CHEMICAL ENGINEERING TRANSACTIONS
VOL. 56, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim

ISBN 978-88-95608-47-1; **ISSN** 2283-9216
DOI: 10.3303/CET1756082

Effect of Zeolite 4A to Marine Microalgae Culture

Afifi Zainal*, Liyana Yahya, Muhammad N. Chik, Nur K. Hussien, Mohd H. Boosroh

Renewable Energy & Green Technology Unit, TNB Research Sdn. Bhd, No. 1, Lorong Ayer Itam, Kawasan Institusi Penyelidikan Bangi, 43000 Kajang, MALAYSIA
afifi.zainal@tnbr.com.my

As a photosynthetic organism, microalgae curbs carbon dioxide (CO_2) emission via carbon up-take either in active or passive transport trough it cell wall. Nonetheless, the bottleneck factor of CO_2 fixation trough microalgae is due to CO_2 dissolution in water. Apart from the dissolution of CO_2 from air into water is too slow to replace the assimilated CO_2 by microalgae, the solubility of CO_2 in water decreases with increasing of salinity. Hence this paper describes the initiative using nanomaterial to increase the dissolution of CO_2 in marine microalgae culture. Marine microalgae culture has been inoculated in 10 liter photobioreactor (PBR). The ambient temperature has been set at 25 °C and in 12 h / 12 h dark-light photoperiod. 10 g of zeolites 4a as nanomaterial has been used to increase the dissolution of CO_2 in the saline cultured solution. Through this study, growth rate for culture added with zeolite was μ_{Z4A} was 0.35 O.D.day^{-1}, and cell doubling time $T_{d\text{-}Z4A}$ was 1.96 day. In contrast the control culture growth rate $\mu_{control}$ was 0.22 O.D.day^{-1}, and for cell doubling times $T_{d\text{-}control}$ it takes 3.15 day. The highest concentration of inorganic carbon in solution in microalgae culture with zeolite was 23.3 ppm while the control culture was only 15.4 ppm. Thus proof that zeolite 4A hastens the dissolution of CO_2 in marine microalgae culture, therefore enhancing carbon capture trough biological means.

1. Introduction

Microalgae, a photosynthetic organism assemblage required light, CO_2 and nutrient to growth (Razzak, et al., 2013). Most commonly microalgae can be found water, be it fresh water, marine, or brackish. However, they can also be found in almost every other environment on earth (Lee, 2008). The algal biomass is seen as an alternative for a sustainable diversified feedstock to various industries either for energy, food, fine chemical industry (Harun et al., 2014) or agriculture and aquaculture feeds (Yaakob et al., 2014). Thus, apart from intended for harvesting its high potential biomass, it is beneficial if the mass culturing facilities to be run in parallel for mitigating carbon emission. Microalgae culturing as the instrument for mitigating anthropogenic carbon dioxide (CO_2) has been well received among researcher, furthermore this endeavour envisage a new pathways for microalgae biomass valorisation (Van Den Hende et al., 2012). Recent findings from National Oceanic and Atmospheric Administration (NOAA) shows that on year 2015, CO_2 concentration in the atmosphere has already hit the records, achieving beyond 400 ppm (Dlugokencky and Tans, 2015). In Malaysia land transport combine with CO_2 extensive industries such as oil & gas, palm oil, energy sectors are expected to contribute 86 % of total CO_2 emission in 2020 (Harris, 2012). These CO_2 extensive industries generated about 5 – 20 % of CO_2 from its flue gas thus offer better mitigation potential, with commensurate increase in algal biomass production (Brennan and Owende, 2013). Hence, by implementing microalgae biotechnology for capturing and utilized inorganic carbon waste from industrial flue gas, high yield and valuable algal biomass can be produced.

1.1 Phycoremediation for carbon capture technology

Phycoremediation, a process whereby microalgae being used for biotreatment either for waste water treatment especially on nutrient removal process (Olguin, 2003), domestic sewerage, (Rawat et al., 2010), industrial effluent (Zainal et al., 2012) or to be used as parts of carbon captures for industrial flue gas treatment (Yen et al., 2015). Though phycoremediation for nutrient and organic removal has been well received among researcher (Colla et al., 2010; Rao et al., 2011), more research development is needed in area of carbon capture through microalgae. One of the bottle neck issues in carbon capture through microalgae is due to slow dissolution of

Please cite this article as: Zainal A., Yahya L., Chik M.N., Hussien N.K., Boosroh M.H., 2017, Effect of zeolite 4a to marine microalgae culture, Chemical Engineering Transactions, 56, 487-492 DOI:10.3303/CET1756082

CO_2. When CO_2 dissolves in an aqueous medium, it reacts through a set of chemical equilibriums which mainly consist of species of CO_2, carbonate, bicarbonate and carbonic acid. (Van Den Hende et al., 2012). Upon achieving equilibrium, the hydration process of CO_2 in the water took longer time. Consequently, the available dissolve inorganic carbon from CO_2 gas was too slow to be ready to replace the assimilated carbon by microalgae. Therefore this situation leads to some CO_2 freely escape to the atmosphere during the cultivation process. In addition, the solubility of CO_2 in water decreases with increasing of salinity, thus less CO_2 retained in the solution cultured with marine microalgae (Markou et al., 2014).

1.2 The way forward

In carbon capture technology, incorporating nanomaterial and zeolite in the membrane layer matrix as parts of separation process has gained much attention such as in inorganic microporous membrane (Li et al., 2015), MFI membrane (Sjöberg et al., 2015), modified nanoporous silica (González-barriuso et al., 2016) and novel porous solid (Puccini et al., 2016). Although research development on phycoremediation incorporating zeolite and nanomaterial with microalgae culture is still new, there is an attempt of using zeolite as nutrient removal in microalgae culturing. Study reveal that zeolite may influence microalgae yield in marine microalgae due to changes in culture medium (Fachini et al., 2004), whereas zeolite too has been study as parts of biofilm rotating photobioreactor for nutrient removal through phycoremediation (Young, 2011), while hydrogel has been used to immobilized microalgae for environmental application (González-delgado et al., 2016). Hence, this paper describes the preliminary study towards overcoming slow CO_2 dissolution by incorporating zeolite as catalyst as well as adsorbent in the marine microalgae culture. The aim of this article is to evaluate the potential of zeolite 4A in improving CO_2 dissolution reactivity in marine microalgae culture, therefore assisting microalgae to fixed CO_2 as well as improved its growth.

2. Materials and methodology

2.1 Microalgae strains

A consortium of native marine microalgae species were used in these experiments. The native species consists of *Chlorella sorokiniana* (NCBI KR869729), *Chlorella pyrenoidosa* (NCBI KT852374), and *Amphora sp*. The consortia was isolated from the sea water outfall at Sultan Azlan Shah Power Station, Manjung Perak at west coast of Malaysia Peninsular, 4° 9’ 31.158”S latitude and 100° 38’ 30.3396” E longitude. The initial inoculum was set at 0.4 optical density (O.D) at 560 nm absorbance. In addition TNBR medium (Yahya et al. 2015) and artificial saline water, Red Sea Salt (Houston, USA) were used as a growth solution for the microalgae.

2.2 CO_2 dissolution

The dissolution of CO_2 was determined through inorganic carbon (IC) analysis, General Electric InnovOx Analyzer (Colorado, United States). In this study nanomaterial zeolite type 4A was used to enhance CO_2 dissolution on marine microalgae culture. To verify Zeolite 4A capacity in enhancing dissolution of CO_2 in saline water, a setup of 1 L column filled with artificial saline water, Red Sea Salt (Houston, USA) was added with 10 g of zeolite 4A. The saline water solution was aerated via aeration pump and purged intermittently with CO_2 that being regulated by pH controller at pH range 6.3 – 7.0. Simultaneously, a blank setup without zeolite 4A was run as a control parameter. The IC concentration obtained versus time for both setup was then plotted in a graph.

2.3 Materials and procedures

Microalgae were cultured in 10 L laboratory photobioreactor as shown in figure 1. In this study, 10 g zeolite 4A, Sigma Aldrich (Missouri, USA) was put in a sack and affixed directly to the air sparger at the bottom of PBR column. In addition, a similar setup of marine microalgae culture without addition of zeolite 4A was run as a control medium.

The effect of zeolite 4A towards microalgae growth was observed trough optical density using HACH DR2800 Spectrometer (Colorado, USA) at 560 nm absorbance. Microalgae growth curved was plot hence, the specific growth rate μ, was calculated according to Eq. (1) where N_1 and N_2 represent the optical density at time T_1 and T_2 respectively.

$$\text{Growth rate, } \mu = \ln(N_2/N_1)/(T_2-T_1) \quad (1)$$

While the cell doubling time Td, was calculated according to Eq. (2) where μ represent specific growth rate.

$$\text{Doubling time } Td = \ln 2/\mu \quad (2)$$

The ambient temperature for the experiment was fixed at 25 ^oC (± 2 ^oC) and in 12 h / 12 h dark-light photoperiod. Culture was aerated with air and pure CO_2 (99 %) was influx intermittently and been regulate by PINPOINT pH

controller, American Marine Inc., (Ridgefield, USA) at range pH 6 to 7. The experiment was run in duplicate for a period of seven consecutive days.

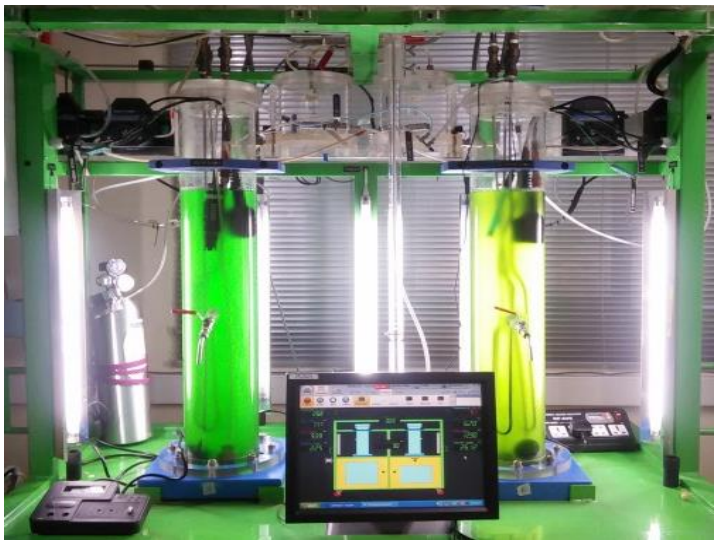

Figure 1: Two set of 10 L laboratory photobioreactor setup

3. Result and Discussion

3.1 Zeolite 4A as CO_2 dissolution enhancer

Initial study on effect of zeolite 4A to the dissolution of CO_2 was conducted on artificial seawater. CO_2 dissolution was observed through concentration level of inorganic carbon. Based from Figure 2 it is certain that zeolite 4A helps to retained CO_2 in artificial seawater water. It was observed that maximum IC concentration in blank artificial seawater solution was 27.3 ppm. In parallel the artificial seawater solution that contained zeolite 4A has higher IC concentration at 44.4 ppm.

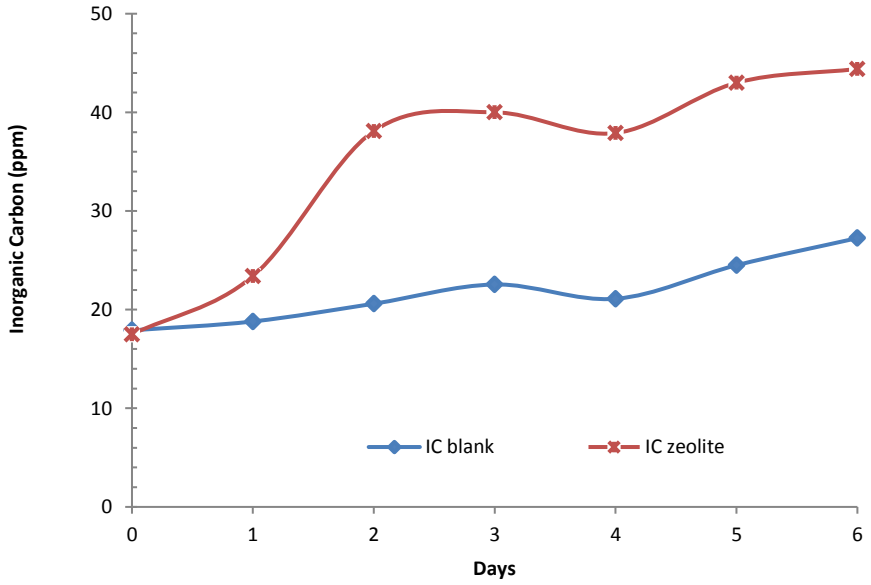

Figure 2: Concentration of inorganic carbon (IC) in artificial seawater

The result shows that zeolite 4A has hastened the time required to increase IC concentration. These can be seen in Figure 2 which illustrates that between first initial two days the IC in the saline solution added with zeolite 4A has increase remarkably compared to the blank solution. Due to zeolite 4A has approximate pore diameter

of 4 Å, it capable to adsorb CO_2 trough it molecular sieve (Hauchhum and Mahanta, 2014; Myers and Sircar, 2003). Zeolite 4A helps to prolong the retention time of CO_2 in the solution, in parallel it act as catalyst to speed up the reaction of CO_2 into form of ion (Myers and Sircar, 2003). As such Zeolite 4A accelerate CO_2 dissolution process and resulted more dissolve inorganic carbon available in the saline solution thus less CO_2 gas escape to the atmosphere.

3.2 Zeolite 4A effect on algae growth and inorganic carbon in microalgae culture

In Figure 3 it shows that microalgae thrive better with addition of zeolite 4A. The algae growth was observed through light absorbance at 560 nm optical density whereas the CO_2 dissolution was observed through inorganic carbon. After one week of culturing and aerated with pure CO_2 and air, the optical density for microalgae algae culture added with zeolite has increase from 0.4 OD to 0.915 OD, while the maximum OD for control culture only achieved 0.533 OD. Based from Eq(1) and Eq(2), growth rate for culture added with zeolite was $\mu_{z(day1-2)}$ was 0.35 O.D / d, and cell doubling time T_{dz} was 1.96 day. In contrast the control culture growth rate $\mu_{c(day5-6)}$ was 0.22 O.D / d, and for cell doubling times T_{dc} it takes 3.15 day.

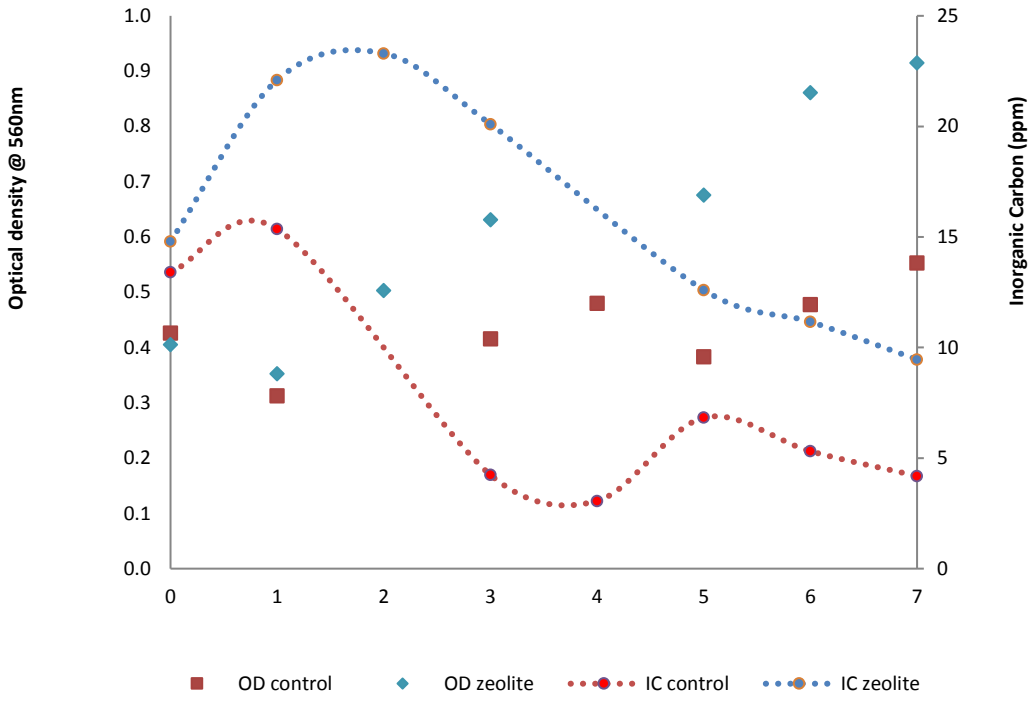

Figure 3: Zeolite 4A effect towards optical density and Inorganic carbon

From Figure 3 it can be seen after two days of culturing, it shows that there's step increase of IC in microalgae culture added with zeolite 4A with concentration of 23.3 ppm before it starts to gradually decreased. This can be understood as in the initial stage of microalgae culturing, the concentration of microalgae cell is lesser, as such amount of CO_2 added in the PBR supersede the CO_2 uptakes by the microalgae. However when algae starts to grow and the concentration of microalgae cell gets higher, the IC concentration shows a decreasing trend as capacity of CO_2 uptake from microalgae cell gets higher (Lam, et al., 2012). Meanwhile, though the control experiment gave nearly similar trend of IC in the initial stage, the magnitude of IC concentration in the microalgae culture is lesser due to more low mass transfer rates of CO_2 to the water cause CO_2 escape to the air (Pires, et al., 2012) thus leads to low performance in algae growth. This can be co-relating with low OD, which indicates low microalgae growth when compared to the culture added with zeolite 4A.

4. Conclusions

Throughout this study, the addition of nanomaterial Zeolite 4A helps to increase dissolves CO_2 in terms of available inorganic carbon in microalgae culture. Addition of zeolite in the culture has assist the reaction process for CO_2 gas dissociates to the form of ion, thus stay longer in the microalgae culture. Furthermore through this

study zeolite 4A shows no adverse effect to microalgae growth and in parallel it shows that better microalgae growth with addition of zeolite 4A compared to the control experiment. This phenomenon indicates that limitation issue of available dissolve CO_2 in microalgae culture that hinder the growth performance of microalgae are now able to be unlocked with the addition of nanomaterial, Zeolite 4A. This finding has leads to an improvised culturing method in utilizing algal biotechnology as instrument for CO_2 capture and utilization. Thorough research should be conduct in future, especially in the area zeolite selectivity that performs better in the sorption of CO_2 as well as able to synergized algae growth.

Acknowledgments

The authors would like to thank TNB Research Technical Board Committee for approving a seeding fund no. TNBR / SF0180/2015 in supporting the research on carbon capture, utilization and storage using biological approach.

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