



Cell to substratum and cell to cell interactions of microalgae



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ABSTRACT

This paper reports the cell to substratum and cell to cell interactions of a diverse group of microalgae based on the Extended Derjaguin, Landau, Verwey, Overbeek (XDLVO) approach using the previously reported physico-chemical surface properties. The microalgae included 10 different species of green algae and diatoms from both freshwater and saltwater environments while the substrata included glass, indium-tin oxide (ITO), stainless steel, polycarbonate, polyethylene, and polystyrene. The results indicated that acid–base interactions were the dominating mechanism of interaction for microalgae. For green algae, if at least one of the interacting surfaces was hydrophobic, adhesion at primary minimum was predicted without any energy barrier. However, most diatom systems featured energy barriers for adhesion due to repulsive van der Waals interactions. The results reported in this study are expected to provide useful data and insight into the interaction mechanisms of microalgae cells with each other and with substrata for a number of practical applications including prevention of biofouling of photobioreactors and other man-made surfaces, promotion of biofilm formation in algal biofilm photobioreactors, and developing bioflocculation strategies for energy efficient harvesting of algal biomass. Particularly, *Botryococcus braunii* and *Cerithiopsis fusiformis* were identified as promising species for bioflocculation and biofilm formation in freshwater and saltwater aquatic systems, respectively. Finally, based on the observed trends in this study, use of hydrophilic algae and hydrophilic coatings over surfaces are recommended for minimizing biofouling in aquatic systems.

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1. Introduction

Microalgae are a diverse group of photosynthetic microorganisms that find numerous biotechnological applications from the production of valuable bioproducts [1,2] to removal of environmental pollutants from wastewaters [3,4]. In these applications, efficient cultivation and harvesting of microalgae has been central to achieving energetic and economic viability, both of which significantly rely on the cell to cell and cell to surface interactions.

On the cultivation side, biofouling of photobioreactor (PBR) walls lowers the system productivity by preventing effective light penetration into the suspension and by making algae attached on the walls inaccessible for harvesting [2,5]. Thus, it is desirable to prevent the biofouling of these systems. More recently, microalgae biofilm cultivation has been gaining attention as an alternative to suspended growth of microalgae for metabolite production and wastewater treatment, as large biomass concentrations can be reached with minimal energy and water consumption using these systems [6–12]. Moreover, attached algae cultivation also finds applications in photosynthetic microbial fuel cell systems

(MFCs) for bioelectricity production. In these systems, the photosynthetic microorganisms are cultivated as biofilms over the anode and electrons generated from water splitting by the photosynthetic microorganisms are harvested at electrode creating and electrical current [13,14]. Thus, in these systems promotion of algal attachment to selected substrata is desirable.

On the harvesting side, a large amount of energy is being spent for processes such as centrifugation, filtration, electrocoagulation, and flocculation using flocculating chemicals to recover algal biomass from dilute suspensions [15]. The use of these energy and chemical intensive processes is a major bottleneck for production of low value products, such as biofuels [15]. Thus, alternative methods such as bioflocculation has been receiving increased attention [16–19]. In bioflocculation, flocculation of cultivated algae is induced by the addition of other flocculating microorganisms and algal species. This method has advantages over conventional means of algae harvesting as it is energy efficient and it does not require addition of chemicals that can potentially contaminate the biomass [19].

Finally, benthic microalgae growth on manmade structures in aquatic and aerial systems is mostly considered as a nuisance [2,20–22]. For instance, algal growth over ship hulls can increase the skin friction of ships by up to 80%, decreasing fuel efficiency and increasing maintenance costs [20]. In thermal cooling systems algal

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Nomenclature

A	area, m ²
a	equivalent algal cell radius, m
d	separation distance, m
e	electron charge, 1.602×10^{-10} C
k	Boltzmann constant, 1.3807×10^{-23} J K ⁻¹
n	concentration of ions, # m ⁻³
P	perimeter, m
T	temperature, K
z	charge number of ions

Greek symbols

ϵ	permittivity of the liquid medium, F m ⁻¹
γ	surface free energy, J m ⁻²
κ^{-1}	double layer thickness, m
ν	hydration layer associated with algal cells, m
λ	correlation length, m
ψ	surface potential, V

Superscripts

AB	refers to acid–base, i.e. polar component
EL	refers to electrostatic component
LW	refers to Lifshitz–van der Waals, i.e. dispersive component
+	refers to electron acceptor parameter
–	refers to electron donor parameter

Subscripts

l	refers to liquid medium
m	refers to algae
s	refers to surface

biofouling decreases the heat transfer and increases the pumping power requirements [22]. In addition, microalgal biofilms are also undesirable in potable water storage and water pipes due to undesirable taste and odor they cause [21]. Moreover, algal biofilms can grow over building walls and monuments where they corrode metals and create an untidy look [21].

Thus, accurate knowledge of the cell to substrata and cell to cell interaction mechanisms are very important in developing energetically and economically feasible algal biomass production and harvesting technologies as well as developing coatings and mitigation strategies for protecting manmade surfaces from biofouling. Studies reported in the literature to date mostly focused on the effects of surface energy of substrata alone on the adhesion density and adhesion strength of microalgae [23–27]. Although not universal, a general trend is that higher adhesion density is observed over hydrophobic [23,24,28,29]. In our previous work we have performed an extensive experimental study quantifying and reporting a comprehensive set of physico-chemical surface properties of a wide range of fresh and saltwater microalgae, including exemplary green algae, diatoms, and cyanobacteria [30]. In an other study, we focused on the adhesion characteristics of the hydrophobic green algae *Botryococcus sudeticus* and the hydrophilic green algae *Chlorella vulgaris* over hydrophobic and hydrophilic substrata [31]. In the latter study, we first quantified the adhesion and desorption rates of these microalgae under controlled hydrodynamic shear rates using a parallel plate flow chamber and compared the experimental results to the predictions of thermodynamic, Derjaguin, Landau, Verwey, Overbeek (DLVO), and Extended Derjaguin, Landau, Verwey, Overbeek (XDLVO) approaches. The results indicated that the rate and strength of adhesion was larger for the hydrophobic green algae *B. sudeticus* and XDLVO model was the most accurate

model in explaining the observed adhesion density and adhesion strength of these microalgae [31]. To the best of our knowledge, there is no comprehensive study reporting the cell to substrata and cell to cell interactions of a diverse group of microalgae from a fundamental perspective, taking into account the physico-chemical surface properties of both the microalgae and the substrata. This study addresses this gap in the literature, by reporting a detailed modeling study on the interaction of a diverse group of microalgae with each other and with a diverse group of substrata based on the XDLVO method using the previously reported physico-chemical surface properties.

2. Analysis

In this study the 10 different microalgal species from fresh and seawater systems as well as 6 different substrata representative of glassy, metallic and polymeric surfaces were considered. Specifically, these species included the freshwater green algae *Ankistrodesmus falcatus* var. *stipitatus* (UTEX B 242), *B. braunii* (UTEX 572), *B. sudeticus* (UTEX B 2629), *C. vulgaris* (UTEX 2714), *Nannochloris oculata* (UTEX LB 1998), and *Scenedesmus dimorphus* (UTEX 1237); the saltwater green algae *Nannochloris* sp. (UTEX LB 1999); and the saltwater diatoms *Amphora coffeaeformis* (UTEX B 2036), *Cylindrotheca fusiformis* (UTEX B 2085), and *Nitzschia frustulum* (UTEX B 2042). All freshwater species were considered to be in the nutrient medium BG-11 featuring a pH of 7.42 and an ionic strength of 21 mM whereas all the saltwater species were considered to be in ASP-M medium featuring a pH of 7.53 and an ionic strength of 584 mM [30]. In this study, we used the morphological and physico-chemical surface properties of these microalgae that were experimentally quantified and reported by Ozkan and Berberoglu [30]. These included the equivalent cell radii (*a*) of these species, their surface potentials (ψ) as well as their surface free energy components, i.e., the Lifshitz–van der Waals (γ^{LW}), electron donor (γ^{-}), electron acceptor (γ^{+}) parameters based on van Oss et al.'s method [30]. These data were based on contact angles that featured standard errors less than 3.6% over at least 9 measurements and zeta potential that featured standard errors less than 3.0% over at least 25 measurements for all species. [30]. Similarly, the physico-chemical surface properties of the substrata used were compiled from the literature [31–36]. Specifically, these substrata included glass, indium-tin oxide (ITO), stainless steel (SS), acrylic or polycarbonate (PC), polystyrene (PS), and polyethylene (PE). Finally, applicability of XDLVO approach was validated experimentally by Ozkan and Berberoglu [31]. Thus, this study focuses on using the experimentally measured physico-chemical surface properties along with the XDLVO model to analyze the cell to substrata and cell to cell interactions of a diverse portfolio of microalgae.

3. Extended Derjaguin, Landau, Verwey, Overbeek (XDLVO) approach

In XDLVO approach microbial adhesion is described as a balance between van der Waals (LW), electrostatic (EL), and acid base (AB) interactions [37]. LW forces originate from instantaneous asymmetrical distribution of electrons in molecules and it is usually attractive [38]. EL interactions are the result of the Coulomb interactions between surfaces, which are usually repulsive as both the algal cell and substrata commonly carry negative charges [39]. Finally, AB forces originate from electron transfer interactions between polar components of cell and substrata surfaces. AB interactions can be attractive (hydrophobic attraction) or repulsive (hydrophilic repulsion) based on the free energy of cohesion of the interacting surfaces [40]. The total interaction energy

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