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What kind of surface is required for algal adhesion: impact of surface properties on microalgal cell–solid substrate interactions

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ABSTRACT

Microalgae cell adhesion plays an essential role in biofilm wastewater treatment, photobioreactor material selection, and surface biofouling control. The interaction energy between microalgae cells and solid substrate behind the cell adhesion phenomenon is the key to boost these issues. Surface properties, including surface potential and surface free energy components, have a significant influence on the adsorption capacity of algal cells on the substrate. According to the extended Derjaguin-Landau-Verwey-Overbeek (eDLVO) theory, the impact degree and trend of surface properties of cells and solid substrate on the total interaction energy were discussed via sensitivity analysis. The results revealed that when algae cells and solid substrate own same property charges, increasing the surface potential of solid substrate (ξ^s) or reducing the surface free energy electron donor components of solid substrate (γ_s^-) is the most effective measure to promote cell adhesion. When algae cells and solid substrate own dissimilar property charges, reducing the surface potential of the algae cells (ξ^m) or enhancing the γ_s^- is an effective way to prevent excessive algae cell adhesion. Overall, the research provides direction for the selection of surface-modified, solid substrate, and algal cells to control cell adhesion under different demands.

Keywords: microalgae cells, adhesion, surface properties, sensitivity analysis, eDLVO

NOMENCLATURE

Abbreviations	
SEF	Surface free energy

Symbols	
d	A separation distance between cells and solid substrate
d_o	The minimum separation distance between cells and solid substrate
a	Algae cell radius
λ	Correlation length of molecules in liquid medium
ε	Permittivity of media
κ	Debye constant
γ_s^{LW}	an der Waals component of abiotic SEF
γ_m^{LW}	Van der Waals component of algae cell SEF
γ_m^+	Electron-acceptor components of algae cell SEF
γ_m^-	Electron-donor components of cell SFE
γ_s^+	Electron-acceptor components of solid substrate SEF
γ_s^-	Electron-donor components of solid substrate SFE
ξ^s	Surface charges of the solid substrate
ξ^m	Surface charges of the algal cells

1. INTRODUCTION

Microalgae biomass is known as the source of third-generation renewable energy due to its high photosynthetic efficiency, abundant lipid contents, and enormous potential in wastewater treatment.[1, 2] Biofilm is very common during microalgae usage, which formed by microalgae cells immobilized on the solid substrate, including artificially cultivated biofilm and naturally formed biofilm.[3] For biofilm cultivation, the strong interaction of microalgae cells and surfaces was required at the biofilm formation.[4] However, not all biofilm is beneficial. For microalgae suspension cultivation, the excessive adhesion of microalgae cells on the transparent wall of the photobioreactor limits the light penetration into the cultivation medium, leading to a decrease in the productivity of microalgae biomass.[5] Moreover, a large amount of microalgae cells adhesion onto the wall enhance drag and are responsible for the impaired function of underwater detectors, especially optical sensors and signal collector. All in all, the above phenomena and consequences are related to the formation and control of microalgae biofilm. Thus, it is significant to explore the mechanism cells adhesion onto the solid substrate.

During the formation of microalgae biofilms, the cells first move to the solid substrate with the hydrodynamic force and then attached onto the solid substrate via interaction between algae cells and the solid substrate.[6] The force between microalgae cells and substrates are mainly dominated by Waals interaction (LW)， Lewis acid-base interaction (AB), and electrostatic interaction (EL), which are affected by surface properties of the solid substrate and algae cells, such as wettability, surface charges, and the hydrogen bonding energy.[7] Aiming to understand the interaction between algal cells and solid substrate, many effects have been made. For example, Altan Ozkan et al.[8] pointed out that hydrophobic algae have better adhesion performance on the hydrophobic surface than that of the hydrophilic surface. Zhang et al.[9] revealed that the adhesion performance of microorganisms on the substrate should increase as decreasing the surface free energy difference between cells and substrate based on the thermodynamic model. Similarly, Cui et al.[10] considered the dispersive surface energy and polar surface energy, and established a thermodynamic model for predicting surface energy and characteristics of algae cells adhesion.

Nevertheless, the thermodynamic model has limited applicability due to the strong interaction of the electrostatic interaction between the microalgae cell and the solid substrate in some systems. According to eDLVO theory, the surface properties, including surface charges and surface free energy components, firstly affect the Lifshit-van Waals interaction, Lewis acid-base interaction, and electrostatic interaction forces between the algal cells and the solid substrate, and then the total interaction energy determined by these forces would be affected.[11] However, to date, the influence degree and trend of surface property parameters that cause changes in cell adhesion have rarely been systematically discussed.

Herein, the influence of change in LW, AB, and EL component of interactions between cells and surfaces on the microalgae cell adhesion is analyzed based on the eDLVO theory. Besides, the key factors affecting the cell attachment onto surfaces were found via sensitivity under different conditions. Finally, the optimization direction for the performance improvement of microalgae cell attachment onto the solid substrate in different demands is proposed, which provides guidance for microalgae biofilm formation, substrate selection, and surface modification.

2. THEORY AND CALCULATION

2.1 The eDLVO approach of algae cells attachment onto solid substrate

The eDLVO theory could be better used for the microorganisms adhesion since interactions of AB, LW, and EL during the microorganisms attach onto the surface are considered.[12] The total interaction energy (G^T), which is used to evaluate the energy change during the process of microalgae cell adhesion onto the surface, is defined as Eq.(1)[13]:

$$G^{T}(d) = G^{LW}(d) + G^{EL}(d) + G^{AB}(d) \quad (1)$$

While a negative G^T is attraction, a positive G^T is repulsion. The G^{LW}, G^{AB}, and G^{EL} interaction force between microalgae cells and solid substrate could be calculated by Eq.(2)-(7)[13].

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

$$A = -12\pi d_0^2 \Delta G^{LW} \quad (3)$$

$$\Delta G^{\mathrm{LW}} = -2\left(\sqrt{\gamma_{\mathrm{M}}^{\mathrm{LW}}} - \sqrt{\gamma_{\mathrm{L}}^{\mathrm{LW}}}\right)\left(\sqrt{\gamma_{\mathrm{S}}^{\mathrm{LW}}} - \sqrt{\gamma_{\mathrm{L}}^{\mathrm{LW}}}\right) \quad (4)$$

$$\Delta G^{AB}(\mathrm{d}) = 2\pi a \lambda \Delta G^{AB} exp\left(\frac{\mathrm{d}_0 - \mathrm{d}}{\lambda}\right) \quad (5)$$

$$\Delta G^{\mathrm{AB}} = 2\left[\sqrt{\gamma_{\mathrm{L}}^{+}}\left(\sqrt{\gamma_{\mathrm{M}}^{-}} + \sqrt{\gamma_{\mathrm{S}}^{-}} - \sqrt{\gamma_{\mathrm{L}}^{-}}\right) + \sqrt{\gamma_{\mathrm{L}}^{-}}\left(\sqrt{\gamma_{\mathrm{M}}^{+}} + \sqrt{\gamma_{\mathrm{S}}^{+}} - \sqrt{\gamma_{\mathrm{L}}^{+}}\right) - \sqrt{\gamma_{\mathrm{M}}^{-}\gamma_{\mathrm{S}}^{+}} - \sqrt{\gamma_{\mathrm{M}}^{+}\gamma_{\mathrm{S}}^{-}}\right] \quad (6)$$

$$G^{EL}(\mathrm{d}) = \pi\varepsilon \mathrm{a}(\zeta_{\mathrm{m}}^2 + \zeta_s^2)\left[\frac{2\zeta_m\zeta_s}{\zeta_m^2 + \zeta_s^2}\ln\frac{1+\exp(-\kappa \mathrm{d})}{1-\exp(-\kappa \mathrm{d})} + \ln\{1-\exp(-2\kappa \mathrm{d})\}\right] \quad (7)$$

2.2 Classification of surface properties of algal cells and solid substrate

The range of surface properties including the surface potential of algae cells and substrate (ξ^m and ξ^s) and the surface energy components of algae cells and substrate are classified as shown in Table 1.[7, 14-16] For example, the ξ potentials of almost all algae cells and solid substrate ranged from -1 to -60 mV, whereas the modified solid substrate surfaces by positively charged coat ranged from 1 to 60 mV. Besides, the major γ^{LW} values of a solid substrate and microalgae cells ranged from 30 to 50 mJ m^{-2}. Moreover, the major electron acceptors γ$^+$ values of a solid substrate and microalgae cells ranged from 0 to 10 mJ m^{-2}, whereas that of γ$^+$ values are rarely greater than 10 mJ m^{-2}. More importantly, the electron donor γ- values of solid substrates and microalgae ells the main scope was between 1 and 50 mJ m^{-2}, whereas that of γ- values rarely lower 1 mJ m^{-2}.

Table 1. Surface properties of algal cells and solid substrate

	ξ (mV)	γ^{LW}(mJ m^{-2})	γ$^+$ (mJ m^{-2})	γ$^-$ (mJ m^{-2})
solid substrate	-1- -60 1- 60 (surface modification)	20 -30 fewer 30 -50 major	0 - 1 major 1 -10 major >10 fewer	0 - 1 fewer 1 - 50 major >50 fewer
algae cells	-1 - -60	20 - 30 fewer 30 - 50 major	0-1 major 1-10 major >10 fewer	0 -1 fewer 1 - 50 major >50 fewer

2.3 Sensitivity analysis method

Sensitivity analysis was applied to assess the impact degree and influence trend of each surface property parameter on the interaction energy. The value of the input distribution can be obtained by increasing and decreasing the input parameters by 50%. The changes in the output distributions were computed by the rate of Q changes can be determined by Eq. (8):

$$Q_{\%} = (Q_{altered} - Q_{initial}) / Q_{initial} \times 100\% \quad (8)$$

Where $Q_{initial}$ and $Q_{altered}$ represent the initial output value and the altered output value, respectively. To ensure that the results of the analysis are reasonable, the values of the surface property parameters are always within the range of Table 1.

RESULTS AND DISCUSSIONS

3.1 The effect of change in surface properties on the force component during the process of the algae cells adhesion onto solid substrates

As shown in Fig. 1, the force component during the process of the algae cells adhesion onto the solid substrate was calculated from the summary of surface properties (see Table 1) based on eDLVO theory. The interaction energy components (G^{LW}, G^{AB}, G^{EL}) is related to the separation distance between algae cells and solid substrate.[17, 18] For the electrostatic interaction (G_{EL}), the repulsion is caused by the fact that the same property charges between algae cell and solid substrate, and the attraction is attributed to the dissimilar property charges in algae cell and solid substrate. Moreover, the Lifshit-

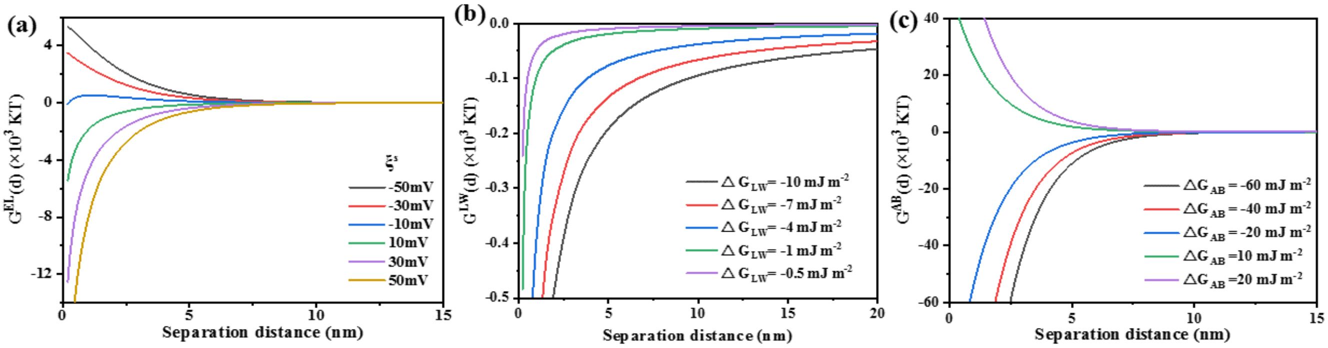

Fig.1 Interaction energy components in algae cells adhesion onto substrata (a) G^{EL}, (b) G^{LW}, and (d) G^{AB}.

van Waals interaction (LW) interaction is attractive and it reduces as nonpolar free energy change (ΔG_{LW}) decreases. Furthermore, the AB interaction appears as attraction or repulsion and it depends on the polar free energy change (ΔG_{AB}).

As shown in Fig. 2, the results clarify that the effect of changes in surface properties on interaction energy components during the process of algae cell adhesion

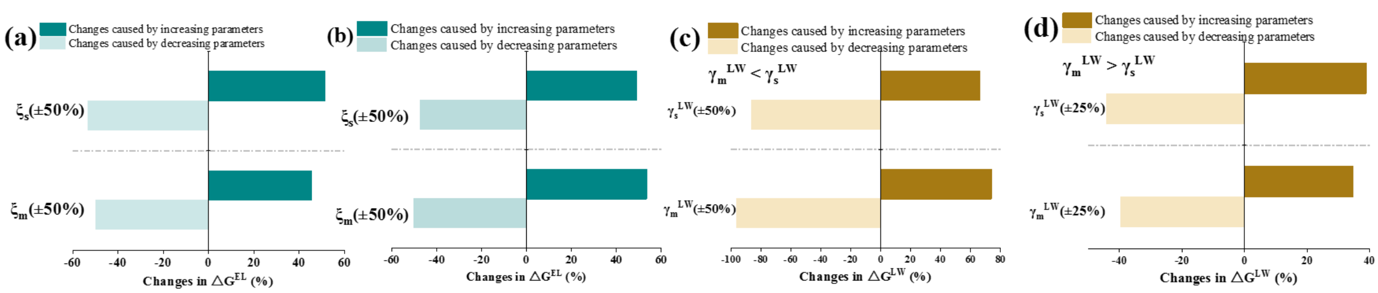

Fig.2 The effect of changes in surface properties on interaction energy components in algae cells adhesion.

onto solid substrate. When algae and solid substrate own the same property charges, changes of electrostatic interaction (G_{EL}) caused by altering the surface potential of solid substrate (ξ^s) were greater than that for the surface potential of algae cells (ξ^m). On the contrary, the effect of change in the surface potential of algae cells (ξ^m) on the electrostatic interaction (G_{EL}) was better than that for the surface potential of solid substrate (ξ^s). Besides, the smaller one of the van der Waals component of algae cell surface free energy (γ_m^{LW}) and van der Waals component of solid substrate surface free energy (γ_s^{LW}) has a major impact on nonpolar free energy change (ΔG_{LW}).

3.2 Analysis of the total interaction force and sensitivity factors during the process of the algal cells adhesion onto solid substrate

As shown in Fig. 3, as the surface potential of the solid substrate is reduced from 50 mV to -50 mV, the total interaction energy (G^T) decreased from 67 kT to -3566 kT at the 3 nm. Besides, total interaction energy dropped from 37 kT to 67 kT when the nonpolar free energy change (ΔG_{LW}) from -0.5 mJ m^{-2} to -10 mJ m^{-2} at 3 nm. More importantly, the total interaction energy changed from 55.0 mJ m^{-2} to 34.9 mJ m^{-2} with the ΔG_{LW} decrease from -0.5 mJ m^{-2} to -10 mJ m^{-2} at the 18 nm, whereas the change of electrostatic interaction has almost negligible influence on total interaction energy at the same position. Thus, change in the surface properties that determine the AB and EL interaction main have a significant effect on total interaction energy as separation distance is very close (usually less than 5 nm).[19] In the case of algal cells close to the solid substrate, the surface properties that determine the Lifshit-van Waals interaction play a major role when separation distance is 15 nm and beyond).[20]

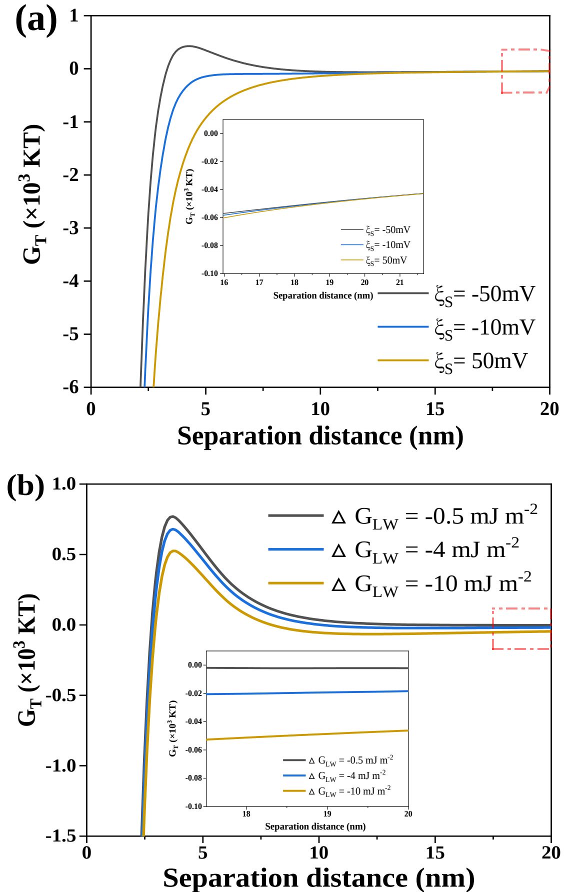

Fig. 3 The total interaction energy (G^T) during the process of algae cells adhesion onto the solid substrate (a) ξ^s, (b) ΔG_{LW}.

3.3 Changes in surface properties that determine the adhesion effect of algae cells on the substrate

As shown in Fig. 4, altering the value of surface potential (ξ^m, ξ^s) and electron donor component of surface free energy (γ_s^-, γ_m^-) were relatively sensitive compare to others surface free energy component. When algae cells and solid substrate own the same property charges, the direction of change of the surface property parameters (except for γ_s^{LW} and γ_m^{LW}) is the same as the direction of change in the total interaction energy. Notably, the second sensitive factor beyond the

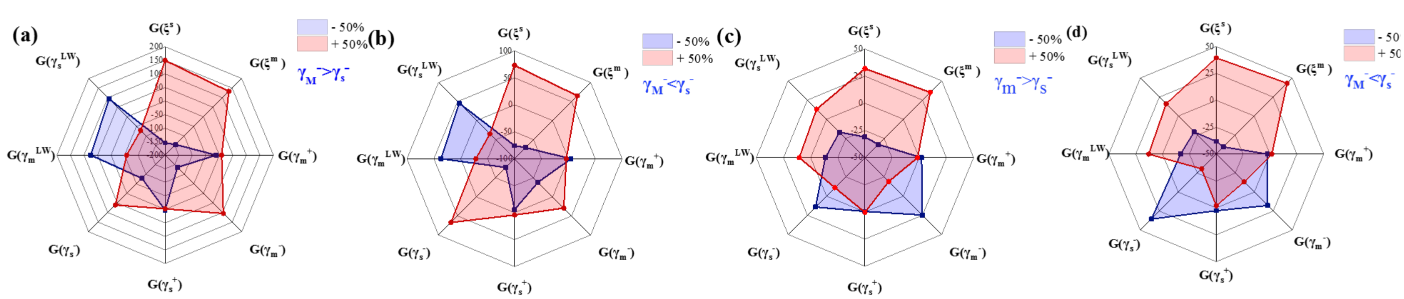

Fig. 4 The effect of change in the surface properties on total interaction energy. When the algal cell and substrata own same property charges (a) $\gamma_m^- > \gamma_s^-$, (b) $\gamma_m^- < \gamma_s^-$, and cells and substrata own dissimilar property charges: (c) $\gamma_m^- > \gamma_s^-$, (d) $\gamma_m^- < \gamma_s^-$.

surface potential is the larger one of electron-donor components of solid substrate and algae cells (γ_s^- and γ_m^-). When algae cells and solid substrate own dissimilar property charges (see Fig. 4c and d), an increase or decrease in surface potential (ξ^m and ξ^s) causes a corresponding increase or decrease in the negative value of total interaction energy. In contrast, decreasing values of electron-donor components of solid substrate (γ_s^-) or microalgae cells (γ_m^-) correspond to increasing negative values of total interaction energy. This suggests that the reduction of γ_s^- or γ_m^- favors that system towards the adhesion of algal cells onto abiotic surfaces. Altering the surface properties from these perspectives could strengthen algal cell adhesion, on the contrary, unnecessary adhesion would be weakened.

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REFERENCE

[1] Chen H, Qiu T, Rong J, He C, Wang Q. Microalgal biofuel revisited: An informatics-based analysis of developments to date and future prospects. Applied Energy 2015;155:585-98.

[2] Chiaramonti D, Prussi M, Buffi M, Rizzo AM, Pari L. Review and experimental study on pyrolysis and hydrothermal liquefaction of microalgae for biofuel production. Applied Energy 2017;185:963-72.

[3] Coh BHH, Ong HC, Cheah MY, Chen WH, Yu KL, Mahlia TMI. Sustainability of direct biodiesel synthesis from microalgae biomass: A critical review. Renewable & Sustainable Energy Reviews 2019;107:59-74.

[4] Mantzorou A, Ververidis F. Microalgal biofilms: A further step over current microalgal cultivation techniques. Sci Total Environ 2019;651:3187-201.

[5] Genin SN, Aitchison JS, Allen DG. Design of algal film photobioreactors: Material surface energy effects on algal film productivity, colonization and lipid content. Bioresource Technology 2014;155:136-43.

[6] Talluri SNL, Winter RM, Salem DR. Conditioning film formation and its influence on the initial adhesion and biofilm formation by a cyanobacterium on photobioreactor materials. Biofouling 2020;36:183-99.

[7] Yuan H, Zhang XR, Jiang ZY, Chen XH, Zhang XX. Quantitative Criterion to Predict Cell Adhesion by Identifying Dominant Interaction between Microorganisms and Abiotic Surfaces. Langmuir 2019;35:3524-33.

[8] Ozkan A, Berberoglu H. Adhesion of algal cells to surfaces. Biofouling 2013;29:469-82.

[9] Zhang X, Zhang Q, Yan T, Jiang Z, Zhang X, Zuo YY. Quantitatively Predicting Bacterial Adhesion Using Surface Free Energy Determined with a Spectrophotometric Method. Environmental Science & Technology 2015;49:6164-71.

[10] Cui Y, Yuan W. Thermodynamic modeling of algal cell–solid substrate interactions. Applied Energy 2013;112:485-92.

[11] Meireles A, Goncalves AL, Gomes IB, Simoes LC, Simoes M. Methods to study microbial adhesion on abiotic surfaces. AIMS Bioeng 2015;2:297-309.

[12] Sirmerova M, Prochazkova G, Siristova L, Kolska Z, Branyik T. Adhesion of Chlorella vulgaris to solid surfaces, as mediated by physicochemical interactions. Journal of Applied Phycology 2013;25:1687-95.

[13] Yuan H, Zhang X, Jiang Z, Chen X, Zhang X. Quantitative Criterion to Predict Cell Adhesion by Identifying Dominant Interaction between Microorganisms and Abiotic Surfaces. Langmuir 2018;35:3524-33.

[14] Ozkan A, Berberoglu H. Physico-chemical surface properties of microalgae. Colloid Surf B-Biointerfaces 2013;112:287-93.

[15] Ozkan A, Berberoglu H. Cell to substratum and cell to cell interactions of microalgae. Colloid Surf B-Biointerfaces 2013;112:302-9.

[16] Ozkan A, Berberoglu H. Adhesion of algal cells to surfaces. Biofouling 2013;29:469-82.

[17] Bos R, van der Mei HC, Busscher HJ. Physico-chemistry of initial microbial adhesive interactions - its mechanisms and methods for study. Fems Microbiology Reviews 1999;23:179-230.

[18] Vu Tuan N, Chia TWR, Turner MS, Fegan N, Dykes GA. Quantification of acid-base interactions based on contact angle measurement allows XDLVO predictions to attachment of Campylobacter jejuni but not Salmonella. Journal of Microbiological Methods 2011;86:89-96.

[19] Prochazkova G, Jirku V, Bartovska L, Branyik T. Using Physico-Chemical Approaches to Predict Microbial Adhesion. Chemicke Listy 2011;105:856-63.

[20] Yu YX, Ma LQ, Xu HX, Sun XF, Zhang ZJ, Ye GC. DLVO theoretical analyses between montmorillonite and fine coal under different pH and divalent cations. Powder Technology 2018;330:147-51.