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Adsorption Capacity and Phosphate Removal Efficiency of Oyster Shells and its Implications to Chemistry Learning

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Abstract

The aquaculture sector of the Philippines which includes fish pond culture systems faces many challenges and issues such as high concentration of phosphate which does not only affect water parameters but also triggers the occurrence of Harmful Algal Blooms. Hence, this study was conducted to evaluate the adsorption capacity and phosphate removal efficiency of oyster shell powder (OSP) using brackishwater under laboratory conditions as learning resources of chemistry learning. This quantitative research study used Completely Randomized Design (CRD) with three treatments: T1 (Control/Commercial) – 1.5g Calcium carbonate ($CaCO_3$); T2 – 1.5g Oyster Shell Powder (OSP); T3-2.5g Oyster Shell Powder (OSP). Results revealed that in terms of surface morphology, the photographs showed irregularity of shapes and different sizes, implying heterogeneity of OSP while, in terms of elemental composition, Calcium and Oxygen are the major elemental composition of the OSP. Further, in terms of Phosphate Adsorption Capacity, One Way ANOVA revealed significant differences (p-value <0.01) among treatments. Further analysis using LSD revealed that commercial calcium carbonate has significantly higher adsorption capacity than oyster shell powder, however, 1.5 g OSP has higher adsorption capacity than 2.5g OSP. Furthermore, in terms of phosphate removal efficiency, One Way ANOVA revealed no significant differences (p-value <0.05). This means that the phosphate removal efficiency of OSP is comparable to commercial calcium carbonate ($CaCO_3$). Moreover, the study's findings act as an educational resource, facilitating a profound comprehension of the practical applications of chemistry principles. It encourages chemistry learners to engage in critical evaluation and practical application of their knowledge, particularly in addressing pressing environmental challenges.

Keywords: Chemistry Learning, Adsorption Capacity, Calcination, Oyster Shell, Phosphate Removal Efficiency

INTRODUCTION

The Philippines, having more than 7,000 islands with rich biodiversity and natural resources, ranked 8th among the top fish-producing countries in the world, contributing 4.354 million metric tons of fish, crustaceans, mollusks, and aquatic plants (including seaweeds), which constitutes 2.06% of the total world production of 211.87 million metric tons (Bureau of Fisheries and Aquatic Resources, 2020). Aquaculture contributed 2.3 million metric tons or 52.79% of the country's total production, while commercial fisheries constituted 25.05% and municipal fisheries 22.16% (BFAR, 2021).

Aquaculture, the sector that gives light to the fisheries industry of the Philippines and the world, stabilized the production of aquatic species when capture fisheries were down (Retuya, 2020). The aquaculture sub-sector provides one-third of the country's fisheries production, making it the country's center of fisheries production. It is expected to fill the increasing demand for the supply of aquatic organisms in the market. From 2014 to 2018, it consistently tops the sector with over 2 million metric tons. It remains the primary Philippine production source as municipal fisheries are more or less unchanged throughout the years, and capture fisheries continue to decline in the same years (PSA, 2019). Philippine Aquaculture ranked 11th in the world in 2019, contributing 0.826 million metric tons of aquaculture production of fish, crustaceans, and mollusks (1.01%). The major produced commodities of the sector are seaweeds *(mainly Kappaphycus* and *Eucheuma* spp*)*, Milkfish *(Chanos chanos)*, Tilapia *(mainly Oreochromis* spp.*)* and shrimps/prawns *(Peneaus* spp., *Metapenaeus* sp., *and Macrobrachium* sp.*)*, which comprised 96.64% of the total sector production in 2019, 2020).

Milkfish, locally called "Bangus," is considered the Philippines' official national fish (Bagarinao, 1998) and the second most produced species of the aquaculture sector, comprising 13% (BFAR 2019, BFAR, 2020; PSA, 2019). Farming of this fish species has been carried out in Southeast Asia, including the Philippines, for over 50 decades and is now considered the most important farmed fish (Yap et al., 2007). Milkfish are cultured in brackish water, freshwater lakes, estuarine areas, and coastal marine waters using various culture systems like ponds, cages, and pens (Yap et al., 2007). Pond culture systems, specifically brackishwater ponds, constitute most of the commodity's production.

The aquaculture sector of the Philippines, which includes fish pond culture systems, faces many challenges, such as pests and diseases, water quality degradation, occurrence of algal blooms, and lack of capital and government support. Water quality degradation issue in ecosystems that support aquaculture has remained one of the main problems for the sector as it triggers and causes an increase in the concentration of phosphates and nitrates, which could lead to deleterious effects because studies found that when the concentration of these materials are beyond the recommended level can cause adverse effects on dissolved oxygen concentrations of the site, trophic state and ultimately the well-being of the fauna and flora of the site (UN Water, 2015). For example, Manila Bay was found to be unsuitable for fish culture, although its temperature, DO level, and pH were within the safe levels, because its Phosphate and nitrate contents are too high (1.02 mg/L – 2.42 mg/L, and 0.90 mg/L – 2.35 mg/L) (Baldoza et al., 2020).

Several factors contribute to the increased phosphate concentrations in these areas such as the following: (a) Water discharges from different sources such as agricultural run-offs and agrochemical-based agricultural activities, have caused simultaneous releases of arsenic and phosphorus contained in water and wastewater into natural environments from point and non-point sources (Jung et al., 2021); municipal wastewater treatment plants (Maccoux et al., 2016); slaughterhouse effluents are also contaminated with nitrogen (including nitrates) and phosphates from the feces of slaughtered animals, detergents, disinfectants, pathogenic and non-pathogenic organisms (Gnowe et al., 2020), domestic wastes due to human wastes and household detergents (Arslanoglu, 2021), and overfeeding using commercial feeds.

High concentrations of phosphates and nitrates affect water parameters and trigger the occurrence of Harmful Algal Blooms (HABs). HABs are also considered the main problem in aquaculture areas and have been a problem for the last decades. It has been identified as the leading cause of fish kills in most of Luzon in recent years (De Vera-Ruiz, 2021). Further, the occurrence of HABs also has a significant impact on the national economy of the country as well as threatening public health. For example, concerning public health, from 1983 to 2002, there were 2,122 cases of paralytic shellfish poisoning with 117 deaths associated with HABs. Furthermore, in the same year duration, HABs also resulted in the following: a) economic losses and damages amounting to 2.2 million pesos, b) extensive economic damages, c) problems in the international trades, d) unemployment of many shellfish industries, and e) displacement and losses of livelihood for thousands of fishers (BFAR, 2021).

Several methods and techniques have been used to address these high Phosphate concentrations, such as adsorption biological and chemical processes. All have shown potential and capacity to reduce phosphate concentration, but some have consequences or drawbacks. For example, the drawbacks found for the biological process are that bioconversion is a slow process, and it needs a long start-up time to initiate the treatment process (Karri et al., 2018), while for chemical treatment, centers for high chemical costs (Fulazzaky et al., 2015). Fortunately, adsorption was found to be technologically simple and economically feasible while producing high-quality water with pollutant concentrations under the legal limits for discharge waters (Crini et al., 2019). This method is also simple in operation, inexpensive, and highly efficient processes.

For the past three decades, several materials have been examined for their adsorptive performance, such as the development of new materials, including new carbons produced from wastes or natural by-products, natural or synthetic adsorbents or sorbents, and biological materials or biosorbents (Crini et al., 2019). This ranges from the use of calcined dolomite, alkaline residue, fly ash, and red mud (Mangwandi et al., 2014; Yan et al., 2014; Li et al., 2006) to the use of biomaterials such as collagen fibers (Liao et al., 2006), wood particles and agricultural residues (Zhang et al., 2020) to the use of eggshells (Torit & Phihusot, 2018), use of rice straw (Luo et al., 2019), and lately the use of seashell wastes which includes crab carapace (Pap et al., 2020), cockle shells (Kim et al., 2018), mussel shells and oyster shells (Nam et al., 2017).

Worldwide, the commercialization of mollusks, including oysters, placed second in seafood production with 16.1 million tons (19 billion US$) production annually. Asia is the most important producer of mollusca followed by Europe and America (Food and Agriculture Organization of the United Nations, 2016). However, with the continuous increase of oyster production and even consumption worldwide, different problems have arisen. One of which is the amount of residue generated. Most shell wastes are deposited in landfills, abandoned on land, or returned to the sea, thus causing incalculable environmental impacts. These waste products contaminate and attract animals due to the strong odor when deposited in the soil. At the same time, when deposited in the sea, they cause grounding and infect the marine population. Further, the lack of regulation and inspection in several oyster-producing countries also reflects this sector's significant environmental impact (Shumway, 2011). Hence, appropriate utilization and management of oyster shell wastes must be implemented.

Oyster shells are studied to be a potential adsorbent material for phosphate and other heavy metal materials as they showed efficiency for removal and are inexpensive, easy to use, and highly available (Khan et al., 2020). Several studies, such as those of Kwon et al. (2004), Yu et al. (2010), Onoda & Nakanishi (2012), and Tran et al.(2020), all concluded the applicability of oyster shells as phosphate adsorbents. However, limitations were observed in using actual water samples collected from brackish water ponds identified with high phosphate levels. Hence, this study was designed to determine the performance of oyster shells on phosphate adsorption using different dosages and compared it to commercially used adsorbent – calcium carbonate (CaCO3). The study also used samples from brackish water ponds instead of synthetic solutions to evaluate its performance.

METHOD

Design

This study used Completely Randomized Design (CRD) following experimental research. The independent variable of the study was the dosage of adsorbents using three treatments, namely; T1 (Control/Commercial) – 1.5g Calcium carbonate (CaCO3); T2 – 1.5g Oyster Shell Powder (OSP); T3 – 2.5g Oyster Shell Powder (OSP) in three replicates in three trials.

Preparation of Oyster Shell Powder

The oyster shell powder was prepared following the procedure utilized in Tran et al. (2020) and Nguyen et al. (2020) study. Raw oyster shells collected from Sto. Tomas, La Union was washed thoroughly with tap water, sun-dried, crushed, and sieved into 0-2 mm sizes (Nadeem, 2018), and calcined and thermal pre-treated at the Department of Science & Technology - Regional Standards and Testing Laboratory, San Fernando City, La Union for calcination and thermal pre-treatment (Bi et al., 2020; Panagiotou et al., 2018; Park et al., 2021). The calcined oyster shell powder was characterized by chemical composition and surface morphology using a Scanning Electron Microscope with Energy Dispersive X-ray or SEM-EDX.

Phosphate Adsorption Analysis

A total of 27 conical flasks (125 mL) containing 100 mL of water samples were collected from a brackish water pond at Santo Tomas La Union. In these flasks, adsorbent doses were placed (1.5 g CaCO3, 1.5 g OSP, 2.5 g OSP). After which, samples were shaken in an orbital shaker at 100 RPM for 2 hours (Torit & Phihusot, 2018). Then, the supernatant in each treatment flask was filtered to separate the adsorbents from the solution. Finally, phosphate concentration was determined through the Ascorbic Acid Method.

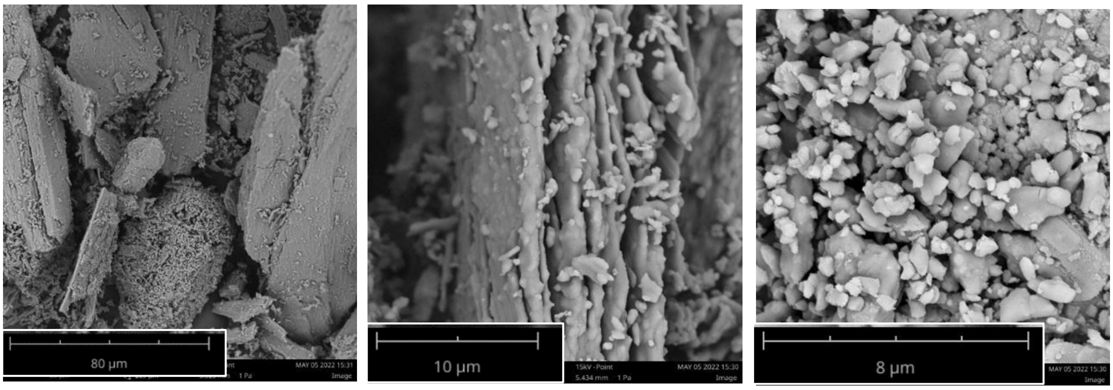
RESULTS AND DISCUSSION

Physico-Chemical Properties of Oyster Shell Powder

The physico-chemical properties of oyster shell powder (OSP) in terms of surface morphology and elemental composition were identified through SEM-EDX analysis at DLSU-Phenom Lab. Determination of the surface morphology of the adsorbents is important as it affects the phosphate adsorption performance. According to Nguyen et al (2020), the change on the microstructure of the oyster shells after treatment, changed its adsorption performance. Figure 1 presents the SEM photographs at 1000x, 5000x, and 10000x magnification of oyster shell powder. The photographs showed irregularity of shapes and different sizes of granular particles. This implies that OSP has heterogeneous distribution as compared to commercial calcium carbonate which has more uniformed particles (Hamester et al., 2012). Heterogeneity and homogeneity of particles affect its surface area, indicating effects on the phosphate removal of the adsorbents.

The presence of larger particles is associated with the properties of the adsorbents used, like for the case of oyster shells, they have high concentration of silica in their shells that increases their shell hardness (Hamester et al., 2012) resulting to difficulty on crushing and achieving uniformed sizes. According to Hamester et al. (2012), the preparation of commercial calcium carbonate consists of grinding in different stages in several grinding systems until it reaches the average particle size most appropriate to use. In the present study, manual crushing using mortar and pestle and sieving materials were used which did not ensure uniformity of the particles.

Further, as shown in Figure 1, porous surface is not observed and no holes were visible as compared to the previous study of Nguyen et al (2020) who also used oyster shells in their study. Their findings revealed that the oyster shell modified with EDTA have more porous structure than calcined and uncalcined oyster shells and also have higher chromium adsorption efficiency. This means that the modification improves the porosity of the oyster shells and improve its adsorption efficiency which implies that treatment of the oyster shells affects their microstructure and their adsorption efficiency. In 2016. Calugaru et al. (2016) found that calcination increased the surface area of the adsorbents.



(a) (b) (c)

Figure 1. SEM photomicrograph of OSP at (a) 1000x, (b) 5000x and (c) 10000x magnification.

Elemental Composition

Elemental composition of oyster shell powder is important as the adsorption relationship between mussel shells and oyster shells and phosphate ions (PO_4^3) could be categorized as chemical adsorption (Salim, 2020). Chemical adsorption greatly depends on the chemical reactions between the adsorbate and the surface sites of the adsorbent (Worch, 2012). This implies that chemical or elemental compositions of adsorbents affect their adsorption performance.

In terms of elemental composition of OSP, analysis revealed that Calcium (Ca) (40.39%) and Oxygen (O) (38.79%) are the major elemental compositions while minor elemental compositions were Carbon (C) (10.34%) and Niobium (Nb) (10.47%). Calcium and Oxygen are commonly found on adsorbents used for phosphate adsorption such as in the study of Munar-Florez et al. (2021), where the major elements present on the palm shells and two types of biochar are Ca and O. However, the result of Hamester et al. (2012) found carbon to have higher weight composition in raw snail shells than Oxygen. In terms of other shellfish such as mussel shells, Calcium is also found as the major elemental composition. This implies that adsorbents used for phosphate adsorption commonly composed of calcium and oxygen, while the minor elemental compositions vary, as other factors such as environmental difference may intervene.

Further, the present study recorded a mass percent of Niobium which is not commonly found on oyster shells as revealed by other studies. Niobium is a rare gray-white metal typically used for the production of high-temperature-resistant alloys and special stainless. In the environment, it can be found on plants (small traces) and also in some mosses and lichens (Nowak & Ziolek, 1999). At present, no negative environmental effect has been recorded.

Furthermore, in terms of chemical composition of commercial $CaCO_3$ and the oyster shell powder, studies reveal that CaO is mainly composed the two wherein former have a weight percent of 99.1% (Hamester et al, 2012), while oyster shells and mussel shells have 54.31% (Yu et al, 2010) and 87.90% (Salim et al, 2021) respectively. This implies that commercial $CaCO_3$ and the oyster shell have similar chemical compositions and can be both used as phosphate remover.

Table 1. Elemental Compositions of Oyster Shell Powder

Element	Mass%	Atom%
Calcium (Ca)	40.39 ± 0.87	19.55 ± 0.61
Oxygen (O)	38.79 ± 1.38	55.02 ± 1.96
Niobium (Nb)	10.47 ± 0.51	22.87 ± 0.49
Carbon (C)	10.34 ± 0.32	2.56 ± 0.12

Phosphate Adsorption Capacity

Table 1 shows the result on phosphate adsorption capacity (PAC) of commercial CaCO3 and oyster shell powder. Results revealed that Treatment I obtained the highest adsorption capacity among treatments with a mean value of 0.011 mg/g followed by Treatment II with PAC of 0.008 mg/g and Treatment III with PAC of 0.005 mg/g respectively.

Table 2. Phosphate Adsorption Capacity of the Treatment Groups

Treatment	Initial Phosphate Concentration (mg/L)	Phosphate Concentration in the Solution (mg/L)	Phosphate Adsorption Capacity (M ± SD)
1.5 g CaCO3	0.353	0.187	0.011 mg/g ± 0.0012[a]
1.5 g OSP	0.353	0.224	0.008 mg/g ± 0.0006[b]
2.5 g OSP	0.353	0.223	0.005 mg/g ± 0.0006[c]

Letter scripts in column are significantly different at 0.01 level of significance

Analysis of Variance showed significant ($p < 0.01$) difference among treatments (*Appendix N)*. Further analysis using Least Significant Difference revealed that Treatment I is significantly different with Treatment II and Treatment III (*Appendix O)*. This implies that $CaCO_3$ is significantly higher compared to 1.5g and 2.5g OSP in terms of adsorption capacity. Comparing the two dosages however, showed that 1.5g OSP has significantly higher adsorption capacity than 2.5g OSP. The higher Adsorption Capacity of $CaCO_3$ could be attributed to its physical properties. In the actual observation, the CaCO3 has fine and powdery texture than OSP. This difference on the texture can be associated with their specific surface affecting their adsorption performance, as concluded by Ha et al (2019), the texture of the calcite in limestone and oyster shells is a more important factor that controls the calcination temperature and specific surface area of the calcination products than their chemical compositions. Further, $CaCO_3$ and OSP both have CaO chemical compositions which are important for adsorption mechanism.

Furthermore, treatments vary from phosphate adsorption capacity as reflected on the data obtained wherein lower doses have higher adsorption capacity while higher dose have lower adsorption capacity. Present result of the study corroborates with the result of Vieira et al. (2019) wherein dosage of CaCO3 resulted to lower adsorption capacity of adsorbents. Present results also complement in the study of Salim et al (2021) which found that as the adsorbent doses increases, the adsorption capacity gradually decreases. Further, according to Ribas et al (2014), the adsorption capacity decreases as mass of adsorbent increases because at high Iron-Coated Waste Mussel Shells (ICWMS) adsorbent dosages, the available number of phosphate ions (PO4-3) solute in aqueous solution is insufficient to completely bind with all available surface binding sites on the ICWMS adsorbent. However, these results are contradicted by the study of Nguyen et al (2020) where they concluded that as weight of the oyster shell adsorbents increases, adsorption of chromium (Cr (IV)) increases.

Phosphate Removal Efficiency

Table 3 presents the result on Phosphate Removal Efficiency of commercial and experimental CaCO3. Results revealed that Treatment I obtained the highest removal efficiency with 28.01% followed by Treatment II and III with 21.44% and 19.83% PRC respectively.

Table 3. Phosphate Removal Efficiency of the Treatment Groups

Treatment	Initial Phosphate Concentration (mg/L)	Phosphate Concentration in the Solution (mg/L)	Volume of Solution (L)	Mass of Absorbent	Phosphate Removal Efficiency (%)
1.5 g $CaCO_3$	0.353	0.187	0.1	1.5	28.01 % $\pm$ 5.40
1.5 g OSP	0.353	0.224	0.1	1.5	21.44 % $\pm$ 1.67
2.5 g OSP	0.353	0.223	0.1	2.5	19.83 % $\pm$ 2.46

Analysis of Variance revealed no significant (*$p<0.05$*) differences among treatments (Appendix Q). This means that phosphate removal efficiency of $CaCO_3$ is comparable to OSP. This further means that the removed phosphate from the solution by $CaCO_3$ is significantly the same with the removed phosphate of OSP. The present result corroborates with the result of Kwon et al (2021), Yu et al. (2010), Onoda & Nakinishi (2012) and Tran et al. (2020) which all concluded that oyster shells or addition of oyster shells to other materials (such as biochar) has removed phosphate and arsenic and is potential to be used as adsorbents for phosphate and arsenic.

Relevance to Chemistry Education

Table 4 presents the key findings of the study and its relevance in the context of Chemistry Education. The table underscores the practical application of chemistry principles in real-world scenarios, providing chemistry learners, valuable insights into the dynamics of adsorption process. This finding when applied to real scenario, encourages students to apply their knowledge in addressing problems or research gaps such as environmental challenges.

Table 4. Relevance to Chemistry Education

No.	Findings	Relevance in Chemistry Education
	The SEM-EDX analysis revealed that the surface morphology of oyster shell powder (OSP) is heterogeneous compared to commercial calcium carbonate. The heterogeneity is influenced by application of manual crushing method, affecting particle distribution, and consequently, surface area.	This finding underscores the importance and effects of processing techniques in the adsorption performances of "adsorbents". For Chemistry learners, this insight offers comprehensive understanding of fundamental chemistry principles and their practical applications in real word. Specifically, students can use this knowledge to design efficient adsorption process by consideration of the intricates and properties of materials involved.
2.	The elemental composition of OSP, particularly the presence of Calcium and Oxygen. Calcium and Oxygen are typically found on adsorbents used for phosphate adsorption.	This finding helps the chemistry learners understand the relationship of elemental composition and chemical adsorption.
	Oyster Shell Powder and Commercial Calcium Carbonate, despite comparable chemical compositions, revealed different adsorption capacity performance.	This finding emphasize that similar chemical composition does not result to similar adsorption capacities, indicating importance and effects or physical properties and modification techniques and processes.
	Inverse relationship between oyster shell powder dosage and phosphate adsorption capacity	The observation that lower doses of OSP lead to higher adsorption capacity, with a decrease in capacity at higher doses, introduces chemistry learners to the concept of optimization in material applications. This insight encourages students to go beyond merely considering the dosage of adsorbents and prompts them to take into account additional factors, such as the availability of binding sites

Implications to Chemistry Learning

The findings of the study offer broad implications not only for fisheries management, but also for chemistry education. This study serves as a learning material for chemistry education as it underscores the intricate relationship between material properties and adsorption performance, emphasizing the importance of surface morphology, elemental composition, and chemical modifications like calcination. Chemistry learners can glean valuable insights into the diverse factors influencing the behavior of adsorbents, from the significance of preparation methods on surface morphology to the impact of elemental composition on chemical adsorption. The study revealed that modification procedures for oyster shell powder, specifically calcination in this study, alter the microstructure of the oyster shells, resulting in a change in their adsorption performance.

Further, the dosage-dependent adsorption capacity and comparative efficiency of OSP with commercial calcium carbonate provide practical lessons on the optimization of adsorption processes and the potential of environmentally friendly materials. This finding has the potential to encourage chemistry students consider the sustainability aspects associated with the utilization of materials, including both unused, e.g. oyster shells and used materials in chemistry-related applications. Also, the identification of uncommon elements, such as Niobium, prompts students to explore the interdisciplinary nature of chemistry, linking it to environmental and materials science.

Furthermore, this study serves as a rich educational resource, fostering a deeper understanding of the real-world applications of chemical principles and encouraging students to critically evaluate and apply their knowledge in addressing environmental challenges.

CONCLUSION

Based on the research results, it can be concluded that Phosphate Removal Efficiency of Oyster Shell Powder is comparable with the commercial calcium carbonate. While in terms of Phosphate Adsorption Capacity, oyster shell powder's adsorption capacity is inversely related with the dosage of oyster shell powder. The lower the dosage, the higher the phosphate adsorption capacity. Further, the study's findings serve as a rich educational resource, fostering a deeper understanding of the real-world applications of chemical principles and encouraging chemistry learners critically evaluate and apply their knowledge in addressing environmental challenges.

SUGGESTIONS

Further analysis on the phosphate adsorption performance using other test parameters is suggested in the study. Further, application of oyster shell powder in brackish water ponds using different rates of application is also suggested.

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