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Proceeding

The 2nd International Conference of the Indonesian Chemical Society 2013

ICICS 2013

Research in Chemistry for Better Quality of Environmental

Universitas Islam Indonesia, Yogyakarta, Indonesia
October, 22 - 23th 2013

Abdul Kahar Muzakkir, Conference Hall
Universitas Islam Indonesia (UII), Yogyakarta.
Kampus Terpadu, Jl. Kaliurang KM 14,5 Sleman, Yogyakarta.

Preface

The international conference is an annual conference of the Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI). In the year 2013, the mandate of the organizing committee was given to the HKI Yogyakarta branch and also supported by Department of Chemistry of Universitas Negeri Yogyakarta (UNY), Department of Chemistry of Universitas Gadjah Mada (UGM), Department of Chemistry of Universitas Islam Negeri Sunan Kalijaga (UIN Suka), National Nuclear Energy Agency (BATAN Yogyakarta), and Volcano Investigation and Technological Development Center (BPPTK Yogyakarta). For the year 2013, ICICS 2013 is hosted by Department of Chemistry, Faculty of Mathematics and Natural Sciences, Islamic University of Indonesia, Yogyakarta from October 22 – 23, 2013. This conference was also prepared to celebrate 70th anniversary of Universitas Islam Indonesia.

The Sicentific Programme of ICICS2013 comprises the following:

1. Invited Speaker 11 papers
2. A total 256 paper for parallels sessions
    a. Organic Chemistry 32 papers
    b. Inorganic Chemistry 43 papers
    c. Physical Chemistry 37 papers
    d. Analytical Chemistry 68 papers
    e. Education Chemistry 23 papers
    f. Biochemistry 43 papers

The breakdown of the presentation is as follows:

Session	Oral	Poster	Total
Invited Speaker	11	0	11
Organic Chemistry	25	7	32
Inorganic Chemistry	38	5	43
Physical Chemistry	31	6	37
Analytical Chemistry	61	7	68
Education Chemistry	22	1	23
Biochemistry	34	8	43
Total	**222**	**34**	**256**

Yogyakarta, 25th November 2013

Editors

Welcoming Address by The Organizing Committee

Assalamu'alaikum Wr. Wb.

Honorable Rector of Universitas Islam Indonesia
The distinguished invited speakers, and
All participants of the ICICS 2013

Welcome you at the 2nd International Conference of the Indonesia Chemical Society 2013 (ICICS 2013) this morning here at the Auditorium Kahar Muzakkir Universitas Islam Indonesia, Yogyakarta. The international conference is an annual conference of the Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI). In the year 2013, the mandate of the organizing committee was given to the HKI Yogyakarta branch and also supported by Department of Chemistry of Universitas Negeri Yogyakarta (UNY), Department of Chemistry of Universitas Gadjah Mada (UGM), Department of Chemistry of Universitas Islam Negeri Sunan Kalijaga (UIN Suka), National Nuclear Energy Agency (BATAN Yogyakarta), and Balai Penyelidikan dan Pengembangan Kegunungapian (BPPTK Yogyakarta). For the year 2013, the honor of hosting ICICS 2013 has been given to the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia, Yogyakarta. This conference was also prepared to celebrate 70th anniversary of Universitas Islam Indonesia.

The conference comprises both oral and poster presentation in English and Indonesian with optional post conference publication of full papers in English in the Procedia Chemistry (Elsevier, ISSN: 1876-6196) and Proceeding Conference for Indonesian language. There are 211 papers presented orally and 34 papers presented by poster covering wide-variety subjects of chemistry. We invited 6 Indonesian invited speakers, 2 Japan invited speakers, 1 Australian invited speakers, 1 Saudi Arabia invited speakers, and 1 Malaysian Invited speakers.

We hope you will enjoy a pleasant and valuable seminar at Universitas Islam Indonesia

Wassalamu'alaikum Wr. Wb.

Riyanto, Ph.D.

Chairman

Opening Speech from the Rector of Universitas Islam Indonesia

Assalamu'alaikum Wr. Wb
The distinguished invited speakers, and
All participants of the ICICS 2013

Firstly, I would like to express my great appreciation to the Department of Chemistry UII as one of the organizers of the program The 2nd International Conference of the Indonesian Chemical Society 2013 (ICICS 2013) with the theme "Research in Chemistry for Better Quality of Environmental". I am proud that this interesting event is being organized and held in Yogyakarta.

As the biggest and the oldest private university in Yogyakarta, University Islam Indonesia is committed to the excellence in research and teaching. Recently, we are preparing UII as one of the world class universities.

Knowing that committee has selected outstanding speakers from various prestigious institutions. I believe that all of the participants will enjoy the discussion of issue covered by the topic of this seminar. Scientist have shown that the environment's condition is increasingly critical, and human industrial activities are largely to blame. In fact that environmental damage is a crisis we caused together, therefore, a responsibility we all share together. We are deeply concerned with the issues and opportunities in the internationalization of sciences for better life, sciences have to make better quality of environmental.

Finally, I would once again like to thank the organizer for organizing this event, and to thank all the participants attending this ICICS 2013 event as well as delivering their scientific presentations. I do really hope that you can enjoy this seminar and have excellent stay in Yogyakarta.

Wassalamu'alaikum Wr. Wb

Prof. Dr. Edy Suandi Hamid, M.Ec.
Rector of Universitas Islam Indonesia

Remarks by the Chairman of the Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI)

Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI) is an independent, nonprofit organization founded in February 1962 to facilitate communication among Indonesian chemists and other professionals from chemistry related fields, and to promote the advancement of science, education, and application of chemistry to support the better life of mankind. HKI organize activities to enhance communication and collaboration among chemists in various institutions in Indonesia, to disseminate new knowledge and research results in chemistry and related fields, to improve the knowledge and skills of chemists working in schools, universities, industries, research institutes, and other sectors, to nurture a scientific temper on school children to ensure strong capabilities of future chemists that are needed for humankind, and other activities that support its missions. HKI holds various academic conferences, publishes several journals, supports the development of scientific information systems in Indonesian; organize training for chemists in various sectors, etc.

The 2013 International Conference of the Indonesian Chemical Society will be the 2nd event in the ICICS conference series, started in 2012, that brings together individuals involved in chemistry-related fields (chemistry, pharmacy, environmental science, chemical engineering, molecular biology, material science, education chemistry, etc.) or institution in chemistry-related sectors. The First International Conference of the Indonesian Chemical Society 2012 is organized by East Java Branch of HKI in collaboration with chemistry departments at several universities in East Java: ITS, UB, UIN Maliki, UM, UMC, Unair, Unej, and Unesa.

ICICS 2013 will be organized by the Indonesian Chemical Society Yogyakarta branch. The international conference was supported by the Indonesian Chemical Society (Himpunan Kimia Indonesia, HKI), Department of Chemistry of Universitas Negeri Yogyakarta (UNY), Department of Chemistry of Universitas Gadjah Mada (UGM) and Department of Chemistry of Universitas Islam Negeri Sunan Kalijaga (UIN Sunan Kalijaga). For the year 2013, the honor of hosting ICICS-2013 has been given to the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia (UII), Yogyakarta, Indonesia.

Congratulations to the ICICS 2013 committee for this conference.

Dr. Muhamad Abdulkadir Martoprawiro
Chairman of the Indonesian Chemical Society

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4. Rector of Gadjah Mada University
5. Rector of Yogyakarta State University
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CONTENT

Invited Speaker

Paper of Education Chemistry

Graphene Supported Oxide Systems for Catalytic Oxidation of Organic Compounds in Aqueous Solution for Water Treatment

Shaobin Wang, Stacey Indrawirawan, Yunjin Yao, Hongqi Sun

Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth WA 6845, Australia

Introduction

Organic contaminants in water have been a big group of pollutants which are toxic and persistent. Presently, a great development has been achieved in decomposing these organic pollutants in wastewaters by advanced oxidation processes (AOPs), involving various chemical, photocatalytic, electrocatalytic methods.Among various techniques of catalytic oxidation for water and wastewater treatment, Fenton reaction is one of the cost-effective technologies where hydroxyl radicals (•OH) are usually main highly reactive oxidizing species generated to degrade organic contaminants. Similar to the activity of hydrogen peroxide for the degradation of organic pollutants, alternative oxidants such as peroxymonosulphate (PMS) have been found to be highly effective in chemically mineralizing various organic contaminants.

Graphene, a single layer of carbon atoms tightly packed into a two-dimensional honeycomb sp^2 carbon lattice, possesses a large surface area, open porous structure, flexibility, chemical stability, and very high electrical conductivity, which warrant it as a good candidate for constructing graphene-based composite materials with metal oxides. Here, we present synthesis of metal oxides (Co_3O_4 and $CoFe_2O_4$) and reduced graphene oxide (rGO) via a chemical deposition of Co_3O_4 and $CoFe_2O_4$ NPs onto GO, followed by reduction of GO to graphene in hydrothermal solution.These composites were tested in the catalytic performance in heterogeneous activation of peroxymonosulfate (PMS) for decomposition of phenol.

Experimental

GO was synthesized using the Hummers method through oxidation of graphite powder. In a typical synthesis of the Co_3O_4-rGOand $CoFe_2O_4$–rGO hybrids, firstly, cobalt and iron precursor were dispersed in distilled water, and GO was dispersed in 250 mL water by sonication for 2 h to achieve uniform dispersion of GO. Then, precursor solution was gradually added to the GO solution. Meanwhile, ammonia (28%) or NaOH solution was added to the above solution, which will be used for precipitation and GO reduction. Finally, the mixture was transferred into an autoclave for hydrothermal treatment at 180 ℃ under static condition for 12 h. The solid product was separated by centrifugation, washed thoroughly with water and absolute ethanol to remove any impurities.

The crystallographic structure of the catalysts was investigatedon a Bruker D8-Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å), with accelerating voltage and current of 40 kV and 40 mA, respectively. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 with a resolution of 4 cm^{-1} in transmission mode at room temperature. The morphology of the materials were characterized by FESEM (Zeiss Neon 40EsB FIBSEM) equipped with EDS and TEM (JEOL 2011 TEM). TGA was performed by heating the samples in an air flow at a rate of 100 mL/min using a Perkin-Elmer Diamond TG/DTA thermal analyzer with a heating rate of 10 ℃/min. The surface area, total pore volume, and pore size distribution of all samples were determined by N_2 adsorption at -196 ℃ using Autosorb (Quantachrome Corp.). All samples were degassed at 100 ℃ for 4 h, prior to the adsorption experiments. The Brunauer-Emmett-Teller (BET) surface area and pore volume were obtained by applying the

BET equation and p/p_0=0.95 to the adsorption data, respectively. The pore size distribution was obtained by the Barrett-Joyner-Halenda (BJH) method.

To study the activity of the catalytic oxidation of phenol, batch experiments were carried out in a 150 mL batch reactor. All reactions were initiated without the pH being controlled by mixing appropriate concentrations of phenol, oxone and a catalyst. Fixed amount of oxone was added to a phenol solution and allowed to dissolve before the reaction. Later, catalysts were added to start the reaction. The reaction was carried on for 1 h and stirred at different temperatures (25, 35 and 45 ℃). At predetermined time intervals, 0.5 mL liquid was withdrawn using a syringe filter into a HPLC vial, and 0.5 mL of methanol was added to quench the reaction. The concentrations of phenol were analyzed using a HPLC with a UV detector at the wavelength of 270 nm. The column used was C-18 and the mobile phase was solution of 30% CH_3CN and 70% water.

Results and discussion

The phase structure of as-synthesized samples was firstly determined by XRD. The results indicate that the hybrids consist of disorderedly stacked graphene sheets and well crystallized Co_3O_4 or $CoFe_2O_4$. The average crystallite sizes of Co_3O_4 in Co_3O_4–rGO and $CoFe_2O_4$ NPs in $CoFe_2O_4$–rGO were estimated to be 32.7 and 23.8 nm, respectively, which were consistent with the TEM observations (Fig.1).According to the TGA analysis, mass loss in Co_3O_4–rGO and $CoFe_2O_4$–rGO showed about 58% and 63.6 wt% of metal oxide deposited on the surface of graphene.

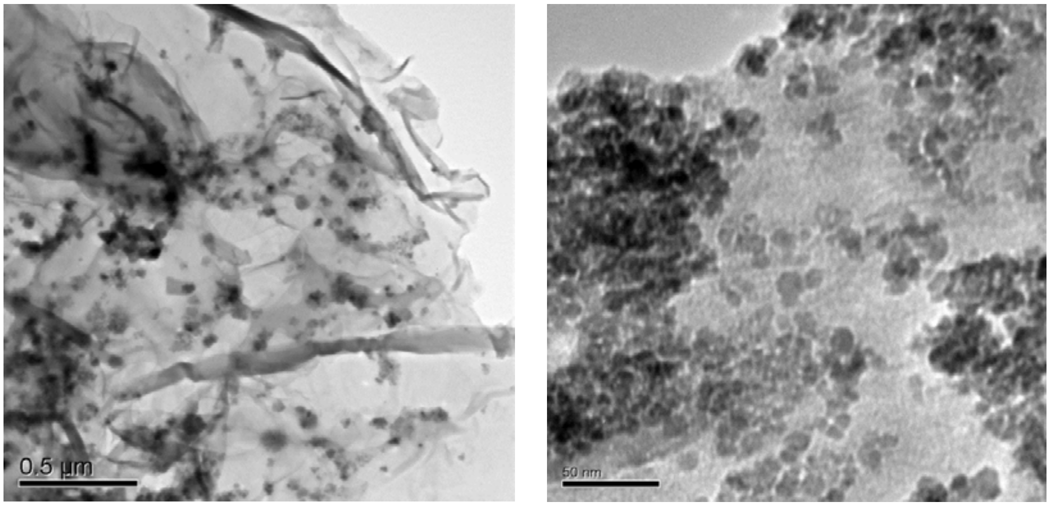

Fig. 1TEM images of Co_3O_4–rGO and $CoFe_2O_4$–rGO.

The catalytic performances of rGO, Co_3O_4,$CoFe_2O_4$, Co_3O_4–rGO and $CoFe_2O_4$–rGO hybrids in the catalytic oxidation of phenol in the presence of PMS are shown in Figure 2. Nearly 23% of phenol (20 mg/L) was removed in 60 min in the presence of rGO, suggesting minor reaction of phenol degradation could occur. For pure Co_3O_4 sample, 100% of phenol was removed in 60 min while for $CoFe_2O_4$ sample, 51% of phenol was removed in 60 min. meanwhile the degradation rate of phenol with $CoFe_2O_4$–rGO and Co_3O_4–rGO hybrids was extremely fast and took around 30 and 20 min, respectively,for complete phenol oxidation under the same conditions.

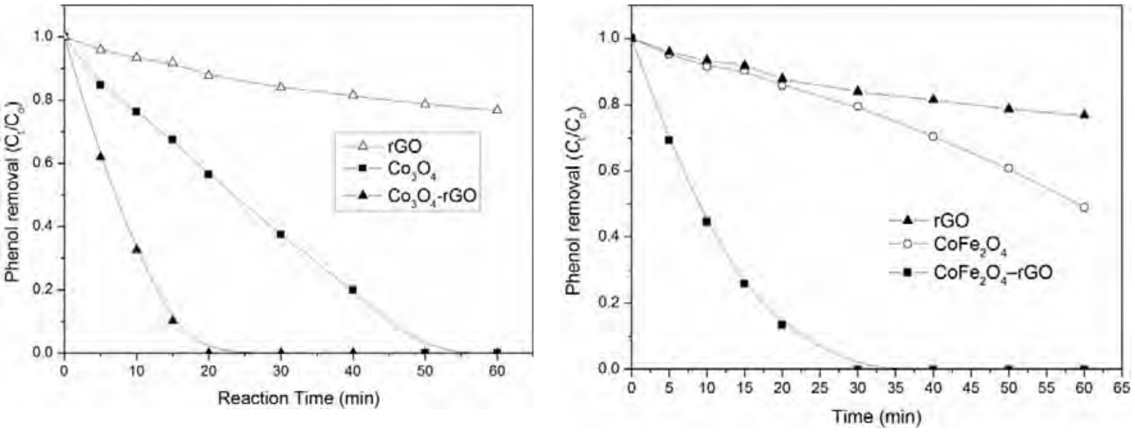

Figure 2. Phenol degradation using different catalysts (Reaction conditions: [Phenol] = 20 mg/L, [PMS] = 0.3 g/150 mL, [Catalyst] = 10 mg/150 mL)

The catalytic performance of Co_3O_4–rGO/PMS and $CoFe_2O_4$–rGO/PMS at different temperatures are shown in Figure 3.As can be seen the rate of disappearance of phenol increased at increasing temperature.It was found that phenol degradation in Co_3O_4–rGO/PMS process is well formulated by the pseudo-zero-order kineticsand that $CoFe_2O_4$–rGO/PMS process is well formulated by the pseudo-first-order kinetics.The activation energy (Ea) values for Co_3O_4–rGO and $CoFe_2O_4$–rGO were obtainedas 26.5 and 15.8 kJ mol^{-1}, respectively.

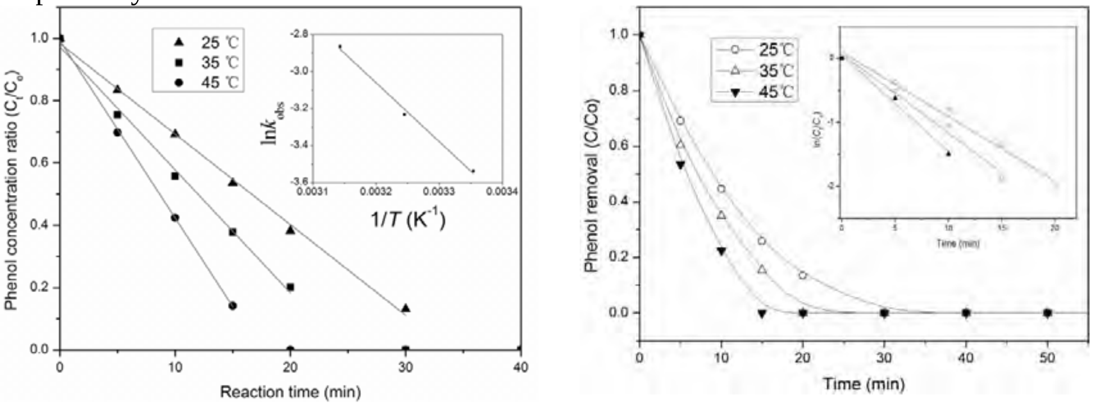

Figure 3. Effect of reaction temperature on phenol degradation using Co_3O_4–rGO/PMS and$CoFe_2O_4$–rGO/PMS.

Acknowledgement

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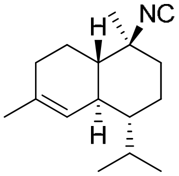
Chemistry and Biology of Brominated Compounds from Marine Algae *Laurencia* spp.

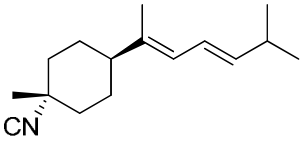
Tatsufumi Okino

Faculty of Environmental Earth Science, Hokkaido University, Sapporo, 060-0810, Japan
(okino@ees.hokudai.ac.jp)

Fouling organisms such as barnacles and mussels cause decrease of fuel efficiency of ships. Antifouling coatings are urgently needed to prevent fouling organisms, to reduce carbon dioxide emissions from ships, and to prevent invasive organisms. Especially international treaty of the International Maritime Organization (IMO) to ban the use and existence of ship's hull of organic tin compounds as antifouling agents went into effect in 2008. A number of antifouling marine natural products have been reported in the past decade. Previously we screened marine invertebrate for antifouling against barnacle larvae. As a result, we found several antifouling compound such as isocyano compounds. For example, 10-isocyano-4-cadinene (**1**) is one of potent compounds, of which total synthesis was completed recently. In addition, 3-isocyanotheonellin (**2**) was explored as a leading compound. Over 90 compounds were synthesized and one of them was selected for the field test. Since the result was promising, we are currently collaborating with a paint company to pursue industrial application. Also their mode of action is being studied.

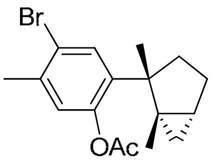


1



2

Recently we screened marine algae for antifouling activity against barnacle larvae using *Amphibalanus amphitrite*. Especially we focused on red algae *Laurencia* spp., because they have precedent antifouling compounds. For example, elatol is a well-known example, but it was not pursued in industry due to its toxicity. Laurinterol is another example. We found laurinterol acetate (**3**) is more active (EC_{50} = 0.37 g/mL). A triterpenoid, thyrsiferol (**4**) also showed a potent antifouling activity (EC_{50} = 0.11 g/mL).



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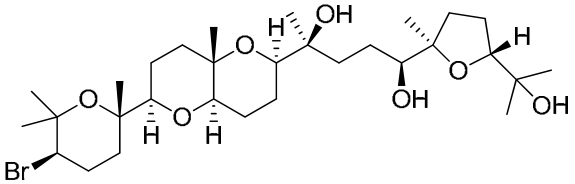
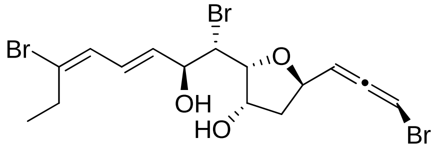


4

A new compound, omaezallene (**5**) showed EC_{50} of 0.22 g/mL and LC_{50} of 3.4 g/mL against barnacle larvae. Determination of planar structure of omaezallene was straight forward by comparing spectroscopic data with literature data of a known bromoallene. Absolute configuration of bromoallene moiety was predicted by Lowe's rule. Lowe's rule is an empirical rule to predict absolute configuration of simple allenes, which was applied for fungal metabolite, diyneallene moiety containing compounds. If the optical rotation is positive, allene is *S*. If negative, allene is *R*.To clarify relative configurations of other parts, omaezallene was derivatized into an acetonide. NOESY experiments of the acetonide indicated relative configurations of other chiral centers except C-9. Total synthesis of proposed structure was achieved by using D-glucose as a starting material. Both epimers at C-9 were synthesized. Comparison of NMR data and optical rotation concluded all absolute configurations of omaezallene. Interestingly epimers of C-9 showed opposite sign of optical rotation. All bromoallenes which were isolated from *Laurencia* so far followed Lowe's rule. 9-*epi*-omaezallene is only exception. In fact, Lowe mentioned that the rule could not be applied if the substituent of bromoallene contained configurational asymmetry.



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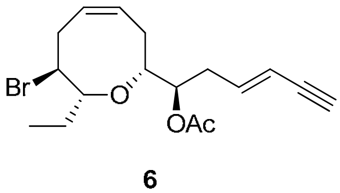
The well-known acetogenin, laurencin from *L. nipponica* also showed potent antifouling activity against barnacle larvae (EC_{50} = 0.23 g/mL), but did not show any toxicity even at 100 g/mL. We tested ecotoxicities of laurencin against the copepod *Tigriopus japonicus*, the water flea *Daphnia magna*, the medaka *Oryzias latipes* juveniles and the clown fish *Amphiprion ocellaris* larvae and juveniles. These toxicities of laurencin were 10 – 100 times weaker than those of currently available antifouling agent copper pyrithione.



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Laurencia is one of the richest producers of brominated secondary metabolites. Biosynthesis of brominated compounds such as laurencin, have been studied since late 1990s. Nevertheless, it remains poorly understood. We conducted cDNA cloning and heterologous expression of vanadium dependent bromoperoxidase (VBPO) from *L. nipponica*. Properties of recombinant enzymes were characterized. In addition, bromination activity to a proposed natural precursor of laurencin was observed. The results suggest that VBPOs are pivotal candidates of biosynthetic enzymes that catalyze the bromination of secondary metabolites in*Laurencia* spp.

Chlorophyll and Carotenoid Prospects on Food, Health and Energy

Heriyanto and Leenawaty Limantara*

*Ma Chung Research center for Photosynthetic Pigments
Universitas Ma Chung
Villa Puncak Tidar N-1 Malang, East Java, Indonesia,
*email: leenawaty.limantara@machung.ac.id

Abstract

Indonesia is rich in biodiversity with the abundant natural resources. Most of Indonesia natural resources, i.e. plant, algae, microorganism, have potency as pigment sources. Chlorophyll (Chl) and carotenoid (Crt) are the main pigments in photosynthesis process and have been known to be responsible for health benefits as antioxidant, pro-vitamin A, anti-cancer, anti obesity, etc., and also natural colorants. Basic experiments of Chl and Crt, that is extraction and purification of pigment, content of pigment, composition of pigment, chemical and physical properties of pigment, have been extensively investigated to get fruitful experimental results for the prospect of these pigments. Three prospects of Chl and Crt are pigment on food, health, and energy. The prospect of pigment on food applies Chl and Crt as natural food colorants which have additional health benefits. Pigment on health utilizes Chl and Crt for better health and improved quality of life such as Vitamin A deficiency (VAD), and iron deficiency anemia (IDA). Another subject of this prospect is invention and improvement of stable Chl-based photosensitizer in photodynamic therapy for cancer and tumor. The last prospect of Chl and Crt is for energy. Optimization of design principle of natural systems in light harvesting, energy transfer and energy conversion could be used for the next generation of solar cells.

Keywords: chlorophyll, carotenoid, antioxidant, pro Vitamin A, anti cancer, anti obesity, photosensitizer, solar cell

Introduction

Photosynthesis is a fundamental process for living organisms. Chlorophyll (Chl) and carotenoid (Crt) are photosynthetic pigments which play important roles in this process (Telfer *et. al.,* 2008; Berera *et. al.,* 2009). The former pigment performs a light harvesting (LH) role and serves to funnel absorbed solar radiation to reaction center where photochemical reaction occurs. The latter is also involved in LH and plays photo-protective roles by quenching Chl triplet state and scavenging singlet oxygen. These pigments are naturally found in photosynthetic organisms, for example plant, bacteria, and algae which abundantly occur in Indonesia natural resources. In addition, Crt is present in human and animal as well (Gross, 1991). Britton *et. al.,* (2004) listed more than 700 known naturally occurring Crts that have been isolated from natural resources. The major Crts, that is beta-carotene (β-carotene), fucoxanthin, bixin, crocin, safranal, lycopene, lutein, zeaxanthin and asthaxanthin, are well known as provitamin A, food colorant, antioxidant, etc.

The functions and abundance of these pigments in nature attract us to perform comprehensive experiments from basic to applied fields. Experiments in the basic level have been conducted to gain fruitful information for the next steps of experiments. Limantara *et. al.*, (1994; 1996) applied a series of isotopes-labelled bacteriochlorophyll (BChl; Chl form in photosynthetic bacteria) to determine the excited states of BChl. The invention of BChl excited states has an important contribution to the usage of BChl and its derivatives as photosensitizers in photodynamic therapy (PDT) for cancer and tumor treatments (Limantara *et. al.*, 2006). Other basic experiments on chemical and physical properties of BChl and its derivatives, such as: photostability (Limantara *et. al.*, 2006; Susanti *et. al.*, 2007; Limantara and Heriyanto, 2010b), aggregation, coordination state, and pH effect (Limantara *et. al.*, 1997; *Koyama et. al.*, 2006; Santosa *et. al.*, 2008; Heriyanto *et. al.*, 2009) were carried out to determine the best photosensitizer.

Material and Method

Photosynthetic organisms, i.e. indigenous plants, macroalgae, microalgae, photosynthetic bacteria, were used as samples for Chl and Crt experiments. The screening of potential Indonesian natural resources as pigment sources was conducted based on the pigment content, tha is relatively Chl content of leaves was determined by portable chlorophyll meter (Rahayu and Limantara, 2005; Heriyanto and Limantara, 2006b) and nitrogen meter (Tantono *et. al.*, 2013), in vitro Chl and Crt contents were determined from crude pigment extracts by spectrophotometry (Madalena *et. al.*, 2007) and high performance liquid chromatography (HPLC) (Limantara and Heriyanto, 2010a) methods; and pigment composition was determined by thin layer chromatography (TLC) (Heriyanto and Limantara, 2006a) and HPLC (Limantara and Heriyanto, 2010). Column chromatography and HPLC were applied for pigment purification (Sukoso *et. al.*, 2010; Pringgenies *et. al.*, 2011) then the purified pigment was identified by UV-Vis spectrophotometer, TLC, HPLC, and nuclear magnetic resonance (Limantara *et. al.*, 1995; Sukoso *et. al.*, 2010). Tests of pigment stabilities against thermal and irradiation treatments (Heriyanto and Limantara, 2010b; Wijaya *et. al.*, 2010; Prihastyanti *et. al.*, 2010) and pH values effect (Heriyanto *et. al.*, 2004; Kusmita and Limantara, 2009;) were performed for the purified pigment and crude pigment extract.

Biopigment research

Sources of major pigments have been well recognized, that is carrot (contain(s) β-carotene), tomato (lycopene), brown seaweed (fucoxanthin), photosynthetic bacteria (BChl a), leafy vegetable and *Chlorella sp*. (Chl a), saffron '*Crocus sativus*' (crocin and safranal), *Bixa orellana* (Bixin), salmon fish and *Haematococcus pluvalis* (astaxanthin). Rahayu and Limantara (2005) revealed that *katuk* (*Sauropus androgynus*) and *suji* (*Pleomele angustifolia* N.E. Brown) leaves have relatively high Chl content from several green leafy plants. Fucoxanthin is known as the main Crt in brown seaweed and *Padina australis* has the highest fucoxanthin content from 5 species of brown seaweed (Limantara and Heriyanto, 2010). Optimization of fucoxanthin extraction efficiency by several organic solvents in *P. australis* was done by Limantara and Heriyanto (2011a) and methanol was the best solvent for fucoxanthin extraction. Indrawati *et. al.*, (2010b) did a similar experiment for simultaneus BChl and Crts extraction in *Rhodopseudomonas palustris*. Some experiments on pigment composition have been conducted for brown seaweeds (Limantara and Heriyanto, 2010; Indrawati *et. al.*, 2010a), *Kappaphycus alvarezii* (de Fretes *et. al.*, 2011), leafy plant (Christanti *et. al.*, 2011), palm oil (Syahputra *et. al.*, 2008). Chl a is the dominant Chl in brown seaweeds, *K. alvarezii*, leafy plant, while fucoxanthin, zeaxanthin, lutein are their main Crts, respectively. Syahputra *et. al.*, (2008) concluded that β-carotene is the main Crt in palm oil. Lycopene, neurosporene, γ-carotene, β-carotene and phytoene are Crts of *Neurospora Intermedia* which is purified from Indonesian fermented peanut cake (Priatni *et. al.,* 2010).

Chl *a* is unstable pigment towards acid, temperature, and light (Gross, 1991). The addition of other compounds as Chl *a* protector and chemical modifications of Chl *a* could improve its stability. Kartikaningsih *et. al.,* (2010) used fucoxanthin as a photoprotector for Chl *a* against irradiation treatment. Absorption spectra of Chl *a* and fucoxanthin in acetone are shown in Figure 1a. Intensity of Qy band (at 662 nm) of Chl *a* decreased after Chl *a* solution was exposed to the light. Decreasing this intensity of Chl *a* (Figure 1b) was bigger than that of mixture of Chl *a* and fucoxanthin (Figure 1c). This result indicates the photoprotection function of Crt. Photoprotection function of β-carotene and lutein against Chl *a* was investigated by da Costa *et. al.*, (2007). Chemical modifications of Chl *a* at its central metal and peripheral chains to be chlorophylin increased its solubility in aqueous solution and its stability (Sumpana, 2013).

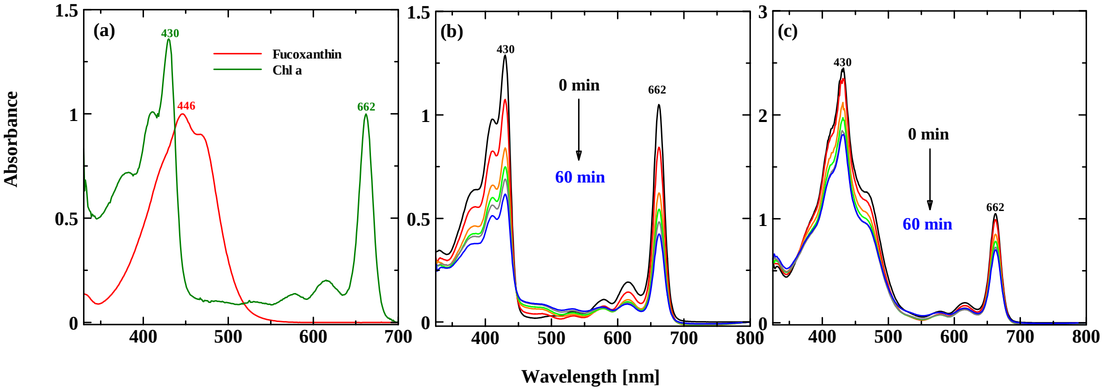

Figure 1. Absorption spectra of fucoxanthin and Chl a in acetone (a), photostability tests of Chl *a* (b), mixture of fucoxanthin and Chl *a* (1:1, mol/mol) (c) during irradiation treatment for 60 minutes.

Application of pigment on food, health and energy

Ingested Chl and Crt are directly obtained from natural food especially vegetables and fruit. In their development, these pigments are applied to food industry as natural food colorants. Chl and Crt have been proven to have health benefits as antioxidant, anti-cancer, anti-inflammation, anti-obesity, pro-vitamin A, and in age-related degenerative diseases. Therefore Chl and Crt are highly potential to be used as healthy food ingredients and functional food. In Indonesian traditional snacks, pigment extracts from *P. angustifolia* and *pandan* (*Pandanus amaryllifolius* Roxb.) leaves are commonly used for natural green colorant. Recently, Arifin (2013) made prototype of natural green food colorant powders and investigated their stabilities and pigment composition. The addition of *Chlorella pyrenoidosa* and *Monascus purpureus*, which is rich in pigments, into the tea as functional drink increased the antioxidant activity and acceptability by the panellist (Megawati *et. al.*, 2013). In addition, the occurrence of red colour in red palm oil, coming from Crts, is becoming the healthful choice for oil cooking.

Indonesia has been known as the world's largest exporter of crude palm oil (CPO) and also one of the most important exporters of seaweeds and some of decapods crustaceans. However, these natural resources have not been maximally exploited as the source of β-carotene, astaxanthin, fucoxanthin, Chl, etc., which are important for maintaining healthcare. Astaxanthin is a potential antioxidant, because of this Crt has the strongest antioxidant activity compared to other natural antioxidants, such as: vitamin E and β-carotene (Shimidzu *et. al.,* 1996 ; Bagchi, 2001). Therefore, astaxanthin is used as cosmetic ingredient due to its antioxidant and photo-protector functions (Andyka *et. al.,* 2013). Herbal medicine containing *P. australis* and *Sprirulina platensis*, which contain fucoxanthin, lutein, Chl *a* and Chl *b* as dominant pigments, showed anti-atherosclerotic (Indrawati *et. al.,* 2013). The potency and efficacy of astaxanthin as anti-cholesterol was reviewed by Wijaya *et. al.,* (2013). PDT is photo-chemotherapy combining the use of light, oxygen and photosensitizer. Recently, there are a number of efforts to invent and develop the stable Chl-based photosensitizer in PDT for cancer and tumors. Zn-pheophorbide *a* is a very promising low-cost, synthetically easily accessible, second generation photosensitizer against human cancer (Jakubowska *et. al.,* 2013).

There are increasing numbers of pigment application to energy utilization especially solar cells. Dye-sensitized solar cell (DSSC) is one technology of solar cells which mimics a basic principle of photosynthesis (Heriyanto and Limantara, 2010a). Synthetic dyes, i.e. ruthenium complexes, are commonly applied to this solar cell as sensitizers for gathering solar energy with the conversion efficiency of sunlight to electric power up to 11% (Gratzel, 2004). Besides the usage of synthetic dyes, photosynthetic pigments, that is Chl and its derivatives (Tributsch and Calvin, 1971; Wang *et. al.,* 2010), Crts (Wang *et. al.,* 2005; Yamazaki *et. al.,* 2007), have been used as sensitizers with a low cost, although their values of the conversion efficiency are lower than the use of synthetic dyes. Currently, bio-hybrid solar cells, a novel photo-nano-device, have been constructed from LH complexes of photosynthetic bacteria on metal surface. Plasmon excitation in metallic nanoparticles provide an excellent way to control the optical properties of matter and enhance the productive photochemistry of the LH complexes (Bujak *et. al.,* 2011 and 2012). Fiedor *et. al.,* (2004) and Akahane *et. al.,*. (2004) modified native LH complexes by reconstitution approach to enhance the efficiency of singlet energy transfer from Crt to BChl.

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Nanoscale Pore Space Science for Sustainable Chemistry

Katsumi Kaneko

Research Center for Exotic Nanocarbons, Nagano, 380-8553, Japan
kkaneko@shinshu-u.ac.jp

Abstract

The unique nanoscale pore structures of nanocarbon and high surface area carbon, which induce highly dense adsorbed state, are shown. The superhigh pressure-compression effect and stabilization effect of unstable phase of nanoscale pore spaces are given using the examples of 1D atomically 1D metallic sulfur chain crystals, KI nanocrystals and CH_4, respectively. The quantum fluctuation of light molecules such as H_2 and CH_4 should not be neglected in the nanoscale spaces; the quantum fluctuation induces an evident quantum molecular sieving effect on adsorption in nanoscale pores for their isotopes. The intensive confinement of ions in the nanoscale pore spaces gives rise to a partial desolvation and highly packed structure. These results can contribute to sustainable chemistry.

Keywords: nanoscale pore, metal sulfur, single wall carbon, interfacial solid, desolvation, adsorption, nanoconfinement.

All component carbon atoms of graphene, single wall carbon nanotube (SWCNT), single wall carbon nanohorn(SWCNH), and double wall carbon nanotube (DWCNT) are exposed to the interfaces. Figure 1 shows monolayers on the external and internal wall surfaces of SWCNT; all component carbon atoms can interact with molecules on the external and internal sides. Therefore, these systems are not ordinary solids, but interfacial solids. These carbons can easily vary the local structure depending on the stimuli through the morphological defects.[1] Activated carbon fiber (ACF) or carbide-derived carbon (CDC) can be also regarded as the interfacial solid, because their surface area is close to that of graphene. These materials have an intensive potential for contribution to interfacial science. At the same time, these carbons except for graphene have nanoscale pores which have the deep interaction potential well for molecules, giving rise to a highly dense adsorbed state in the pore spaces and unique functions due to molecule-molecule and molecule-pore wall collective interactions.

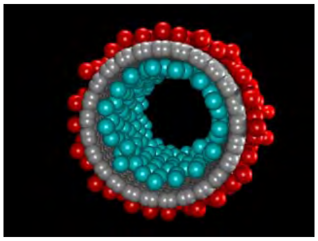

Figure 1. Monolayers on the external and internal tube wall surfaces having opposite sign of nanoscale curvature in SWCNT.

Recently we have obtained clear evidence that confinement of KI nanocrystals below 0.1 MPa induces the solid phase transition into high pressure phase, which occurs above 1.9 GPa for the bulk KI crystals; this remarkable effect is named super high pressure effect.[2] Thus, phase transition can be influenced remarkably by the nanoconfiment of substances. We measured the rotational-vibration spectra of methane in single walled nanoscale pores near the boiling temperature (111.5 K). The rotational structure almost disappears around 111 K, although the vibration spectrum of methane in the bulk phase has a clear rotational structure. The rotational structure can be observed at 140 K, showing the elevation of boiling temperature of methane adsorbed in the nanoscale tube spaces by 30 K[3]. Very recently, we obtained intensive evidence on the in-pore superhigh pressure effect of the tubular carbon spaces. It is well-known that solid sulfur consists of 8-member rings, being insulator. We introduce sulfur vapor below 0.1 MPa in the tubular spaces of SWCNT and DWCNT. High resolution transmission electron microscopic (HR-TEM) observation elucidated the presence of a complete one-dimensional sulfur chain in the tubular space. Figure 2 shows the HR-TEM images of the 1D sulfur chain in the tube spaces of DWCNT whose internal tube diameters are 0.68 and 0.60 nm. The zigzag sulfur chain and complete linear chain are observed in the internal tubes of 0.68 nm and 0.60 nm, respectively. Surprisingly we observed clear X-ray diffraction peaks corresponding to the 1D chain structures of sulfur. 4) This facts indicate that the in-pore superhigh pressure corresponds to 90 GPa at least. In case of Se, a unique helix structure is formed.5)

The quantum molecular sieving effect is a representative function of the nanoscale pore spaces. The quantum fluctuation difference between light molecules such as H_2 and D_2 is only 0.03 nm at 77 K, leading to an explicit adsorption difference of more than 5 % for H_2 and D_2.6) The clear adsorption difference of 2 % even between CD_4 and CH_4 was evidenced in the higher fractional filling for 0.7 nm slit-pores. $^{13}CH_4$ and $^{12}CH_4$ can be efficiently separable using the nanoscale pores of SWCNH at 112 K with the quantum molecular sieving.7) The EXAFS study of Rb^+ ions in the slit pores of ACF indicated partial dehydration.8) Also organic ion “solution” confined in the slit pores of ACF and CDC was studied with synchrotron X-ray diffraction analysis, providing a highly oriented molecular packing structure.9)

These carbon nanotube spaces can be electronically modified with the aid of charge-transfer interaction using adsorption of aromatic hydrocarbon molecules. The charge transfer interaction can donate charges to the nanotube walls, changing molecular adsorptivity and dispersion stability in water. Then, these electronically modified SWCNT and/or DWCNT should induce new functions for atoms, ions, and molecules.10,11)

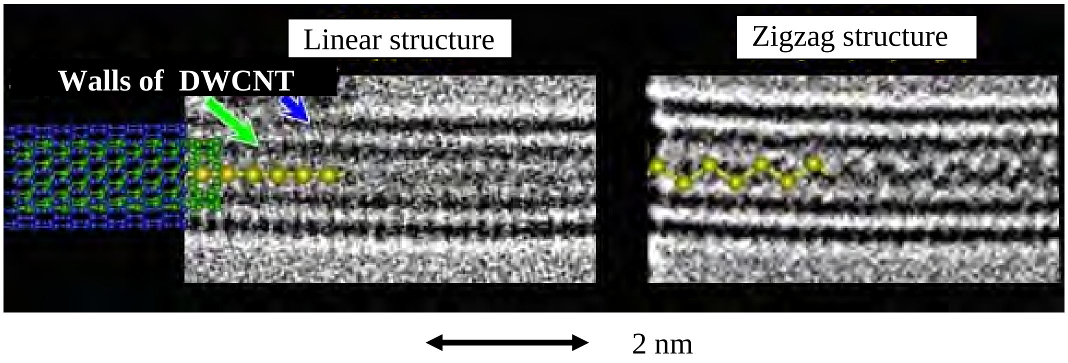

Figure 2. High resolution transmission electron microscopic images of atomically 1-dimensinal metallic sulfur chain crystals in double wall carbon nanotube.

Acknowledgements

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Al_{13} Intercalated and Pillared Montmorillontes from Unusual Antiperspirant Aqueous Solutions: Precursors for Porous Clay Heterostructures and Heptane Hydro-Isomerization Catalytic Activities

Fethi Kooli

Taibah University, Department of Chemistry, POBOX 30002,
Al-Madinah Al-Munawwarah, Saudi Arabia.
E-mail: fkooli@taibahu.edu.sa

We propose to use antiperspirant solution as pillaring agent, containing ACH and other organic modifiers. Montmorillonite clay (Mt) was directly added to an aqueous solution of the antiperspirant dissolved in a certain volume of water at 80 ^{o}C, and at different Al/clay ratios (in weight, R), resulting to Al intercalated Mt precursors (Al-MtR). The amount of Al species incorporated in Al-MtR precursors, depended on the R values, it varied between 8.70 to 19.75 % with a maximum at R value of 12. The pure pillared clays were obtained after calcinations at 500 ^{o}C for R values above 4. For further studies we have selected R value of 6 (Al-Mt6sample).

The thermal stability of Al-Mt6 precursor depended on calcination temperatures. The PXRD patterns indicated that the layered structure was stable up to 800 ^{o}C with a decrease of the 001 intensity's reflection and shrinkage of the basal spacing from 1.94 to 1.72 nm. A complete collapse of the layered structure was achieved at 900 ^{o}C., with an amorphous phase being formed (Figure 1).

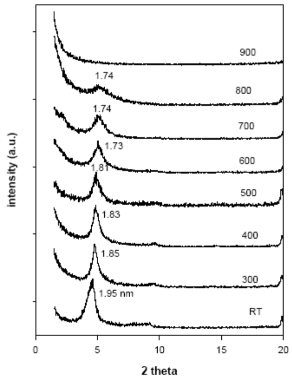


Figure 1. PXRD patterns of Al-Mt6 precursor calcined at different temperatures

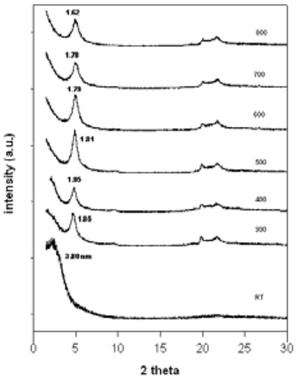


Figure 2. PXRD patterns of PAl-MtCH prepared from Al-Mt6 precursor calcined at different temperatures

^{27}Al-NMR spectral analysis confirmed the presence of Al species in Al-Mt6, with an additional band between 60 and 70 ppm, mostly assigned to the tetrahedral Al from the pillaring species. The position of the Al octahedral peak at 3 ppm shifted to 2.3 ppm. The calcination at 500 ^{o}C resulted to the increase of the tetrahedral peak intensity, with a shift of the octahedral peak at 1.4

ppm, due to the reaction of aluminum species with the Mt sheets. This conclusion was proved by the reaction of the pillared clays with docylamine (C10 amine) solution. After reaction, no expansion of the interlayer spacing was achieved, and it remained constant close to 1.76 nm. Meanwhile, further expansion of the basal spacing was achieved from 1.90 nm to 3.58 nm when the Al-Mt6precursor (no calcined) reacted with C10 amine, and indicated that the intercalated Al species in Mt-Al-6 precursor were easily exchanged with C10 amine molecules.

This finding opened new horizons and the preparation of porous clay heterostructures (PCH) materials was investigated. This method allowed us to minimize the consume of surfactants, by using one directing template (dodecylamine, C12 amine), in order to reduce the organic chemical waste, and to introduce the aluminium species in the mesostructured silica, instead of post grafting in one step reaction, during the preparation of PCH materials.

The synthesis of the PCH samples was achieved by mixing Al-Mt6 precursor or its pillared derivatives with dodecylamine, (C_{12} amine) and TEOS at molar ratios of clay/$C_{12}H_{25}NH_2$/TEOS about 1/20/150. The mixture was stirred for 4 h at room temperature. The organic molecules were removed by calcinations at 550 ^oC in air. The sample is identified as PAl-MtCH. When pillared clays were used, the calcination temperature was added in the sample identification as P-Al-MtXCH,

Figure 2 presents the PXRD of the calcined PCHs, the interlayer spacing of Al-Mt6 increased dramatically from 2.00 nm to 3.80 nm with no multiple reflections. However, only slight variation of the interlayer spacing was observed for P-Al-MtXCHs, and it varied from 1.81 to 1.60 nm. We have noticed that the interlayer spacing of the PAl-MtCH precursor depended on the length of the used amine, it shifted to higher values as the length of the aliphatic chains increased.

The presence of silica was confirmed by XRF data with an increase of its content from 56% to 79%. A significant decrease in Al_2O_3 content was detected from 22 % to 5% for PAl-MtCH. In case of PAl-MtXCH materials, we noticed slight variations in SiO_2 and Al_2O_3 contents. These data confirmed that the alumina species were difficult to be exchanged with C_{12} amine when pillared clays were used.

^{27}Al MAS NMR spectrum of PAl-MtCH material exhibited different feature than Al-Mt6, with a significant increase of resonance at 52 ppm (Al^{IV}), and two resonance peaks related for Al^{VI} at 1.5 and 0 ppm. The last two peaks could be attributed to the Al^{VI} in the clay sheets and to an extra Al^{IV} existing in different environments, for example, within the intercalated silica species. Meanwhile, P-Al-Mt500CH material exhibited a similar spectrum to that reported for the starting pillared clay (described above), indicating that the stability of the alumina species between the clay sheets.

Table 2 summarizes the textural properties of the starting pillared clays and their PCH derivatives. The PAl-MtCH material exhibited a specific surface area (SSA) of 880 m^2/g, with a total pore volume of 0.851 mL/g. This data indicated that our PAl-MtCH was mainly a mesoporous material with an average pore diameter of 3.82 nm (Table 2). The P-Al-MXCH samples exhibited SSA values lower than that of PAl-MtCH, however, higher than those of the starting pillared clays.

The total acidity of the PAl-Mt6CH (using the temperature desorption of cyclohexylamine) reached a value of 0.61 mmol/g, and higher to that of Al-Mt6 precursor and the pillared clays. Using pyridine as probe molecule, The PAl-MtXCH exhibited strong Lewis (1452 and 1617 cm^{-1}) and strong Bronsted (1540 cm^{-1} and 1640 cm^{-1}) acid sites, even at desorption temperature of 300 ^oC . While pillared clays exhibited mainly Lewis acid sites at 300 ^oC.

The hydro-isomerization reaction of heptane requires bifunctional catalysts, based on the cooperation between noble metal particles and the Bronsted acid sites. The conversion of Pt impregnated Al-Mt6 pillared clays was affected by the temperature of the catalytic reaction, and of the calcination of Al-Mt6 precursor itself. Low conversions of 2% at catalytic temperature of 250 ^oC was obtained and reached a maximum of 30 % at 350 ^oC. the calcinations of Al-Mt6 precursor at 600 ^oC and above resulted a loss of catalyst activities, up to 15 % at 350 ^oC. The selectivity to isomers and cracking products were in the range of 60% and 40 %, respectively. At catalytic temperature of 350 ^oC. The impregnated PAl-MtCH catalyst exhibited a maximum conversion of 50 % with selectivity and cracking yields of 63 and 33 %, respectively. The improvement of the conversion could be related to the nature and the strength of the acid sites in this catalyst. However, PAl-MtXCH catalysts exhibited similar conversion values compared to their starting pillared clays, calcined at temperatures higher than 400 ^oC.

The ratio of isomerization to craking (I/C) yields gave an indication on the suitability of the catalysts to the hydro- isomerization reactions. In general the I/C ratios were improved for the PAl-MtCH or PAl-MtXCH products compared to their starting pillared clays, However, the ratios were still lower than the zeolites related catalysts (in the range of 5 to 6). The stability of the catalyst was carried out at 300 ^oC, and by expanding the time on stream. The conversion and selectivity values were unchanged for a period of 12h, then a significant decrease was observed, due to the coke formation which blocked the acid sites. However, the PAl-MtCH catalyst showed a decay in catalytic activities for a period on stream of 18 h, with a mild decrease in conversion and selectivity. In case of PAl-Mt500CH, the conversion values decreased quickly for a period less than 8 h, with an improvement of the cracking products.

In conclusion, the intercalated Al_{13}-montmorillonite precursor was used to prepare pillared clays and porous clay heterostructures (PCHs). The resulting PCH from the intercalated precursor exhibited different physico-chemical properties than the pillared clays. Higher surface areas and pore volumes were obtained. The presence of aluminum in PCH material in different environments were proofed by ^{27}Al MASNMR. Strong Lewis and Bronsted acid sites were detected at temperature of 300 ^{o}C. These sites were able to hydro-isomerize heptane molecules with a conversion of 50 % and selectivity of 63 % at 350 ^{o}C. The cracking products were about 30 %.

Characterization of Surface Area, Pore Volume and Pore Size Distribution of Activated Carbon by Physisorption Methods

Allwar[1]*, Ahmad Md. Noor[2], Mohd Asri bin Mohd Nawi[2]

[1]Chemistry Department, Faculty of Mathematics and Natural Sciences, Islamic University of Indonesia, Indonesia
[2]School of Chemistry, University Sains Malaysia, Malaysia
*allwar@uii.a.cid

Abstract

In this study, oil palm shell as solid waste from palm oil mills was used for the production of activated carbon by chemical activation using 50% $ZnCl_2$ and KOH as activating agents. Determinations of pore structures were carried out by physisorption methods using nitrogen adsorption-desorption isotherm data at 77K. Pore structures of the activated carbon were investigated and tested by variety of methods to differentiate the surface area, pore volume and pore size distribution. The difference of Langmuir shapes obtained between lower relative pressure ($P/Po <0.05$) and wider relative pressure ($P/Po =0.05 – 0.35$) have encountered a problem for characterization of pore structures. The BET, Langmuir isotherm, Dubinin-Radushkevich, Dubinin-Astakhov, t-plot and BJH methods are reliable evidences for determination of pore structures. The highest surface areas of the activated carbon are 889 and 1295 m^2g^{-1} and total pore volumes are 0.35 and 0.74 m^3g^{-1} for $ZnCl_2$ and KOH, respectively. According to the results, activated carbons prepared with KOH have wider micropore size distribution.

Keywords: nitrogen adsorption-desorption isotherm; The BET; Langmuir isotherm; Dubinin-Radushkevich; Dubinin-Astakhov; t-plot; and BJH methods.

Introduction

Well-known porous material called activated carbon has a wide range of properties and physical forms making it to be prominently used in many applications. It is extensively used in variety of industrial and environmental applications (Hu, 2001, Khalili, 2000). The important properties such as surface area, pore volume and pore size distribution including surface chemistry are among of which they are strongly associated to the adsorption capacity. Large surface area and high pore volume are widely used in chemical and gas separation, medicine and catalyst while total surface area may supports the accessibility of active site relating to the catalytic activity (Budinova, 2006). Pore size distribution with the combinations of the micropores (pore diameter < 2nm) and mesopores (pore diameter 2 – 50 nm) are required to improve the transport process of particles or molecules inside porous networks and facilitate the adsorption of larger molecules (Lastoskie, 1993).

Due to its excellent characteristic, activated carbon has increasingly been used in numerous practical applications (Zhang, 2007). Consequently, the world consumption of activated carbon has steadily increased and also not been replaced until now, despite hard competitions from zeolite, polymer and other new-adsorbents. This can be seen from the constant increased in number of publications over the years. Recently, considerable efforts have also been increasingly directed to the comprehensive understanding of porous activated carbon

Activated carbon can be prepared from variety of byproduct solid wastes which are made of carbon-rich materials. However, a well-developed porous structure of the activated carbon depends not only on the type of byproduct solid wastes but also on the appropriate methods used to prepare it. Basically, there are two methods for preparation of activated carbon: physical and chemical activation processes. In physical process, the raw material such as wood, shell, etc. is carbonized or pyrolyzed in the absence of air and any chemicals. This is further followed by the activation process of the rudimentary solid chars in order to improve its porous structure (Guo, 2000). In chemical process, raw material is impregnated by activating agents such as phosphoric acid, potassium hydroxide, sodium carbonate, sodium hydroxide, potassium carbonate, phosphoric acid, zinc chloride, etc (Allwar, 2013). The impregnated sample is pyrolyzed under nitrogen, carbon dioxide or steam. Activation is a very important process in order to initiate a well-developed porosity by cleaning out of tars-clogging, and finally, enlarging the surface area of the activated carbon. Preparation of activated carbon with chemical activation is sometimes preferred due to some advantages in their properties which have been the focus of commercial interests (Jogtoyen, 1998).

Oil palm shell, byproduct solid waste from palm oil mills is usually burned off as solid fuel in the boiler system to produce low-energy resources and electricity, or it is discarded at open area around the mills either both practices are unfavorable to the environments (Alam, 2007). Previous studies had reported that palm shell (endocarp), a final waste from palm-oil processing mills is a prospective precursor for the preparation of high-quality activated carbon because of its high density, relatively high carbon and low ash contents (Jaafar M., 2001, Allwar., 2008).

The purpose of this study is to prepare activated carbon and study its characterization by physisorption methods(Storck, 1998). The methods were applied using nitrogen adsorption desorption isotherm data at 77 K(Sing, 2001c). The Langmuir isotherm method was used to evaluate surface area at lower relative pressure ($P/Po < 0.05$), while the BET (Brunauer, Emmet and Teller) method was applied to estimate surface area at higher relative pressure ($P/Po = 0.05 – 0.35$) (Sing, 2001b). The Dubinin-Radushkevich (D-R) method is the most common way to evaluate the micropore volume and micropore surface area at relative pressure below 0.03(Nguyen, 2001). Micropore volume, micropore area and external surface area were estimated using t-plot method at relative pressure in the range of 0.03-0.3(Hudec, 2002). The determination of total pore volume used at single point that is the highest relative pressure ($P/P_o = 0.99$). The micropore diameter and mesopore diameter were calculated using Dubinin-Astakhov (D-A) and Barret-Joyner and Halenda (BJH) method, respectively (Brunauer, 1938, Lowell, 1984, Barrett, 1951, Guo, 2007).

Experimental

Sample oil palm shell was used for activated carbon production. The oil palm shell was washed with water including with hot water for removing the oil content, and dried under sunlight. The oil palm shell was crushed and sieved into particles size in the range of 0.5 – 1.5 cm.

Approximately, 250 g of each sample was impregnated with 750 ml of 50% $ZnCl_2$ and KOH solution, respectively. The mixtures were refluxed at 85^oC for 24 h. Thereafter, the mixture was filtered and the residue was washed with hot distilled water for several times until pH 6-7 by adding 5 M hydrochloride acid or 5 M sodium hydroxide. The impregnated sample then was dried in oven at 110^oC for 24 h.

Preparation of activated carbon was carried out as following procedure. The impregnated sample was carbonized in two-step process. First, the impregnated sample was loaded into stainless steel reactor and placed into the graphite furnace. Purified nitrogen gas was allowed to flow into the reactor at a constant rate of 200 cm^3 min^{-1}. At the same time, the temperature of graphite furnace was gradually increased with a heating rate 5°C min^{-1} to a specific temperature. The carbonization temperature was set in the range of 500 – 800°C with a contact time 3 h. at each of process. After cooling down to room temperature, the sample was washed with hot water for several times until pH 6-7, and it then was dried in oven at 110°C.

In the second step, similar procedure to the first step was carried out, while the purified carbon dioxide gas was allowed to flow into the reactor instead of purified nitrogen gas with the contact time of 1.5 h. The activated carbon produced was kept in tight-closed bottle for further analysis.

Proximate and ultimate analysis of activated carbon

Proximate analysis of oil palm shell was calculated using the Thermogravimetric analysis (TGA) and CNH elemental analyzer. Carbonized process was applied at temperature 30 – 900°C, under purified nitrogen gas(Luangkiattikhun, 2008). The result was displayed in form of moisture, volatile matters and fixed carbon contents. Ultimate analysis was carried using Elemental analyzer to determine the hydrogen, nitrogen and carbon contents in the sample and activated carbon.

Result and Discussion

Thermal analysis

Table 1 shows the proximate and elemental analysis of the oil palm shell. The result shows that the carbon and oxygen proved having the major components in the oil palm shell while other elements such as hydrogen and nitrogen are presence in a relatively small quantity. The presences of high fix carbon (64.7%) and carbon (50.3%) content may be indicated that oil palm shell will be effective to be used for activated carbon precursor.

Table 1 Proximate and ultimate analysis of raw materials

Raw material	Proximate analysis				Ultimate analysis			
	Moisture (%)	Volatile matter (%)	Fix carbon (%)	Ash content (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)
Oil palm shell	6.7	64.7	26.4	2.2	50.3	5.6	0.3	43.8

Nitrogen adsorption-desorption isotherm

Evaluation of pores structure of the activated carbon were carried out by nitrogen adsorption desorption isotherm data at 77 K. This method is one of the most important factors for estimating the type of porous materials. Series of experiment were conducted in different activation temperatures starting from 500 to 800^{o}C. Figure 1 shows the curves of nitrogen adsorption desorption isotherms at 77 K of activated carbons prepared by chemical activation using 50% $ZnCl_2$ and KOH solution. The explanation of the curves can be separated into three parts. First, the presences of open-ended shapes at temperature 400 to 600^{o}C show a poor-developed porous structure. It may be due to the insufficient heat energy to release volatile matters and finally, some of volatile matters including tar formation may block the porosity. Therefore, the absorbed nitrogen in the adsorption process cannot be completely released from the inside pores during the desorption process (Hussein, 2001). Second, most of the nitrogen adsorption-desorption isotherm shapes at higher temperatures such as at 700^{o}C show close-ended isotherms which indicate a well-porous development. The nitrogen adsorption-desorption isotherms show a steep rise in shape at lower relative pressure ($P/Po<0.05$) and a pronounced plateau at higher relative pressure ($P/Po>0.05$). This model exhibit the Type I isotherm or Langmuir isotherm associated with micropores and relatively small external surface area(Sing, 2001a). Third, for the activated carbon prepared with KOH at 700 and 800^{o}C, the curves show close-ended isotherms at low relative pressure. The isotherm shapes also show a wide knee at low relative pressure and gradually increased to unity of relative pressures indicating a well-porous development. The shapes also show typical Type I isotherms having a small hysteresis loop observed at 800^{o}C with the filling of capillary condensation. This profile indicated the presence of small external surface which is shown by hysteresis loop at near saturation relative pressure region due to the existence of wider micropores and narrower mesopores.

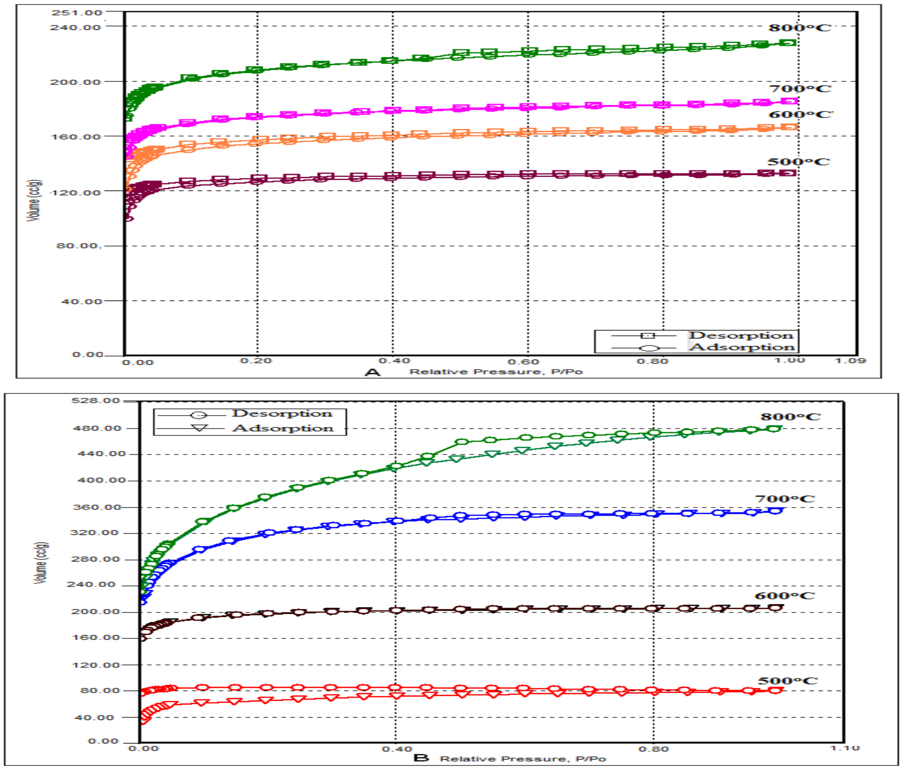


Figure 1: Nitrogen adsorption-desorption isotherms shapes of activated carbons prepared with 50% of (A) $ZnCl_2$; (B) KOH solution

Surface Area and Pore Volume

Surface area and pore volume are the most important properties that can influence the adsorption capacity of porous materials. In their applications, increasing surface area as well as pore volume is usually followed by increasing adsorption capacity. All nitrogen isotherms were observed at lower relative pressure starting from 0 to 0.05, associated with Langmuir isotherm based on the assumption that gasses form only a monolayer (**Go´mez-Serrano**, **2001)**). Consequently, the specific surface area could be better determined by the Langmuir isotherm method. Micropore volume and micropore surface area were calculated by the Dubinin-Raduskevich method based on the Type I isotherm at lower relative pressure. The values of micropores surface area are higher than the Langmuir surface area. These differences can be assumed that the Langmuir surface area were estimated from lower relative pressure (P/Po < 0.05), monolayer, while the micropores surface area can be considered as the total relative pressure consisting of monolayer and multilayer. Table 2 summarizes the textural characteristics involving the specific surface area, micropore volume, micropore surface area and total pore volume of activated carbons.

Table 2: Textural characteristics for the yield of oil palm shell activated carbon

Type of chemical	Temperature (°C)	Langmuir Surface area (m^2g^{-1})	Dubinin-Radushkevich		Total pore volume (cm^3g^{-1})
			Micropore volume (cm^3g^{-1})	Micropore surface area (m^2g^{-1})	
$ZnCl_2$	500	549	0.21	571	0.21
	600	664	0.25	696	0.26
	700	743	0.27	765	0.29
	800	889	0.32	906	0.35
KOH	500	297	0.11	345	0.12
	600	833	0.31	867	0.32

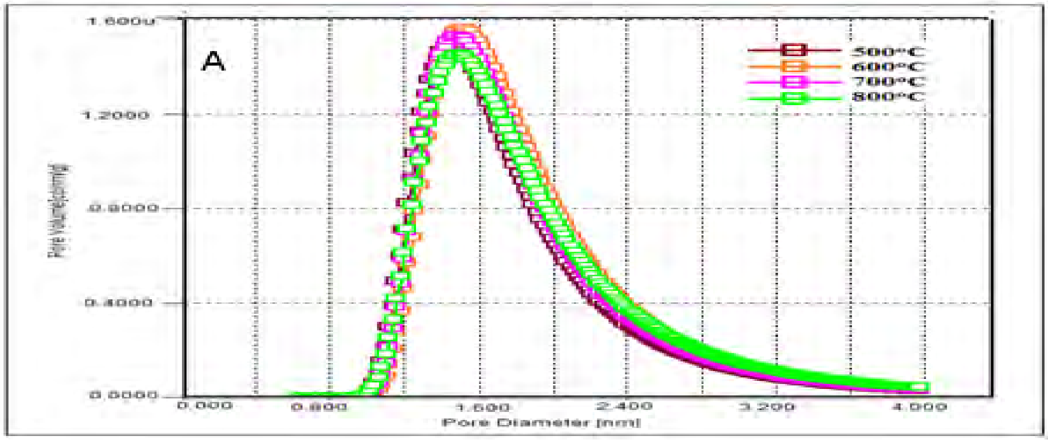
In contrast, the Langmuir isotherm shapes of the activated carbon prepared with KOH at 700 – 800°C were observed at relative pressure in the range of 0.03 – 0.3 which have the correlation coefficient 0.99. This shape is clearly associated to the BET method for determination of surface area, meanwhile the micropore volume, external surface area and micropore area were identified with t-plot methods at the thickness in the range of 0.4- 0.6. Table 3 show the textural characteristics of activated carbon prepared with KOH at activation temperature 700 and 800°C. It is clearly seen that preparation of activated carbon using KOH at higher temperature found the best result. The maximum BET surface area is 1295 m^2g^{-1} obtained at 800°C. The results suggested that the activated carbon may have variety of pores consisting of wide micropores and narrow mesopores.

Table 3: Textural characteristics for the activated carbon prepared by KOH

Type of chemical	Temp (°C)	BET surface area (m^2g^{-1})	t-plot			Total pore volume (p/po= 0.99) (cm^3g^{-1})	Mesopore Volume (cm^3g^{-1})
			Micropore volume (cm^3g^{-1})	Micropore area (m^2g^{-1})	External surface area (m^2g^{-1})		
KOH	700	1126	0.34	897	229	0.55	0.32
	800	1295	0.41	851	444	0.74	0.40

Pore Size Distribution

The measurement of pore size distribution is usually based upon the nitrogen adsorption-desorption isotherms. According to the IUPAC classification, the internal structures of porous materials can be classified into three groups: micropore (pore diameter less than 2 nm), mesopores (pore diameter in the range of 2-50 nm), and macropores (pore diameter more than 50 nm). The Dubinin-Astakhov method is widely used for determining microporous material. Previous study informed that measurement of the micropores which have lower relative pressure (P/Po< 0.05) could be carried out by the Dubinin-Astakhov (D-A) method (Gil, 2003). According to the nitrogen isotherm shapes, all activated carbons prepared with $ZnCl_2$ and KOH (exception on KOH at 700 and 800^{o}C) exhibit lower relative pressures. Figure 2 shows the Dubinin-Astakhov plots of pore size distributions of activated carbon. The maximum peaks of the pore diameter are located between 1.5 – 1.7 nm indication the presences of micropores or narrow micropores (pore diameter < 1.8 nm). This result is agreed with the nitrogen adsorption-desorption isotherm shapes which show Type I isotherm.



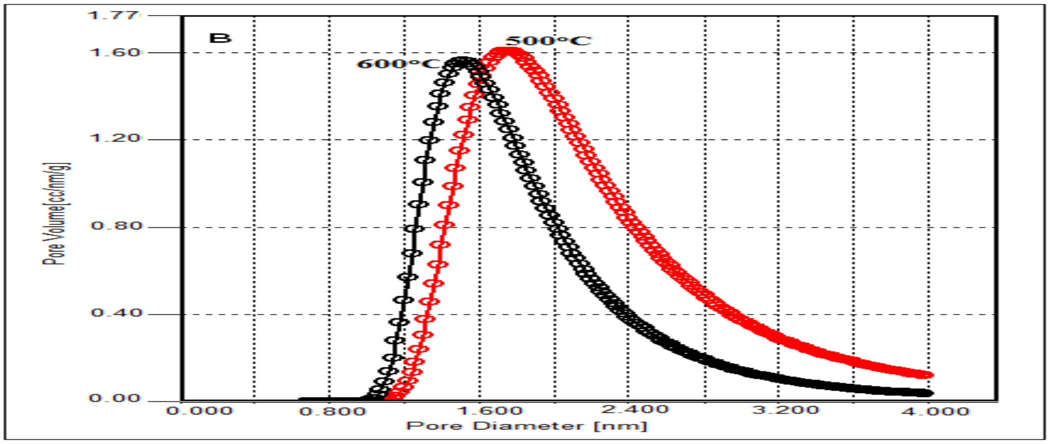


Figure 2: The Dubinin-Astakhov shapes for micropore (A) $ZnCl_2$; (B) KOH

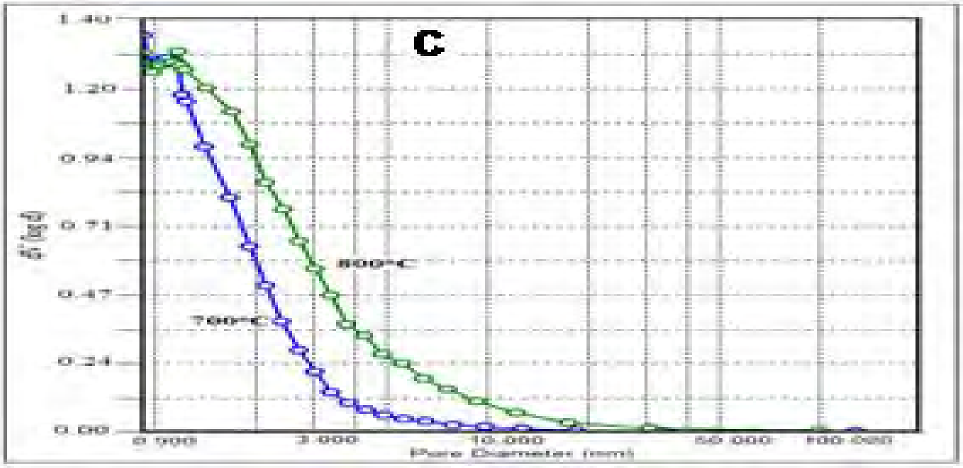


Figure 3: The BJH shape for micro- and mesopores

In contrast, the activated carbons prepared with KOH at 700 and 800°C exhibit the Type I isotherm with a small hysteresis at relative pressure higher than 0.33. It assumed that all the micropores have been filled with nitrogen as adsorbate material. Figure 3 shows the BJH shapes of the activated carbons. As seen in the figures, the shapes of pore diameters of the activated carbons are in the range from 0.9 to 50.0 nm which indicate the presence of micropores (diameter < 2 nm) and small amount of wide micropores and narrow mesopores (diameter between 1.9 – 50 nm). This result is consistent with the previous section in which the nitrogen isotherm show Type I isotherm with a small hysteresis loop.

The D-A method noticed that the quantitative micropores were estimated based on the distribution of adsorption energy (*En)* and parameter distribution (*n*) corresponding to the micropore size distribution. The values of *n* are between 1 and 4 are shown for large porous materials. The values of n > 2 are usually for porous materials with very homogeneous micropores, while the values of n < 2 are used for heterogeneous pores with wide range micropore distributions. In this study clearly shown that the values of n are 1.9 nm which exhibit the more homogeneous pores consisting of the predominantly micropore structures. In contrast, the values of n are between 1.6 and 1.7 consisting of heterogeneous pores with wide size range of micropores. Table 4 describes the distribution of pore diameter.

Table 4: The distribution of micropore diameter of the activated carbon

Type of chemical	Temperature	BJH Average Mesopore Diameter (nm)	D-A Micropore diameter (nm)
$ZnCl_2$	500	-	1.46 (n=1.9)
	600	-	1.52 (n=1.9)
	700	-	1.48 (n=1.9)
	800	-	1.50 (n=1.8)
KOH	500	-	1.76 (n=1.7)
	600	-	1.52 (n=1.9)
	700	7.56	1.70 (n=1.7)
	800	7.87	1.76 (n=1.6)

Conclusion

The model nitrogen isotherm shapes lead the different methods that are used in the determination of pore structures. The Langmuir isotherm method, D-R and D-A methods were reliable to estimate Langmuir pore structures which have lower relative pressure, while The BET, t-plot and BJH methods were applied to estimate pore structures which have wider relative pressure. The highest surface areas of the activated carbon are 889 and 1295 m^2g^{-1} and total pore volumes are 0.35 and 0.74 m^3g^{-1} for $ZnCl_2$ and KOH, respectively. The activated carbon prepared with $ZnCl_2$ clearly show micropore size distribution, while the activated carbon prepared with KOH exhibit heterogeneous-pore size distribution: wider micropores and narrow mesopores

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The Effect of Cooperative Learning on Fathanah Character and Student Achievement in Chemistry

KrisnaMerdekawati[1], TatangShaburJulianto[2]

[1] Chemistry Education Department, Islamic University of Indonesia, Jl. Kaliurang Km 14,5 Yogyakarta
[2] Chemistry Department, Islamic University of Indonesia
Email :krisna.merdekawati@uii.ac.id

Abstract

This study was aimed to investigate the effect of cooperative learning on fathanah character and student achievement in chemistry. This study used experimental method. The subjects were the students of the chemistry department of FMIPA UII that taking course of organic compounds structure elucidation in the 2012/2013 academic year. The instruments used were achievement test and fathanah questionaire. Independent sample t-test statistic tool was used to analyze the data collected. The results of the test indicated that cooperative learning have significant effect on student achievement, but do not have a significant effect on fathanah character.

Keywords: cooperative learning, fathanah character, student achievement in chemistry

Introduction

Courses of Organic compound structure elucidation explain the use of spectroscopy aspects to identify the cluster functions and determine the chemical structure of a chemical compound organic matter. Materials of the courses were on the basics instrumentation: Spectroscopy, Ultraviolet-Visible, Infrared (IR), Nuclear Magnetic Resonance (NMR), Mass Spectra (MS) data interpretation and organic compound structure elucidation technique. The learning achievement of this course is still low. In this course students are expected to be able to read, interpret, and combine the spectral data given by instrumentations. Even though, it was being an effort to make students active. The class' activity is dominated only of students who have high achievement. The activity viewed from a how far they are actively asking or answering questions. To stimulate student activity, often lecturer is trying to appoint a passive students to answer the questions.

Besides academic achievement-oriented performance, the chemistry department of the Islamic University of Indonesia also seeks to equip students with character education. One character is a college student who needs is fathanah (Arabic) character. Fathanah is a character full of intelligence, professionalism, competence. According to Adz-Dzakiey (2004), fathanah character can be developed using methods such as: 1) build effective communication with sincerity of heart, with the language and media that it is easier to understand, communicate the needed and important thing, 2) build the ability to solve problems with quick, accurate, logical, 3) awareness-raising, 4) the ability to create positive change. It was assumed that cooperative learning can give positive influence to develop fathanah character. In the cooperative learning students who have learning experience can build effective communication, look for problem solving, and build intelligence social.

According to Slavin (2000), cooperative learning not only aimed to improve learning achievement. But also to increase internal locus of control, intergroup relations, self-esteem, pro-academic norms. Cooperative Learning is done with forming of the distribution student groups. Unlike in conventional learning, which is often the working and activity groups determine only by a few students. Cooperative learning requires a responsibility of the individual to be able to achieve objectives of the group. Without the responsibility of each individual, group goals to get a higher learning achievement will not be achieved. This was because group work was considered from the performance all members of the group. To get the achievements, each member of the group must have academic attitudes. Students are required to be fathanah character in performing their tasks and studying in the group.

Many studies showed a positive impact of cooperative learning in the achievements cognitive and social skills (Dornyei, 1997; Peklaj,1999 ; Doymus, et al, 2009; Hanze, 2007; Yasemin, et al 2010). In the cooperative learning classroom, the students are expected to help each other, to discuss, argued to increase their knowledge (Dikici and Yavuzer, 2006). It is expected that cooperative learning can improve the student achievements and fathanah character.

Method

This study uses an experimental research method with a quantitative approach. This study will see how far effect of cooperative learning on the student achievement and on the fathanah character. In this research, students are divided into 2, first cooperative learning as experimental class and second group is conventional learning as control classes. Cooperative learning is used by NHT (Numbered Head Together) and STAD (Student Teams Achievement Divisions) type. The samples are students who take courses in organic compounds structure elucidation, in the academic year of 2012-2013.

The research instrument used are: 1) achievement test, 2) a questionnaire measuring of fathanah character. The research instrument was conducted in two phases, the preparation and testing phase. Achievement test instrument using descriptions queryaccording course structure elucidation of organic compounds curriculum’s. Fatahanah inquiry developed from indicators: 1) problem solving, 2) willingness to learn from others, 3) ability to resolve the problem based on knowledge, 4) self-management and group management skills. Students give answers by choosing one of the answer that has been provided. The scoring of questionnaires affective and internal locus of control used scale of 1 to 4.

In the preparation phase, instruments are designed and consulted to expert, and then tested to determine the validity and reliability of the instrument. From the test results, the validity and reliability of the instrument are high.

In the testing phase, learning session in the control classes as well as trial classes was conducted over 7 week periods. At the end of lesson, student achievement and fathanah character were measured in each class. Statistical calculation is then performed to determine whether there is a difference of the two classes. Significance level (alpha level) used in the study was 0.05. All statistical analysis was carried out by SPSS 15 software.

This method begins with cooperative learning groups based on the distribution of heterogeneous academic ability in each group. Each class was conducted with cooperative learning approach NHT and STAD.

NHT basically is a variant of Group Discussions, but there is only one of the students who represent groups but had not been told who will be grouped representatives. This ensures total involvement of all students (Slavin, 2000). At the first, students were divided into groups, which consists of 5 people. Each member of the group was given number from 1 to 5. Lecturer provides questions or cases, students think together to unite their opinion to answer the questions and make sure that all members of the group understood the answer. Lecturer called for a certain number, a student from each group which has the number to answer the question for the whole class. The score achievement of the group depends on the answer of group members who are called. Each member group to makes sure to understand matter.

STAD model consists of five main components, namely the class presentations, team, quiz, individual score progress, team recognition (Slavin, 2000). Learning started with an explanation matter by lecturers. Lecturer provides the opportunity students discussing in groups. The discussion was to discuss questions lecturers and the most important thing is to ensure each member can do a quiz with good. Afterwards, student held a quiz individually. Quiz scores obtained by the students, is the average score of the group. This forced the students to active learning and understood the material, because they have a moral responsibility to the member group.

Result

Table 1 presents t-test results, chemistry student achievement of control classes and experimental classes. Analysis of the test obtained by sig value is less than 0.05, it means that there is huge differences significantly to their scores chemistry between control classes and and experimental classes. Average score in the experimental classes was 81.83, while the control classes was 64.17.

Tabel 1. Independent Sampel Test of Learning Achievement

		Levene's test for equality of variances		t-test for equality of means						
				t	df	Sig. (2 tailed)	Mean difference	Std. Error difference	95% confidence interval of the difference	
		F	Sig.						lower	upper
Score	Equal variances assumed	3,367	0,096	2,300	10	,044	17,667	7,680	,555	34,780
	Equal variances not assumed			2,300	7,565	,052	-17,667	7,680	-,223	35,557

Table 2 presents t-test results, fathanah character score of control classes and and experimental classes. The results of analysis obtained by sig value is more than 0.05, it means there is no difference significantly in the score fathanah character between control classes and trial classes. Average scores in the trial classes were23.17 while control classes 23.00.

Tabel 2. Independent Sampel Test of Fathanah

		Levene's test for equality of variances		t-test for equality of means						
		F	Sig.	t	df	Sig. (2 tailed)	Mean difference	Std. Error difference	95% confidence interval of the difference	
									lower	upper
score	Equal variances assumed	1,453	,256	,108	10	,916	,167	1,537	-3,257	3,590
	Equal variances not assumed			,108	6,253	,917	,167	1,537	-3,557	3,890

Discussion

Generally this study provides good results. The experimental classes occurred equity values and increase the study achievements in courses of organic compound structure elucidation. In control classes, only 50% of the participating students who can gain score over 70. While for the experimental classes 100% of the participants obtained the ≥70. This shows that cooperative learning methods in courses of organic compound structure elucidation have a significant influence

Cooperative learning is not onlystudent achievement oriented, but also develop students' social skills. Cooperative learning developed to reach at least three important learning goals, namely: 1) learning academies, this model excels in helping to understand the difficult concepts, 2) acceptance of individual differences, cooperative learning, provides an opportunity for students from various backgrounds and conditions for working together, learn to respect for each other, 3) development of social skills.

The student achievement with cooperative learning is higher than conventional learning. In cooperative learning, students are more active in the group and individual's scores depend on group achievement. So, each student has a responsibility of the individual. Students who are good should be willing to help students who are less intelligent, in order to achieve a high score group.

From the measurement fathanah character score, in general, the impact of cooperative learning are not significant. Cooperative learning which was given only 7 times is not enough to change the behavior and experience of the students. Individual factors are an important role. When students study in groups, they need personal adaptation to make group working effective . According to Slavin (2000), the effects of cooperative learning not always give a good result. But also, from many study shows that a condition in the cooperative learning is fulfilled, positive influence from the study cooperative achievement.

Conclusion

Based on the analysis and discussion, it can be concluded that cooperative learning have a significant effect on student achievement, but do not have a significant effect on fathanah character.

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