Synthesis of Chitosan-Hydroxyapatite Composite Gel from Waste Crab Shells for Oil Adsorption

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Abstract – Composites consisting of oil adsorbing materials such as chitosan and hydroxyapatite has been proven to be a viable oil adsorbent in treating oil spills. As a waste product, crab shells can be utilized as a source of raw materials for an oil adsorbent. In this study, the oil adsorption capacity of synthesized chitosan-hydroxyapatite composite were investigated and compared. Chitosan and hydroxyapatite were simultaneously extracted from crab shells. The extracted samples were then verified using the Fourier Transform Infrared Spectroscopy. 1:1 ratio of chitosan and hydroxyapatite were prepared in a form of a gel composite.

Introduction. –   Oil is highly essential to man specifically to the energy industry because it is one of the main sources of electricity. However, oil possesses a great threat to the environment if not properly observed. In 2015, records show that approximately 7000 tonnes of oil is spilled globally with portions happening here in the Philippines [1]. The known oil spill in the Philippines happened in the year 2006 where an oil tanker sank just off the coast of the Guimaras and Negros islands. Although oil spills may also happen in land, marine spillage tend to be more common as offshore drilling is better in terms of investment [2].

Oil spills cause pollution to the environment which greatly affects both plants and animals living near the affected area. Surface animals like seabirds and otters tend to be the ones greatly affected since oil floats in water. Not only does the pollution slowly kill the animals but also their floating corpses when they die will lead to more pollution yet less in scale [3].

Methods in cleaning up the oil takes a lot of time and resources which slows down the treatment of the water. Some of the solutions are not advisable due to the consequential effects it withholds. One solution is burning the oil, however, it may increase air pollution due to the combustion process. In addition, oil tends to spread on the surface in a thin film thus having a difficulty in burning. Another solution involves emulsifying detergent, but it does not remove oil from the water as it only separates the oil to fine particles [4]. Leaving the oil alone itself is already a solution as it will naturally break down [5], however in terms of long-term effects, this option is not advisable. Other solutions also include sucking up the oil, containing the spilled area within a large dome and even using bacteria that eat up the oil itself [6].Solutions vary from being industrially-made to eco-friendly alternatives, however majority of these require a huge amount of funding.

Cleaning up oil spillages is difficult to perform as it requires more sophisticated valuable resources and machinery. Although cheap alternatives of cleaning up oil have been found. One of these alternatives are chitosan-hydroxyapatite (chitosan-HAp) composites which can be used as a sorbent for oil cleanup [7] [8]. From related studies, chitosan-HAp composites could solve the problem of water pollution as it can also remove other pollutants [9]. However, it is preferred to utilize natural waste products as a source for composite synthesis not only effective in oil adsorption but also cheap and reduces waste products.

Natural waste products such as waste crab shells can be a possible source for chitosan and hydroxyapatite. Both can be found at the exoskeletons of crabs [10] [11]. In addition, 1,354 tonnes of crab shells is wasted every year which can be utilized for chitin production [12]. By utilizing waste crab shells for the synthesis of the chitosan-HAp composite, not only oil spills can be treated but also levels of crab shells can be reduced. Thus, this study aims to

create a chitosan-HAp composite from waste crab shells that could be effective for oil adsorption.

Chitosan and hydroxyapatite were extracted from the crab shells. A composite in gel form was produced from these two materials with a ratio of 1:1 chitosan-hydroxyapatite. It was then tested for oil adsorption capacity. The chitosan and hydroxyapatite were verified using Fourier Transform Infrared Spectroscopy instrument. Furthermore, personal protective equipment was worn at all times and the chemicals were properly disposed in accordance with the Materials Safety Data Sheet.

There were two (2) batches of the composite with eight (8) samples per batch. Composite A had an adsorption capacity of 0.107 0.177 while composite B had an absorption capacity of 0.049 0.019. Both had the capacity to adsorb oil however, there was no significant difference p-value at 0.065.

Methods. – This study is composed of four phases: extraction, synthesis of composite, testing, and data analysis.

Extraction of chitosan. Five hundred (500) grams of crab shells were cleaned and crushed. The crab shells were put in a 1L beaker with 4% NaOH to boil at 100C for one (1) hour to deproteinize the samples [10]. The samples were cooled down at room temperature. The samples were then pulverised. The pulverised crab shells were sieved using a 0.2 mm mesh sieve to acquire finer particles of crab shell powder. One percent (1%) HCl was added to the sample powder in a ratio of 1:4 w/v powder to HCl for 24 hours. The HCl was drained from the mixture. Two percent (2%) NaOH solution was added to the powder in a 1:2 w/v ratio powder to NaOH solution. This treatment was done for one hour to remove the albumen. The treated powder was washed using distilled water [13] [14]. The sample was then soaked in boiling 50% NaOH for two (2) hours. The powder was filtered from the beaker and cooled down at room temperature for one (1) hour. The powder was washed carefully with 500 mL 50% NaOH. The powder was oven dried at temperature of 120C for 24 hours [15].

Extraction of hydroxyapatite. Five hundred (500) grams of crab shells were cleaned and crushed. The crab shells were boiled in distilled water for two (2) hours to remove adherent meat. The crab shells were filtered from the beaker and air dried. The crab shells were pulverised and then sieved using 0.2 mm sieve to acquire fine particles. The acquired powder was heated in a furnace at 1000C for five (5) hours to form calcium oxide powder. It was cooled down at room temperature. The powder was then mixed with distilled water in a 1:1 w/v ratio solution

The phosphoric solution in 0.6M was added dropwise re-

sulting a 5:3 m_{powder}/v_{H3PO4} solution. The solution was kept at room temperature for 24 hours to precipitate. The precipitate was filtered using a Whatman No. 40 filter paper and washed carefully with distilled water. The precipitate was oven dried at 120C for three (3) hours and sintered by heating it in a furnace at 900C for four (4) hours [16].

Drying. The collected samples were sundried for 6 hours under sunlight and air dried in the laboratory at night for two days until no more moisture was present in the sponge. They were then minced into the finest possible particle that can be obtained.

Synthesis of composite. A ratio of 1:1 chitosan and hydroxyapatite was followed. Twelve (12) grams of chitosan was dissolved with the use of a magnetic stirrer at 600 rev/min in a 250 mL distilled water with 1% v/v acetic acid. Same amount of hydroxyapatite was added slowly to the mixture while stirring. Followed by the addition of 12.5 mL of 2.5% glutaraldehyde solution to the mixture. After the 90 minutes of stirring, 15 g of gelatin powder was added to the mixture while continuously stirred at 40C. While warm, the mixture was poured into eight (8) molds which were divided into two (2) batches, batch A and B. Both batches of the composite were air dried to form completely for 48 hours [17] [18].

Testing. The initial weight of the samples were recorded with the use of an analytical balance. The samples were submerged in crude oil for 30 minutes then removed with a strainer and were weighed. The amount of oil adsorbed was calculated using the following formula [19]:

$$qe = (\frac{w_o - w_e}{M})$$

Where:
$q_e = amount of oil adsorbed per unit weight of adsorbent$
$w_o = initial weight of oil (g)$
$w_e = weight of oil sample after the adsorption process (g)$
$M = mass of adsorbent (g)$

Results. – This study uses Fourier Transform Infrared Spectroscopy Instrument. In figure 1, an infrared spectrum of extracted chitosan is shown. A wide peak is located in 3200-3400 cm⁻¹ wavelength attributed by the vibration of the stretching of O-H and N-H bonds. Additionally, sharp peaks are found at around 1400 cm⁻¹ and 900 cm⁻¹ wavelengths caused by CH-OH and C-O-C bonds respectively.

In figure 2, the infrared spectrum of the extracted hydroxyapatite is shown. Sharp peaks are located at around 900, 1100, and 3600 cm⁻¹ wavelengths due to P-O, P-O, and O-H bonds respectively. Another peak is located at

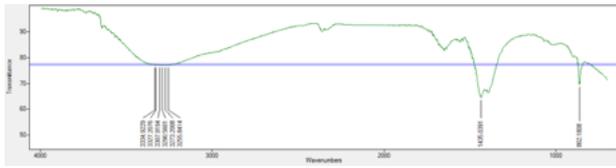around 1400 cm^{-1} wavelength attributed by the C-O bond.

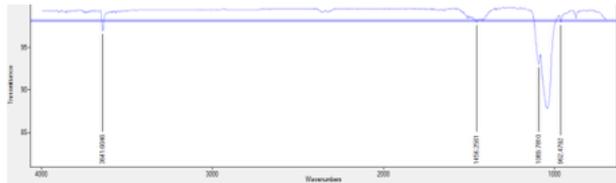Fig. 1: Infrared spectra of extracted chitosan

Fig. 2: Infrared spectra of extracted hydroxyapatite

The adsorption capacity of the composite was measured by weighing the molded composite before and after it was introduced to the crude oil. To identify the significant differences, the Independent Samples t Test statistical tool was used. Table 1 shows the difference between composite A and B. Composite A had an adsorption capacity of 0.107 0.177 while composite B had an absorption capacity of 0.049 0.019. Although composite A had higher adsorption capacity, there is no significant difference between composite A and B with a p-value of 0.065 shown in table 2.

	Composite	N	Mean	Std. Deviation	Std. Error Mean
Weight	A	8	.107200	.1767566	.0624929
	B	8	.048775	.0190642	.0067402

Table 1: Group Statistics

		F	Sig.	t	df
Weight	Equal variances assumed	4.011	.065	.930	14
	Equal variances not assumed			.930	7.163
	Equal variances not assumed			.930	7.163

Table 2: Independent Samples t-Test

Discussion. – In figure 1, a wide peak was located at 3200-3400 cm^{-1} which confirmed the presence of O-H bonds. However, the significant peaks were located at 1400 and 900 cm-1 contrary to 1150 and 1317 cm^{-1} [20]. One possible reason was that the chitosan did not fully convert from the deacetylation of chitin. The C-O bond from the sample maybe from the C=O bond from the chitin which may not have fully converted [21].

In figure 2, sharp peaks were located at 962, 1090 and 3641 cm^{-1} . This was almost identical to the standard hydroxyapatite IR spectrum [22]. Two distinguishable peaks

(962 and 1090 cm^{-1}) were located close to peaks 964 and 1093 cm^{-1} from the reference spectrum which confirmed the presence of P-O bonds. Moreover, another peak at 3641 cm-1 attributed to O-H bond present in hydroxyapatite. From the similarities of peaks, it can be implied that the sample was hydroxyapatite. However, an extra peak was located on wavelength 1456 cm^{-1} . Broad bands at 3432 and 1642 cm^{-1} attributed to the adsorbed water [22].

The composite produced was in a form of a soft gel. There were two (2) batches of the composite in order for the data to be more reliable. Each batch was composed of eight (8) small composites. The adsorption capacity of the composite was measured by weighing the molded composite before and after it was introduced to the crude oil. Composite A had an adsorption capacity of 0.107 0.177 while composite B had an absorption capacity of 0.049 0.019. From the results, it was shown that the chitosan-HAp mixture between the two (2) batches was insignificant with p-value at 0.065 yet both had the capacity to adsorb oil.

Conclusion.. – It was found out that chitosan-HAp composite gel was viable as an oil adsorbent due to its effective capacity to adsorb oil. In addition, there was no significant difference between composite A and B with a p-value of 0.065. For further studies, it is recommended to test various ratios of chitosan-HAp to determine the most effective adsorption capacity of the composite.

Recommendations. – To further improve this study, the use of equipment such as freeze-dryer and other cross-linking chemicals are recommended for the synthesis of the composite for it to form a more stable gel. It is recommended to test various ratios of chitosan-HAp to determine the most effective adsorption capacity of the composite. Additionally, using other forms possible for the composite such as sheets, microbeads and is also recommended. If certain equipment or chemicals are unavailable, it is recommended to use alternative methods for the synthesis.

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