

C.2a.1.7-  
Mohadi\_2018\_J.\_Phys.\_Conf.\_Ser.\_1095  
\_012032.pdf  
*By* Risfidian Mohadi

PAPER • OPEN ACCESS

1  
**Isolation of  $\beta$ -Chitosan from Squid Bone as Raw Material to Synthesize of Hybrid Photocatalysts TiO<sub>2</sub>-Chitosan**

To cite this article: Risfidian Mohadi *et al* 2018 *J. Phys.: Conf. Ser.* **1095** 012032

7  
View the [article online](#) for updates and enhancements.

You may also like

- 8  
- [Extraction of degradable bio polymer materials from shrimp shell wastes by two different methods](#)  
M Faisal, A Elhussieny, K A Ali et al.
- [Extraction and physicochemical characterization of chitin and chitosan isolated from house cricket](#)  
E B Ibitoye, I H Lokman, M N M Hezme et al.
- [Comparison of extraction sequence on yield and physico-chemical characteristic of chitosan from shrimp shell waste](#)  
W William and N Wid



The Electrochemical Society  
Advancing solid state & electrochemical science & technology

## 241st ECS Meeting

May 29 – June 2, 2022 Vancouver • BC • Canada  
Abstract submission deadline: **Dec 3, 2021**

Connect. Engage. Champion. Empower. Accelerate.  
**We move science forward**



## 1 Isolation of $\beta$ -Chitosan from Squid Bone as Raw Material to Synthesize of Hybrid Photocatalysts TiO<sub>2</sub>-Chitosan

Risfidian Mohadi<sup>1,a)</sup>, Nurlisa Hidayati<sup>1,a)</sup>, and Aldes Lesbani<sup>2,c)</sup>

<sup>1</sup> Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sriwijaya University. Jl. Raya Palembang Prabumulih Km 32 Ogan Ilir 30662, South Sumatera, Indonesia

<sup>2</sup> Integrated Research Laboratory, Graduate School, Sriwijaya University, Jl. Padang Selasa, Bukit Besar Palembang 30139, South Sumatera, Indonesia

a) Corresponding author: risfidian.mohadi@unsri.ac.id

b) hidayatinurlisa@yahoo.com

c) aldeslesbani@pps.unsri.ac.id

**Abstract.** Synthesis of hybrid photocatalyst of TiO<sub>2</sub>-chitosan has been done. Chitosan as a raw material was chitosan- $\beta$  obtained from chitosan isolation from squid bone. Chitosan from squid bone has a soft structure and very little to contain minerals and other impurities so easily obtained. Hybrid photocatalyst TiO<sub>2</sub>-chitosan was synthesized by a sol-gel method in which the incorporation of chitosan as a supporting material and TiO<sub>2</sub> having a function as a photocatalytic agent was dispersed on the  $\beta$ -chitosan surface. The hybrid of TiO<sub>2</sub>-chitosan photocatalysts was characterized by FTIR and SEM/EDX shows the functional groups and surface morphologies of hybrid photocatalyst TiO<sub>2</sub>-chitosan covered by uniformly distributed TiO<sub>2</sub> nanoparticles. The FTIR spectrum showed the O-Ti-O absorption bands at the wavenumber of 678.98 cm<sup>-1</sup> and the typical absorption of chitosan the -OH at the wavenumbers of 3425.58 cm<sup>-1</sup>, 3834.49 cm<sup>-1</sup>, and 3873.06 cm<sup>-1</sup>, respectively.

Keywords: chitosan- $\beta$ , photocatalyst, TiO<sub>2</sub>, sol-gel method, nanoparticles

### 1. Introduction

Chitosan is a natural polymer that has a structure similar to cellulose and can be formed into thin films. Chitosan that has the properties of *nontoxic*, *biodegradable*, and *biocompatible* resulting from the deacetylation of  $\beta$ -D-glucosamine by using high temperature and high concentrated alkali solvents [1,2]. Chitosan has the structure of poly  $\beta$ -D-(2-acetamido-2-deoxy-D-glucopyranosyl) units. Chitosan is specific because it has a reactive amine group on C-2 and primary and secondary hydroxyl groups in C-3 and C-6 which cause chitosan to have high chemical reactivity [3,4,5]. The structure of chitin and chitosan have the difference lies in the comparison of the amine group (-NH<sub>2</sub>) with an acetyl group (-CH<sub>3</sub>CO) called the degree of deacetylation [6]. The degree of deacetylation depending on the raw material and the method used in the preparation of chitosan. The degree of deacetylation is a quality parameter of chitosan which shows the percentage of acetyl groups which can be removed from the chitin remainder. The release of acetyl groups on chitin causes the positively charged chitosan, to able to bind negatively charged compounds or



2 Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Published under licence by IOP Publishing Ltd

molecule. Methods for determining the acetyl groups released from chitin include potentiometric titration, ninhydrin test, NMR, titration of hydrogen bromide, IR, and UV-Vis spectrophotometry [7,8]. XRD analysis shows that chitosan has 3 structures, that is structure  $\alpha$ ,  $\beta$ , and  $\gamma$ . Molecule  $\alpha$ -Chitosan has a very dense antiparallel bond because it is stabilized by its intermolecular hydrogen bond. In contrast to  $\beta$  and  $\gamma$  chitosan, where the hydrogen bond in the water increases. The high level of hydration and decreased attachment causes the  $\beta$  and  $\gamma$  chitosan structure to be more flexible and reactive. Chitosan with  $\alpha$  structure is mostly found in animal shells of *crustaceans*, while  $\beta$  and  $\gamma$  chitosan can be found in squid bones and fungi, respectively.

6  
Chitosan is insoluble in water but is soluble in most organic solutions, such as acetic acid, formic acid, and lactic acid, and has a finite solubility in phosphoric acid and is insoluble in sulfuric acid. The commonly used chitosan solvent is an acetic acid with a concentration of 1-2% [9]. Photocatalyst technology used for processing and degraded of wastewater contaminant, efficiently and can be done by using titanium dioxide ( $\text{TiO}_2$ ) through the process photo-oxide the dye into pollutants compounds in the water. The Titanium dioxide ( $\text{TiO}_2$ ) is a semiconductor material that has a relatively high photocatalytic activity. In this study,  $\text{TiO}_2$  will be dispersed into chitosan which acts as a *supporting material*, wherein the chitosan- $\text{TiO}_2$  formed to combine the functions of chitosan as an adsorbent and  $\text{TiO}_2$  that has high photocatalytic activity [10,11].

## 2. Experiment

Materials used in this research were squid bone, hydrochloric acid, sodium hydroxide, nitrogen gas, and distilled water, while instrumentation applied for analysis were spectrophotometer FTIR Shimadzu Prestige-21, and SEM-EDX JEOL JED-2300.

### 2.1. Preparation of Chitosan from Squid Bone

Fresh squid bone washed and dried in the sunlight for about four days. Once the squid bone dry milled using a mortar and sieved to pass 3 the 80 mesh size. Amount of 50 g of 80 mesh squid bone put into a 500 mL beaker glass, then adding 1 M HCl solution 5 with a ratio of 1:10 (w/v) for demineralization process. The mixture is stirred with a magnetic stirrer at room temperature for 3 hours and then filtered through filter paper while continuously washed with distilled water until no residual chloride ion remains in the samples. The washing process is stopped if no turbid solution formed when the filtrate drops with an  $\text{AgNO}_3$  solution. Residue from demineralization put into a 500 mL beaker glass and added with 1 M NaOH solution at a ratio of 1:10 (w/v). The mixture stirred and heated at 60 °C on a hotplate stirrer for 1 hour and then filtered with Whatman 41 $\mu\text{m}$  filter paper. The residue was found on the filter paper was washed with distilled water until the residue namely chitosan in neutral pH. Chitosan was dried in an oven at a temperature of 70 °C until dry to constant weight. Chitosan has been obtained then characterized by FT-IR spectrophotometer to identify the functional groups of chitosan, and determine the degree of deacetylation product by base line method.

The FT-IR spectrum analysis for chitosan does area of functional groups and the fingerprint region with a frequency of 4000  $\text{cm}^{-1}$  - 400  $\text{cm}^{-1}$ . Deacetylation degree of chitosan determined by *base line* by FT-IR spectra, with the formula:

$$DD = 100 - \left[ \left( \frac{A_{1655}}{A_{3450}} \right) \times \frac{100}{1.33} \right] \quad (1)$$

Where,  $A_{1655}$  showed absorption at amide band,  $A_{3450}$  showed absorption at hydroxyl and a factor of 1.33 shows the value of the ratio  $A_{1655}/A_{3450}$  to completely deacetylation degrees of chitosan.

### 2.2. Synthesis of Hybrid Photocatalysts $\text{TiO}_2$ -Chitosan from Squid Bone

Amount of 10 g of chitosan from squid bone added into 100 mL of 0.1 M HCl solution in 250 mL beaker glass, while continuously stirring until it dissolved evenly and the  $\text{TiO}_2$  particle was added with a ratio of 1:1 (w/w). The solution stirred to homogenize for 20 minutes then filtered through Whatman 41 $\mu\text{m}$  filter

paper, then the precipitate obtained is dried in an oven at a temperature of 50°C about 4 h in the form of TiO<sub>2</sub>-chitosan gel. The product of TiO<sub>2</sub>-chitosan gel washed with distilled water until the pH of water residue is neutral, then dried in the oven at a temperature of 70 °C for 12 h to obtain a hybrid of TiO<sub>2</sub>-chitosan. The hybrid TiO<sub>2</sub>-Chitosan characterized by a FT-IR spectrophotometer to see functional groups and the elemental contained by SEM-EDX analysis.

### 3. Results and Discussion

Squid bone powder (80 mesh) that has been prepared was added 1 M HCl to remove mineral content, and continue to the second stage is deproteinize, which in this process aims to break the protein bonds and other crosslinked intramolecular in squid bone chitin using 1M NaOH. The yield produced at this stage is about 65.6% which estimated that the protein content in squid bone around 30-40% [12],13. The deacetylation process of chitin to chitosan by removed of the acetyl group (CH<sub>3</sub>CO) by using a concentrated solution of NaOH 50% (v/v). The process of deacetylation of chitin takes place under alkaline conditions because the N-acetyl group is not removed with an acid reagent without polysaccharides [14]. Thus, in this process the yield obtained from squid bone about 80.15% (w/w) with the texture of chitosan in shaped hydrogel [15].

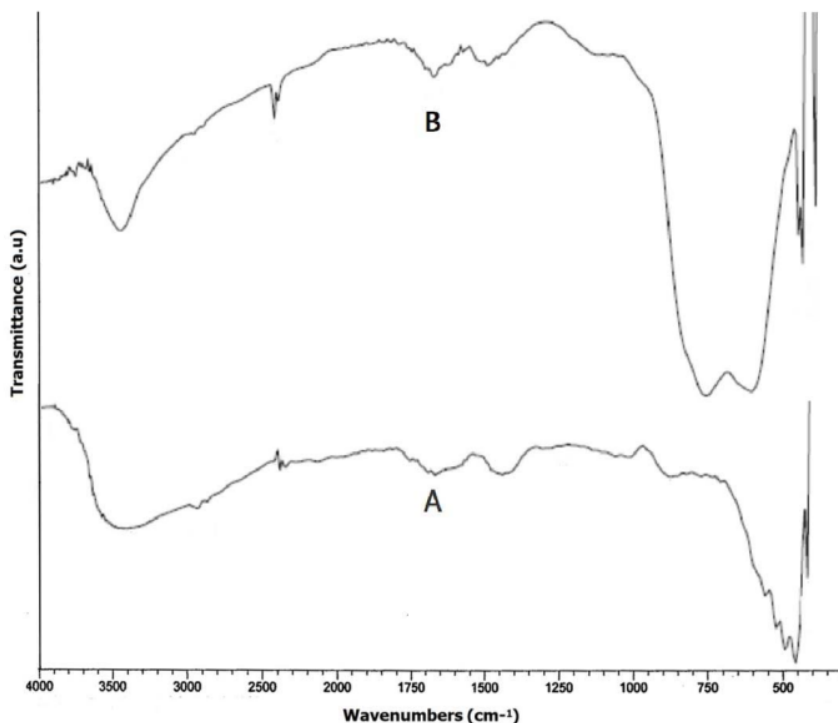
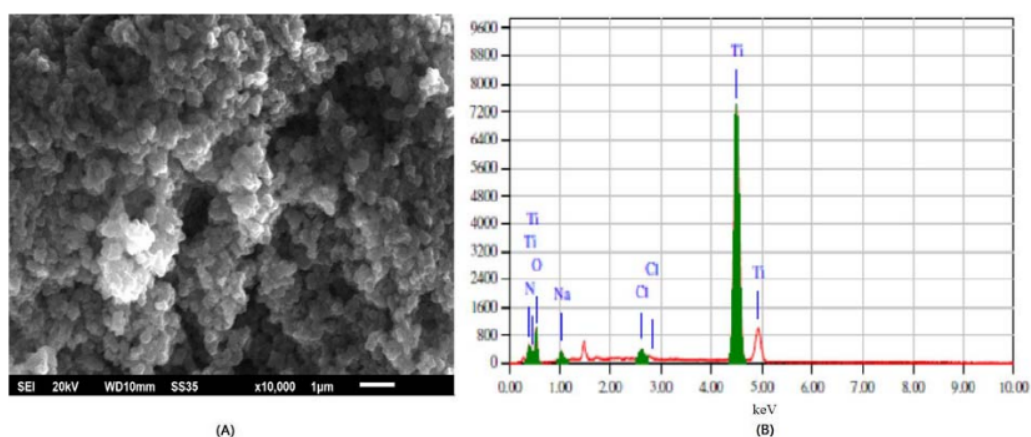


Figure 1. FT-IR spectrum of chitosan (A), and TiO<sub>2</sub>-Chitosan (B)

Based on the FT-IR spectra on Figure 1. (A) and the calculation using equation (1) the degree of deacetylation by methods *base line* on a FT-IR spectrum obtained the degree of deacetylation of chitosan from squid bone ranged around ± 93.6%. The degree of deacetylation levels off at relatively high values while normal commercial chitosan has of ± 80% deacetylation. Figure 1. was confirmed the characterizations of chitosan (A), and a hybrid of TiO<sub>2</sub>-chitosan (B), the presence of carboxyl and

4 hydroxyl groups [16]. The peak at (3380 to 3480)  $\text{cm}^{-1}$  is  $\nu(\text{O-H})$  and  $\nu(\text{NH}_2)$ ; the peak at (2920 to 2940)  $\text{cm}^{-1}$  is from  $\nu(\text{CH}_3, \text{CH}_2, \text{CH}, \text{and OH})$ ; the peak at (1630 to 1650)  $\text{cm}^{-1}$  is from  $\nu(\text{C=O})$  in low absorbances indicate that the C=O group of chitin have had reduced in the form of chitosan [17]. The adsorption band of O-Ti-O for hybrid of  $\text{TiO}_2$ -chitosan from squid bone appear at (524 to 680)  $\text{cm}^{-1}$  showed in **Figure 1**. (B) with presence of  $\nu(\text{O-H})$  and  $\nu(\text{NH}_2)$  stretching vibration overlap at 3425  $\text{cm}^{-1}$  indicate that that functional group is still active as adsorbent in the form of hybrid of  $\text{TiO}_2$ -chitosan.

The hybrid of  $\text{TiO}_2$ -chitosan surface morphology characterized by SEM and the elemental analyses performed by EDX. According to the SEM photograph in **Figure 2**, it is seen that the  $\text{TiO}_2$  particles have had evenly distributed over the surface of chitosan in the hybrid of  $\text{TiO}_2$ -chitosan with particle size almost in nano size. The surface of hybrid of  $\text{TiO}_2$ -chitosan mass percentage had dominated by  $\text{TiO}_2$  particle while the N atom from the aminne group ( $\text{NH}_2$ ) of chitosan confirmed as the active site of the hybrid agrees to the FTIR spectra in **Figure 1**. and the detail of elementals percentage on the hybrid of  $\text{TiO}_2$ -chitosan given in **Table 1**.



**Figure 2.** Scanning Electron Microscope (SEM) photograph of hybrid of  $\text{TiO}_2$ -chitosan from squid bone with (A) 10.000x and (B) spectrum of Energy Dispersive X-ray (EDX)

**Table 1.** The percentage of elements and oxides on hybrid of  $\text{TiO}_2$ -chitosan from squid bone

Elements	% Mass	% Atom	Oxides
O	44.20	62.10	$\text{TiO}_2$
Ti	43.66	20.49	NO
N	9.36	15.03	

The  $\text{TiO}_2$  on a hybrid of  $\text{TiO}_2$ -chitosan from squid bone has 62.10% in oxide form, while the N atom contributes 15.03%, and 20.49% of NO, respectively. That mean 15.03% of nitrogen atom from chitosan exist as aminne group ( $\text{NH}_2$ ) and 20.49% also in the form of oxide. The in oxide form (NO) of chitosan has been by oxidation process when amine direct contacted to the  $\text{TiO}_2$  particle on chitosan surface to form of hybrid of  $\text{TiO}_2$ -chitosan.

#### 4. Conclusions

The product of  $\beta$  chitosan isolated from squid bone gain about 80.15% (w/w) yield. The degree of deacetylation of the  $\beta$  chitosan determined by *base line* methods on a chitosan FT-IR spectra results about  $\pm 93.6\%$  degree of deacetylation.  $\text{TiO}_2$ -chitosan from squid bone was used as raw material to synthesis of

hybrid TiO<sub>2</sub>-chitosan. Base on FT-IR spectra and SEM-EDX analysis the absorbances appear at (524 to 680) cm<sup>-1</sup> and  $\nu(\text{O-H})$  and  $\nu(\text{NH}_2)$  stretching vibration overlap at 3425 cm<sup>-1</sup> indicate that those functional group of NH<sub>2</sub> from  $\beta$  chitosan is still active as adsorbent in the form of hybrid of TiO<sub>2</sub>-chitosan even though TiO<sub>2</sub> particle were distribute evenly on the surface of chitosan.

### 5. Acknowledgments

This research supported from Hibah Kompetitif of Sriwijaya University 2017 through PNPB founding with contract number 9012/UN9.3.1/PP/2017. The authors wish to acknowledge gratefully to all research group members of Inorganic Laboratory Dept. of Chemistry, Faculty of Mathematics and Natural Sciences, Sriwijaya University.

### 6. References

- [1] Chandumpai, A., Narongsak S., Damrongsak F., and Prasait S., *Carbohydr. Polym.* 58, 467-474 (2004).
- [2] Modrzejewska Z., Maniukiewicz W., Wojtasz-Pajak A., *Polish Chitin Soc.*, Monograph XI, 113–121 (2006).
- [3] Jolanta K., Małgorzata C., Zbigniew K., Anna B., Krzysztof B., Jorg T., and Piotr S., *Mar Drugs*. 8(5):1567–1636 (2010).
- [4] Cuong H., Minh N., Van Hoa N., Trung T., *Int J Biol Macromol.* 93:442-447 (2016).
- [5] Alessandro I., Matteo Di G., Simona F., Chiara S., Marianna B., Francesco V., Graziella P., Fabio B., Francesco Z., Matteo C., and Giuseppe F., *Mar Drugs*. 12: 5979–5992 (2014 ).
- [6] Islem Y., and Marguerite R. *Mar. Drugs*, 13, 1133-1174 (2015)
- [7] Muzzarelli R.A.A. *Mar. Drugs*. 9:1510–1533 (2011).
- [8] Kurita K., Kaji Y., Mori T., Nishiyama Y. *Carbohydr. Polym.* 42:19–21 (2000).
- [9] Youn D.K., No H.K., Prinyawiwatkul W. *Int. J. Food Sci. Technol.* 48:571–577 (2013).
- [10] Cardenas G., Cabrera G., Taboada E., Miranda S.P. *J. Polymer Sci.* 93:1876–1885 (2004).
- [11] Tolaimate, A.; Desbrieres, J.; Rhazi, M. *Polymer* 44, 7939–7952 (2003).
- [12] Rinaudo M. *Prog Polym Sci.* 31:603–632 (2006).
- [13] Clasen C, Wilhelms T, Kulicke W-M. 7:3210–3222 (2006).
- [14] Synowiecki J, Al-Khateeb NA. *Crit Rev Food Sci Nutr.* 43:145–171 (2003).
- [15] Zhang Y, Xue C, Xue Y, Gao R, Zhang X. *Carbohydr Res.* 340:1914–1917 (2005).
- [16] Mohadi R., Kurniawan Ch., Yuliasari N., Hadayati N., Lesbani A., *Prog. on Chem. and App. of Chitin and its Deriv.* 20:213-221 (2015)
- [17] Kasaai MR. *Carbohydr Polym.* 71:497–508 (2008).

C.2a.1.7-

Mohadi\_2018\_J.\_Phys.\_Conf.\_Ser.\_1095\_012032.pdf

---

ORIGINALITY REPORT

---

16%

SIMILARITY INDEX

---

PRIMARY SOURCES

---

1	<a href="http://puima.mipa.unsri.ac.id">puima.mipa.unsri.ac.id</a> Internet	112 words — 5%
2	<a href="http://Repository.Unej.Ac.Id">Repository.Unej.Ac.Id</a> Internet	57 words — 3%
3	<a href="http://link.springer.com">link.springer.com</a> Internet	38 words — 2%
4	<a href="http://www.tandfonline.com">www.tandfonline.com</a> Internet	33 words — 1%
5	<a href="http://www.chemijournal.com">www.chemijournal.com</a> Internet	32 words — 1%
6	<a href="http://www.scribd.com">www.scribd.com</a> Internet	22 words — 1%
7	<a href="http://repository.unhas.ac.id">repository.unhas.ac.id</a> Internet	21 words — 1%
8	<a href="http://www.proceedings.com">www.proceedings.com</a> Internet	21 words — 1%
9	<a href="http://media.neliti.com">media.neliti.com</a> Internet	17 words — 1%



---

EXCLUDE QUOTES      OFF

EXCLUDE MATCHES      < 1%

EXCLUDE BIBLIOGRAPHY   ON