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Mechanistic kinetic models describing impact of early attachment between *Chlorella vulgaris* and polyurethane foam material in fluidized bed bioreactor on lipid for biodiesel production

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ABSTRACT

The fundamental mechanism of early attachment between *Chlorella vulgaris* microalgae cells and polyurethane foam support material was unveiled prior to the kinetic study and optimization of operational bed packing volume in fluidized bed bioreactor. All aiming to enhance the lipid accumulation for sustainable biodiesel production. The two-step early attachment mechanism was found starting with the short-range Lewis acid-base interaction before the cells migrating toward the surface of support material induced by the electrostatic attractive force. This mechanism was mainly propelled by the chemisorption stemming from the interactions of cell-to-cell repulsion and cell-to-support material attraction. The electrostatic attractive interaction transpired on the surface of support material was also maneuvering the kinetics of formation of early attachment as reflected by the zeta potential trend via the sequence of pH 9 < pH 7 < pH 5 > pH 3. The rapid early attachment formation in pH 5 culture medium in fluidized bed bioreactor had led to the highest weight of attached growth microalgae biomass attainability as opposed to the other pH mediums. By exploiting the pH 5 culture medium, the maximum yields of microalgae biomass, lipid and later biodiesel were harvested from the bioreactor packed with 6% (v/v) of polyurethane foam support material, confirming optimum packing volume. These yields were initially observed increasing with the increase of packing volume due to the increasing surface area of support material; and unfortunately, decreasing after 6% (v/v) of packing volume due to the congestion factor.

1. Introduction

It is widely recognized that microalgae biomasses emerge to be the next generation feedstock for biofuel productions in order to resolve setbacks associated to the limited biofuels supplies in satisfying the global demands. Liu et al. [1] had also supported the possibility of microalgae biomass feedstock to significantly substitute the petroleum-based fuels in the near future. However, owing to the very dilute microalgae biomass concentration at stationary growth phase, typically lesser than 0.1% solids, and the biomass has comparable density with water culture medium which resists settleability, intensive energy and extensive time are basically needed for biomass harvesting [2,3]. The harvesting processes of microalgae biomass such as mechanical, electrical, biological and chemical based approaches have contributed to very high cost associated with operations and maintenances especially for massive scale setup [4], which accounted about 20% to 30% of the total biofuel production cost [5]. Hence, to reduce the microalgae biomass harvesting cost, attached cultivation method has been investigated in the past few years in which the microalgae biomass is concentrated onto solid substrate surfaces, targeting to ease the microalgae-water separation process [6].

In general, microorganisms favor to grow on solid material surfaces

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[7]. The microbial adhesion to surfaces is intrigued by the initial attraction of cells to the surface followed by the adsorption and attachment [8]. The microbial cell surfaces are both chemically and structurally more convoluted and heterogeneous than most of the inert substratum surfaces [9] which impede the physico-chemical approach of microbial attachment interaction [10]. The physico-chemical approaches can be divided into three forms, namely, (1) thermodynamic, (2) Derjaguin, Landau, Verwey, Overbeek (DLVO) and (3) extended DLVO (XDLVO) approaches. The DLVO approach had proven merits for predicting the microbial attachments under the well-controlled environments for certain bacterial species and strains [11]. Researchers had even used the DLVO approach to model the mechanisms of adhesion of microalgae to glass and indium tin oxide [12], bacteria to quartz sediment grains [13] and disinfection of bacteria with TiO_2 [14]. However, numerous inconsistencies between the DLVO predictions and experimental evidences had questioned the reliabilities of this approach in describing the initial biofilm formations [15]. In considering other phenomena involved during the colloidal adhesion which was neglected by the DLVO approach, the XDLVO approach was later developed [16]. Hereafter, researchers had made comparison between the DLVO and XDLVO approaches to unveil better insights on describing the adhesion mechanisms in their case studies [12,17,18].

The study of various solid substrate support materials to concentrate microalgae biomass from the thermodynamic viewpoints had been recently reported by Mohd-Sahib et al. [19]. The polyurethane foam support material was found could spontaneously adsorb *Chlorella vulgaris* microalgae cells and the adsorbed cells could thereafter successfully grow until stationary growth phase. Alas, the fundamental adsorption mechanism particularly the early attachment formation between *Chlorella vulgaris* microalgae cells and polyurethane foam support material was not reported. Besides, the detailed research works unveiling the early attachment mechanism in tandem with the adsorption kinetics of microalgae cells onto the support material in fluidized bed bioreactor to produce lipid feedstock for biodiesel are still inaccessible at ease. Without considering these aspects, the application of fluidized bed bioreactor to grow attached microalgae biomass could not be optimized even though it can resolve the harvesting issue. This would certainly lead to the poor lipid yield which afflicts the production of biodiesel. In order to conceive the cells adsorption, mathematical models from the DLVO and XDLVO approaches were employed to describe the mechanism and kinetics of early attachment formation between *Chlorella vulgaris* and polyurethane foam support material in fluidized bed bioreactor. The impacts of early attachment on microalgae lipid accumulation for producing biodiesel were also optimized using fluidized bed bioreactors packed with different packing volumes of polyurethane foam support material. The biodiesel is in general consisting of fatty acid methyl esters (FAMEs) mixture which characteristically fulfills the requirements authorized by American Society for Testing and Materials (ASTM D-6751) Standard or European (EN14214) Standard [20].

2. Materials and methods

2.1. Microalgae stock culture

The *Chlorella vulgaris* was employed as a model of microalgae species in the research works reported henceforth. The seed of *Chlorella vulgaris* was initially obtained from the culture collections belong to the Centre for Biofuel and Biochemical Research, Universiti Teknologi PETRONAS. A 5-L mini-photobioreactor with a diameter of 182 mm was loaded with 10% (v/v) of *Chlorella vulgaris* seed culture and 90% (v/v) of Bold's Basal Medium [19]. The pH of culture medium was maintained at 3 throughout the inoculation period to minimalize the occurrence of culture contamination. The inoculated *Chlorella vulgaris* culture was incessantly supplied with ambient air using compressed air and illumination from cool-white fluorescent light (Philip TL-D 36W/865, light intensity of 60–70 μmol/m^2 s). The surrounding temperature was maintained between 25 °C and 28 °C until the stationary growth phase of *Chlorella vulgaris* culture was attained. The biomass of *Chlorella vulgaris* from this growth phase was subsequently used as a microalgae stock in all the investigations outline hereafter.

2.2. Energy of interaction: Derjaguin, Landau, Verwey, Overbeek (DLVO) approach

The DLVO theory was originally developed to describe the adhesion of colloidal particles to solid surfaces by considering the interaction energy between particle and surface of substrates. In the case of cell adhesion based on the DLVO approach, Bos et al. [10] construed the adhesion of microalgae onto solid substrates was an energy balance between Lifshitz-van der Waals (*LW*) and electrostatic (*EL*) forces of interacting surfaces. The *LW* force arises from the instantaneous asymmetrical distribution of electron cloud and this macroscopic-scale force is usually attractive [21]. On the other hand, the *EL* force is resulted from the double-layer interaction between two surfaces which is usually repulsive as the contact areas often carry negative charge [22–24]. The total interaction energy in a function of separation distance [$G^{TOT}(d)$] between microalgae cell and solid substrate contact surfaces is defined as follows:

$$G^{TOT}(d) = G^{LW}(d) + G^{EL}(d) \tag{1}$$

where $G^{LW}(d)$ and $G^{EL}(d)$ indicate the *LW* and *EL* interaction energies, respectively. A positive value of $G^{TOT}(d)$ signifies the repulsive interaction between microalgae cells and solid substrates, while negative value designating adhesion. The values of total interaction energy and associated separation distance determine the extent of reversibility of adhesion. The scale of interaction energy in terms of kT (in J), where k is the Boltzmann constant and T is the temperature of cell medium (in K), is generally preferred in distinguishing various interaction energies between microorganism cells and solid substrates; as 1 kT represents the thermal or Brownian motion energy of microorganisms [10,12].

The component of *LW* free energy of interaction in a function of separation distance [$G^{LW}(d)$] is defined as follows:

$$G^{LW}(d) = -\frac{A}{6}\left[\frac{a}{d} + \frac{a}{d+2a} + \ln\left(\frac{d}{d+2a}\right)\right] \tag{2}$$

where a is the equivalent radius of microalgae cells (in m) in which equals to 2.67 ± 0.33 ($\times 10^{-6}$) m for microalgae cells of *Chlorella vulgaris* [12], d is the separation distance (in m) and A is the Hamaker constant [10] calculated as follows:

$$A = -12\pi d_0^2 \Delta G_{adh}^{LW} \tag{3}$$

where d_0 is the minimum separation distance between two contact surfaces, namely, microalgae cells and solid substrates, in which equals to 1.57×10^{-10} m [10] and $\Delta {G_{adh}}^{LW}$ is the change in *LW* free energy of adhesion. The $\Delta {G_{adh}}^{LW}$ is calculated by taking into account the surface free energy components of microalgae cells, liquid medium and solid substrates as follows:

$$\Delta G_{adh}^{LW} = -2\left(\sqrt{\gamma_m^{LW}} - \sqrt{\gamma_l^{LW}}\right)\left(\sqrt{\gamma_s^{LW}} - \sqrt{\gamma_l^{LW}}\right) \tag{4}$$

where $\gamma^{LW}$is the *LW* surface free energy (in ergs/cm^2) while the subscripts m, l and s indicating microalgae cells, liquid medium and solid substrates, respectively. By using the polyurethane foam support material as solid substrates for *Chlorella vulgaris* microalgae cell adhesion, the γ^{LW} values were found to be 46.0, 21.8 and 23.0 ergs/cm^2, respectively. Detailed procedures of every γ^{LW} determination were delineated in the report published by Mohd-Sahib et al. [19]. Accordingly, the $\Delta {G_{adh}}^{LW}$ was calculated to be -5.37×10^{-4} J/m^2 and Hamaker constant was then computed and found to be 4.99×10^{-22} J, via Eqs. (4) and (3), respectively.

The component of *EL* free energy, [$G^{EL}(d)$] between microalgae cell