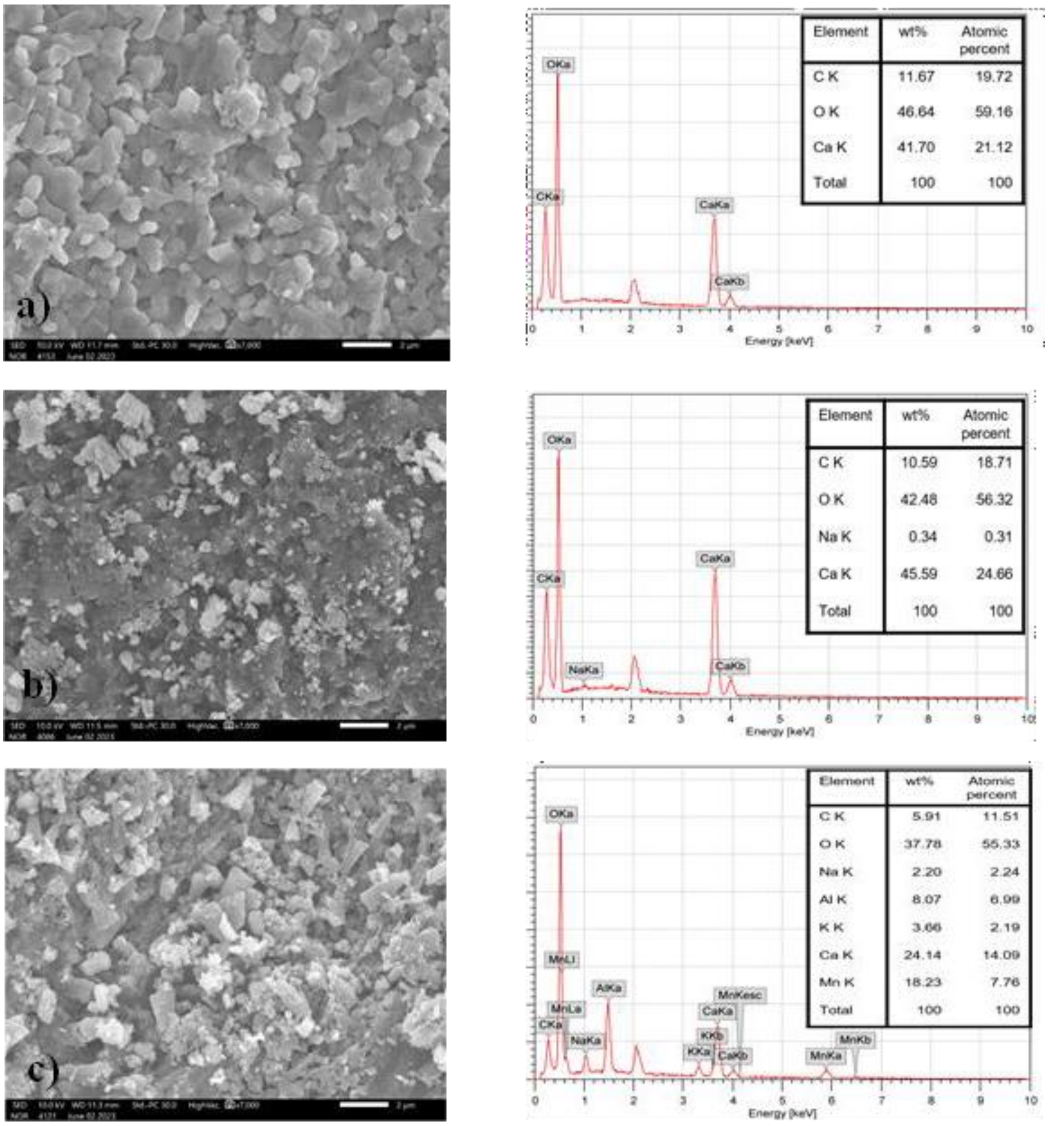

Figure 3. SEM-EDS results of CSP (a), NaOH-CSP (b), and MnO_2-CSP-300°C (c)

The X-ray diffraction (XRD) results of CSP (a) and MnO_2-CSP-300°C (b) in Figure 4 show that after soaking the material in $KMnO_4$ solution and heating it at 300°C, the surface of the material has been coated with MnO_2. This is evidenced by the observation of a color change in the material from its original state. The obtained diffraction peaks were compared to the standard peaks in the database of Joint Committee on Powder Diffraction Standards (JCPDS). The XRD results of both CSP and MnO_2-CSP-300°C show distinct peaks that match with the standard peaks, indicating the presence of specific crystal structures in both materials. The presence of MnO_2 is also confirmed by the appearance of additional peaks in the MnO_2-CSP- 300°C XRD results not observed in the CSP XRD results. Overall, the XRD results verify the successful deposition of MnO_2 onto the surface of CSP after the $KMnO_4$ treatment and heating at 300°C.

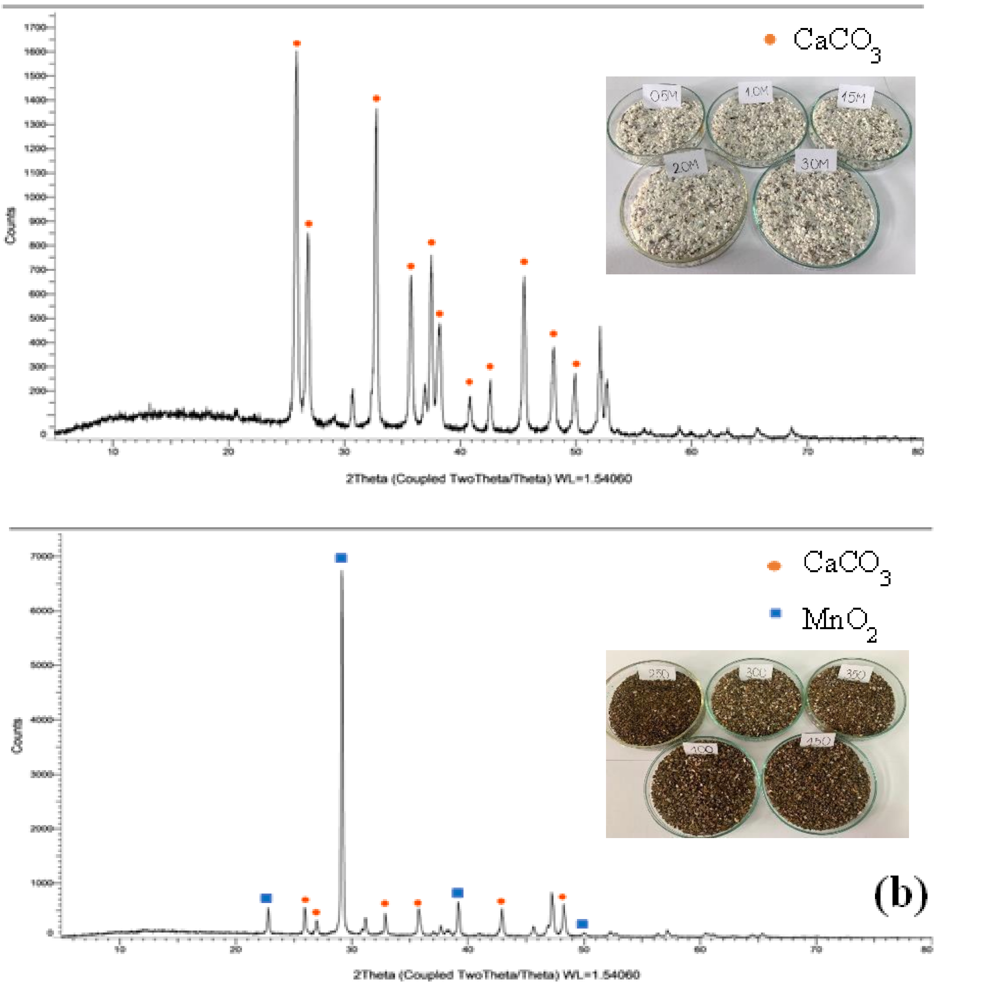

Figure 4. X-ray diffraction (XRD) results of CSP (a), and MnO_2-CSP-300°C (b)

After examining the results outlined in Figure 5a, it is evident that the initial pH of the hard water sample with alkalinity (pH = 8.3) did not see significant changes in columns M0, M1, M2, and M3 after undergoing 60 minutes of experimental operation. These values re- mained within the acceptable range of 6.0-8.5 prescribed by QCVN 01-1:2018/BYT (Vi-etnam).

However, in columns M4 and M5, the pH values exhibited a notable upward trend, be- coming more alkaline and reaching a value of pH = 10.1. This increase in pH exceeded the maximum allowable limit set by QCVN 01-1:2018/BYT by approximately 1.6, which could potentially be attributed to the decomposition of $KMnO_4$ into the inorganic solid K_2MnO_4 dur- ing the heating process. This oxidation reaction creates a strongly oxidizing substance that can alter the pH of the sample. It is possible that during the post-heating material washing with distilled water, this impurity was not completely removed, which could have had an impact on the pH value. In addition, measurement errors associated with the device could have also contributed to the observed difference in pH values.

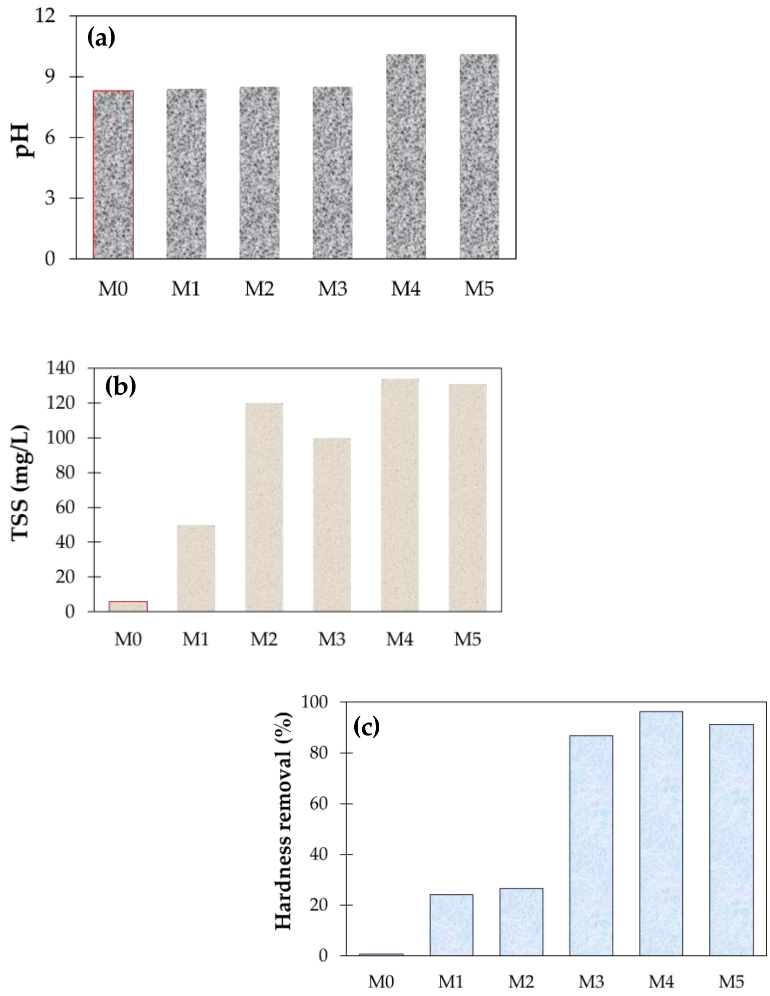

Figure 5. Results of pH (a), TSS (b), and hardness removal efficiency (c) under different column

According to the results presented in Figure 5b, the suspended solid content in columns M1, M2, M3, M4, and M5 increased significantly after passing through the filter layers. Among these columns, column M1 had the lowest increase in TSS content, with an increase of 44mg/L, which was 8.3 times higher than the baseline column M0. Columns M4 and M5 had TSS values of 134mg/L and 131mg/L respectively, corresponding to 22.3 and 21.8 times higher than column M0. As per QCVN 08-MT:2015, Column A1 - Used for domestic water supply, conservation of aquatic plants, and other purposes, the threshold for TSS content in water is 20mg/L. Based on the results, it is concluded that the filter columns are not effective in treating TSS and in fact aggravate the problem by increasing the TSS content in the water above the prescribed limit. This is a critical issue that requires attention and remedial measures.

The results in Figure 5c demonstrated significant differences in the hardness adsorption efficiency of the various models tested. Columns M1 and M2 exhibited similar efficiency, with 24.0% and 27.7%, respectively, after 60 minutes of adsorption. However, it was found that material 1 in column M2 had no ability to adsorb hardness, as confirmed in previous experi- ment through the batch reaction method. Therefore, the remaining material layers were re- sponsible for the observed hardness result in the water sample, rendering the efficiency of columns M1 and M2 relatively similar.

On the other hand, columns M3, M4, and M5 displayed substantially improved adsorp- tion efficiency. Column M4 demonstrated the highest efficiency, with a rate of 96.3%, followed by columns M5 and M3 with rates of 91.3% and 86.7%, respectively. Columns M4 and M5 utilized clam shells soaked in $KMnO_4$ solution and heated at temperatures of 300°C and 350°C, resulting in the decomposition of $KMnO_4$ to form the inorganic compound MnO_2. This compound coated the surface of the clam shell material, thereby enhancing its adsorption surface and overall effectiveness.

4. Conclusions

The study successfully selected and synthesized an adsorbent material from clam shells for use in treating hard water. Material 1 (CSP) was found to be unsuitable for adsorbing hardness, but material 2 (NaOH-CSP) and material 3 (MnO_2-CSP) were successful, with ma- terial 3 being the most efficient. The study also carried out the design and operation of a water softening test model with multiple filtration column models tested. The model with the high- est hardness removal efficiency was Model M4 with the researched material of oyster shells soaked in a 7% $KMnO_4$ solution and heated to 300°C, achieving a treatment efficiency of 96.77%. However, it was noted that the pH level increased towards alkalinity with material 3 and the TSS content after adsorption exceeded allowable limits in some cases. In conclusion, the most promising adsorbent material for removing hardness was clam shells soaked in a 7% $KMnO_4$ solution and heated to 300°C.

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