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Improving Photobioreactor wall Using Optical Brightener: Investigating the Photostability of Coated Layer and Algal Growth

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ABSTRACT

In this work, photostability, absorption and emission intensity of coated polycarbonate (PC) sheets with optical brightener (OB) as a wavelength converter material have been investigated. In addition, this coated sheet was used as a wall for microalgae culture flask, as a small scale photobioreactor, for studying the spectral conversion of UV-A radiation to blue light region and its effect on the biomas productivity of microalga Chlorella sp. For this purpose, the PC sheets coated by different concentrations of OB dissolved in thermoplastic acrylic resin were prepared and placed between the UV-A radiation source and the culture flasks. Results showed that the photostability increases under UV-A and solar radiation by applying two coating systems. Also, higher surface concentration causes an increase in emission intensity of coated sheet. Furthermore, compared with the uncoated sheets, the sheet coated with OB layer exhibited up to 70% higher biomass production of microalga Chlorella sp. Prog. Color Colorants Coat. 13 (2020), 251-260© Institute for Color Science and Technology.

1. Introduction

The Sun, as a sustainable light source, plays an important role in many photochemical reactions such as photosynthesis, photovoltaics, photocatalysis, etc [1, 2]. The spectral power distribution of the light source is a significant parameter in these reactions. For example, although the spectrum of sun at the sea level includes wavelengths of 290–4000 nm, only radiations between 400–700 nm (photosynthetically active radiation, PAR) are suitable for photosynthesis [1]. Also, a small part of the solar radiation is used in photovoltaic devices [3]. If the wavelengths of light are consistent with the desirable absorption curve, it may be possible to achieve higher efficiency for both photosynthetic organisms and photovoltaic devices. Therefore, using spectral conversion facilitates achieving this consistency [3-6].

The spectrum modification is a well-researched topic in physics and chemistry and has been applied, for example, to infrared quantum counter or efficient lamp phosphors [7, 8]. It is also one of the third generation concepts suggested to overcome the classical efficiency limit of silicon solar cells. Many of the materials like quantum dots (QDs), organic dyes, and rare earth ions/complexes demonstrate that down-conversion or photoluminescence is well suited for spectrum modification [2, 3]. Converter materials used for this purpose must exhibit: (i) a high quantum efficiency, (ii) a wide absorption band in the region where efficiency of the cell is low, (iii) a high absorption coefficient, (iv) a narrow emission band coinciding with the peak of the maximum photovoltaic

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efficiency of the cell, (v) good separation between the absorption and emission bands in order to minimize losses due to reabsorption, and (vi) low cost and prolonged photostability [2, 3, 5, 9].

A transparent medium is needed for applying converter materials on solar cells and photobioreactors. There is a lot of research on using polymethyl methacrylate (PMMA) as a solid matrix for fluorescent dyes because this polymer provides a transparent environment for dyes and can improve their photostability [10, 11].

Various methods can be used for applying the coating on the substrate. The type of the method is determined by system parameters and can affect the final product properties. Air spraying is a common method for applying the coating in which the determination of spraying parameters such as fluid flow, fluid pressure and viscosity of the final formulation are important [12, 13].

In the present study, photodegradation, absorption and emission intensity of coating containing an optical brightener (OB) were investigated on a UV-stabilized polycarbonate (PC) sheet. In addition, the feasibility of using a polymer coating containing OB on photobioreactor wall, which can shift the UV-A wavelength to visible region, have been studied for enhancing the growth rate and productivity of the microalga.

2. Exprimental

2.1. UV-A source

A blacklight blue lamp (Philips TL 8W/08, Netherlands) was used as the UV-A source. This lamp showed a peak emission at ~370 nm with a half band width (HBW) of 20 nm (Table 1). The emission spectrum of the UV-A source is presented in Figure 1.

Table 1: Properties of blacklight blue lamp.

Property	Value
Lamp voltage (V)	56
Lamp current (A)	0.15
Lamp wattage (W)	8
UV-A radiation (W)	1.2
Tube length (mm)	288
Tube diameter (mm)	16

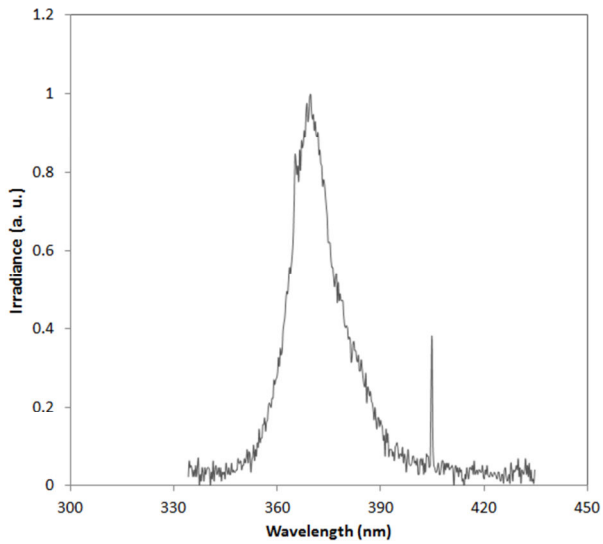

Figure 1: Emission spectrum of blacklight blue lamp.

2.2. Coating the sheet

In order to coat the sheet, UV-stabilized polycarbonate (PC) was used as the substrate and Uvitex OB (2,5-thiophenediylbis(5-tert-butyl-1,3-benzoxazole); BASF, Germany), was used as a light converter material. The OB has been used to enhance the solar cell efficiency and in polymer packing materials [3, 14]. The absorption and emission spectra of the OB is shown in Figure 2. Solutions with different concentrations of the Uvitex OB in a thermoplastic acrylic resin were prepared. Also, 0.15 wt.% surface additive BYK-306 was added to the mixture for removal all eventual. The final mixture was applied on the PC sheets using an air spray gun at 3.5 bars (Iwata W101, Japan). The coatings were then dried after a short flash-off time at 60 °C for 5 min. Absorption and emission spectra of coated layer are shown in Figure 2. Absorption of the uncoated and coated PC sheets are presented in Figure 3.

Since an increase in OB concentration resulted in higher solubility and increased the risk of quenching, coatings were prepared with the maximum concentration of the dissolved OB for achieving a clear solution [15, 16]. However, in order to evaluate the effect of higher concentrations of OB in the coating, the number of deposited layers was increased.

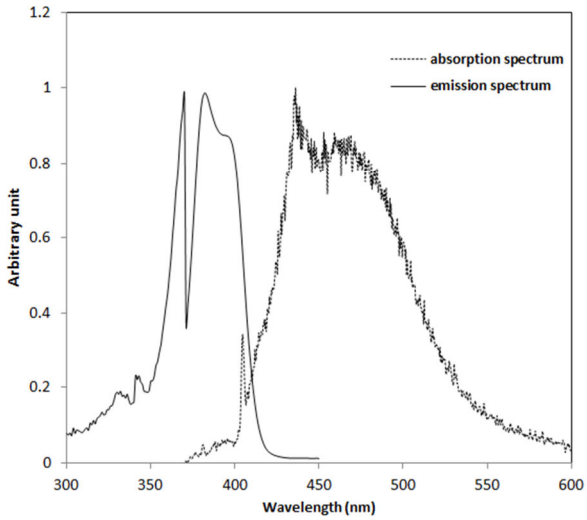

Figure 2: Absorption and emission spectrum of the coated layer.

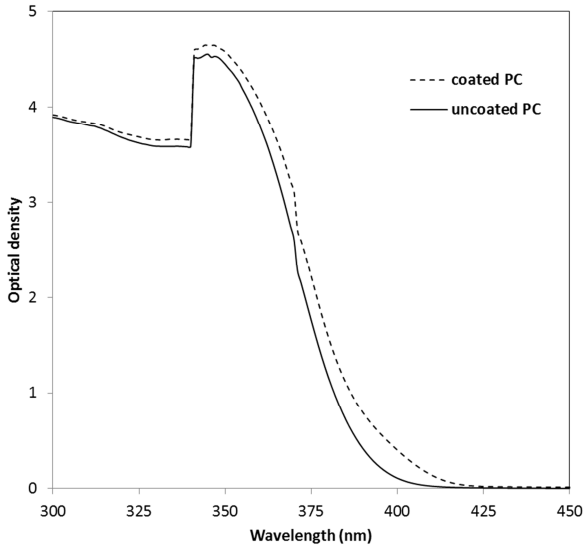

Figure 3: Absorption spectra of uncoated and a coated PC sheet.

2.3. Emission intensity and spectra

Emission spectra of the coated sheet and output spectrum of the light source were determined using a high-resolution spectrometer (HR4000 Ocean Optics, USA).Visible light and UV-A radiation intensity were measured by a light meter (TES-1330A, Taiwan) and a UV light meter (UV-340, Lutron, Taiwan), respectively.

2.4. Absorption spectra

Absorption spectra of the coated sheets and microalga culture were determined using the double beam UV/Vis spectrophotometer (V-550, JASCO, Japan) by considering air as reference. Also, absorption spectra of the coated layers on sheets for different samples were obtained by considering the uncoated PC sheet as reference.

2.5. Photodegradation

To assess the photodegradation of the samples, the coated sheets were exposed to UV-A (4 mW cm^{-2}) and solar radiation from the coated side. Photodegradation tests under UV-A and solar radiation were performed for 15 and 24 days, respectively. Figure 4 shows the sunlight intensity at 14:30 o'clock in 24 days of experiment at N 01°35' E 22°50'.

Photodegradation was characterized using Equation 1 to calculate the rate constant of degradation (K_d, s^{-1}) [17]:

$$K_d = -\frac{1}{t}\ln\left(\frac{OD_f}{OD_0}\right) \quad (1)$$

where OD_0 and OD_f are optical density of coated layer at 380 nm in the first and last day, respectively. Also, t is the time in day.

2.6. Microorganism and culture media

Microalga Chlorella sp. (PTCC 6010) from the Iranian Research Organization for Science and Technology (IROST) was used as a photosynthetic microorganism. This microorganism was pre-cultivated in Rudic's medium (pH~8) [18]. After pre-cultivation in a 250 mL flask (100 mL working volume) under cool white fluorescent light with 25 µmol photons $m^{-2}s^{-1}$, Chlorella sp. was inoculated into a 2000 mL flask (1000 mL working volume) containing 900 mL standard inorganic medium. This medium contained (in mg L^{-1}) 300 $NaNO_3$, 20 KH_2PO_4, 80 K_2HPO_4, 20 NaCl, 47 $CaCl_2$, 10 $MgSO_4{\cdot}7H_2O$, 0.1 $ZnSO_4{\cdot}7H_2O$, 1.5 $MnSO_4{\cdot}H_2O$, 0.08 $CuSO_4{\cdot}5H_2O$, 0.3 H_3BO_3, 0.3 $(NH_4){\cdot}6Mo_7O_{24}{\cdot}4H_2O$, 17 $FeCl_3{\cdot}6H_2O$, 0.2 $Co(NO_3)_2{\cdot}H_2O$, and 7.5 EDTA.

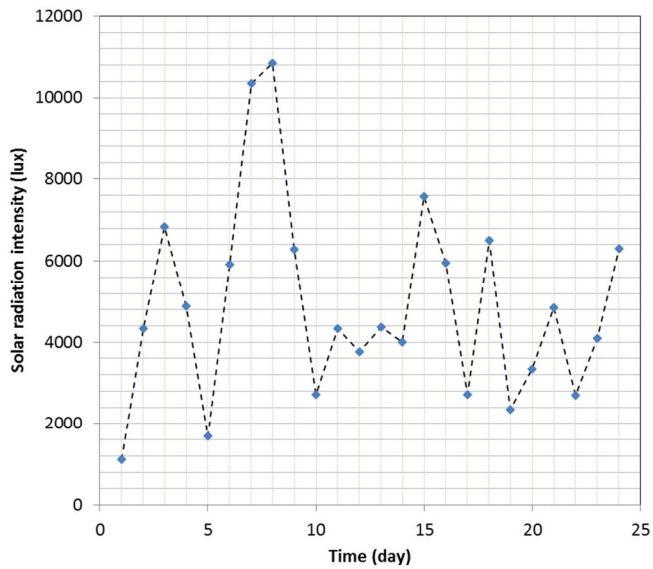

Figure 4: Sunlight intensity at 14:30 o'clock in 24 days of experiment.

After cultivation in a 1000 mL flask, 320 mL of the broth was distributed equally in 8 tissue culture flasks with a capacity of 40 mL each (JET BIOFILVent Cap, China). These flasks and a flat panel photobioreactor are geometrically similar. The reports are presented based on a group of 4 and the rest of the samples were used for accuracy reassurance. The coated and uncoated PC sheets have been put in front of each flask and other faces of the flasks were covered with aluminum foil. Here, the aluminum foil serves as a light reflector. The flasks were then placed in front of the light source. Finally, the whole setup was placed in a black enclosure at 27±2 °C for 360 h.

2.7. Algal growth parameters

Biomass concentration (X, mgL^{-1}) or dry weight of microalga was calculated using Equation (2) [19]:

$$X = 490 \times OD_{560} \quad (2)$$

where OD_{560} is the optical density of broth at 560 nm.

The specific growth rate (μ, day^{-1}) of the culture can be calculated using Equation (3):

$$\mu = \frac{\ln\left(\frac{X_t}{X_0}\right)}{t} \quad (3)$$

where X_t and X_0 are the biomass concentration at time t and the beginning of the experiment, respectively.

The biomass productivity (P, $gL^{-1}day^{-1}$) is estimated by Equation (4):

$$P = \frac{X_F - X_0}{t_F} \quad (4)$$

where X_F is the biomass concentration at the end of the experiment or time t_F.

3. Results and Discussion

3.1. Absorption and emission intensity

For investigating the effect of OB concentration on the absorption and emission of the coated layer, the OB concentration per unit area of PC ($\frac{g-OB}{cm^2}$) was calculated according to Equation (5):

$$C = M \times N \quad (5)$$

where M is the weight of OB dissolved in 30 g of resin ($\frac{g-OB}{30\ gr-resin}$) and N is the weight of deposited layer on 50 cm^2 of PC sheet ($\frac{g-resin}{50\ cm^2}$).

As presented in Table 2, the absorption of the layer in 380 nm (OD_{380}) increases linearly by using more OB in the coating (C). Indeed, the results showed that the emission intensity of the coated plates increased and this increase is significant at higher concentrations. Furthermore, an increase in the amount of M from 0.02 to 0.05 has not remarkably changed the emission intensity and absorption. In fact, the weight of deposited layer (N) decreased by increasing the M, so C remained approximately unchanged.

Since the solubility of OB in the polymer matrix is limited, samples were coated with two layers of maximum concentration (M=0.4) in order to study the effect of higher concentrations per unit area (C). The results showed that emission intensity increases by increasing the surface concentration. However, it is important to note that increasing the number of layers caused more scattering and reflection of the incident light.

Table 2: Emission and absorption data of Uvitex OB in different concentrations.

M	N	C	Emission (lux)	Absorption OD_{380}
0.02	0.060	0.0012	75	0.27
0.05	0.034	0.0017	83	0.30
0.1	0.109	0.0109	134	0.43
0.2	0.081	0.0162	190	0.96
0.4	0.056	0.0279	225	1.58
0.4[a]	0.094	0.0360	264	1.93

[a]Applied as a two-coat system.

3.2. Photodegradation

3.2.1. Under UV-A radiation

The results of the photodegradation of samples with different OB concentrations are shown in Figure 5. These samples were selected because of their high emission intensity. According to Figure 5, the increase in the exposure time caused more damage in samples and lower optical density. Constant degradation rate (K_d) for different samples under UV-A radiation is presented in Table 3. As presented in this table, samples with two coated layers (or higher N value) showed more stability. Almost all fluorophores are photobleached upon continuous illumination, especially where the light intensities are high. The photostability of a dye can be affected by its local environment [20].

The photostability of dye molecules in polymer matrix depends on a number of parameters such as chemical structure of macromolecules, polymerization initiation procedure, concentration of dye in the sample, presence of oxygen in the initial monomer composition, sample temperature and thermal treatment. Among them, the reaction of dye molecules in the excited state with free radicals and any other impurities in the sample, like hydroperoxides and dissolved oxygen, has the most important role [17, 21, 22]. In the coated samples with two layers (increase in N at constant M), the penetration length of the produced radicals and oxygen are limited and more time is required for penetration. Therefore, constant degradation rate is decreased.

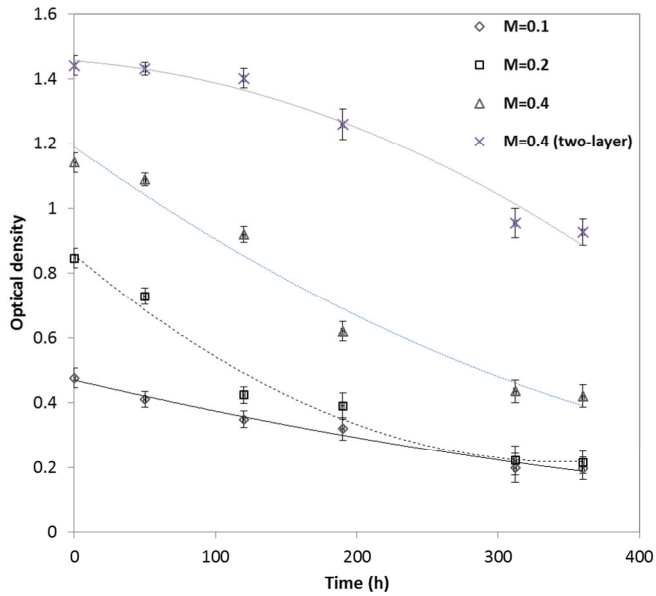

Figure 5: Photo-degradation of polymer coating with different OB concentration under UV-A radiation during 15 days.

Table 3: Constant rate of degradation under UV-A radiation.

M (*gr-OB)/(30gr-resin)*	K_d (day^{-1})
0.1	0.055
0.2	0.094
0.4	0.063
0.4*	0.0012

*Applied as a two-coat system.

3.2.2. Under solar radiation

Photodegradation of samples under solar radiation is shown in Figures 6 and 7. Also, the constant degradation rate of different samples under UV-A radiation is presented in Table 4. As presented in this table, the photostability of samples with two coated layers is obviously better than that of the samples with one layer. Because of high intensity of the solar radiation, there is no significant difference between photostability of the samples that are coated with one layer and different concentrations of the OB. However, the results for samples coated with two layers showed a decrease in constant degradation rate, especially for the samples with high concentrations. This phenomenon is related to the increase in the path length of the photons. However, application of the second layer has accompanied with the loss of surface quality and consequently rising the amount of untransformed light.

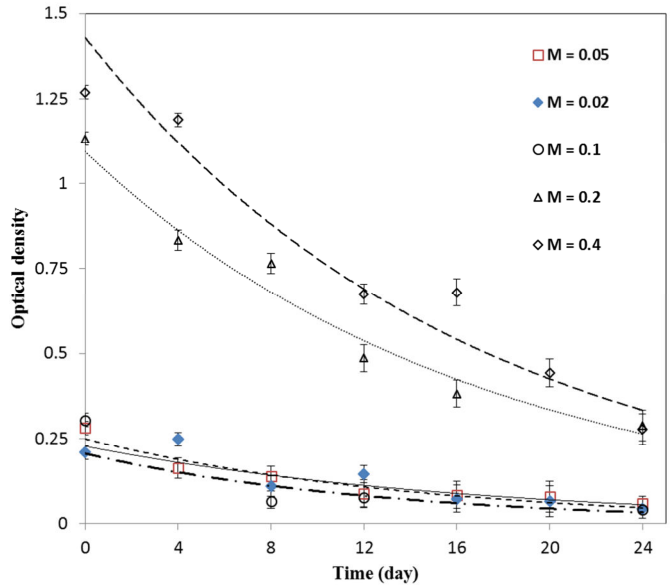

Figure 6: Photo-degradation of coated layer with different concentrations of OB under solar radiation during 24 days, as a one-coat system.

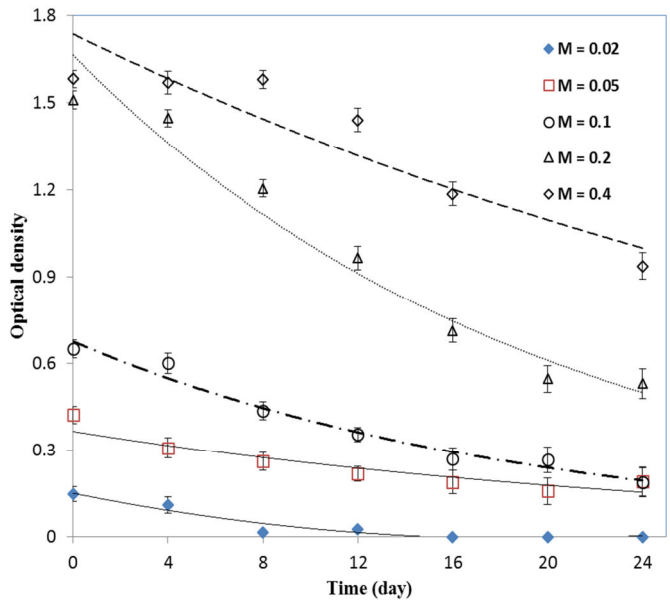

Figure 7: Photo-degradation of coated layer with different concentrations of OB under solar radiation during 24 days, as a two-coat system.

Table 4: Constant rate of degradation under solar radiation.

M (*gr-OB)/(30gr-resin)*	K_d (day^{-1})	
	One-layer	Two-layer
0.02	0.066	0.041
0.05	0.0650	0.033
0.1	0.060	0.052
0.2	0.0570	0.044
0.4	0.063	0.022

3.3. Biomass production

The time course for cell growth of samples is illustrated in Figure 8. The growth parameters of different samples are presented in Table 5. Compared with the uncoated sheets, the panels coated with OB layer increased algal biomass productivity by 54%, 60% and 70% for OD380 of layers 0.5, 1.2 and 1.4 during the same culture period, respectively.

Mohsenpour and Willoughby used luminescent acrylic polymer for the construction of a bubble column photobioreactor [23]. The photobioreactor was equipped with 150 W xenon lamps with the intensity of 250 µmol m^{-2} s^{-1}. They reported that the biomass productivity of *Chlorella vulgaris* was increased for some luminescent sheets. In another work, organic dye solutions of Rhodamine101 (R101) and 9, 10-diphenylanthracene (DPA) were used in a reactor with two layers: one for *Chlorella vulgaris* cultivation and the other for the organic dye solution [24]. Results showed that using R101 and DPA increased photosynthetic efficiency up to 40 and 20%, respectively. However, in our work, coating technique on the reactor wall was considered for increasing the algal growth. The results showed that converting the UV-A radiation passing through the walls of a culture flask into visible light with the coated layer (Figure 9) increases the biomass productivity.

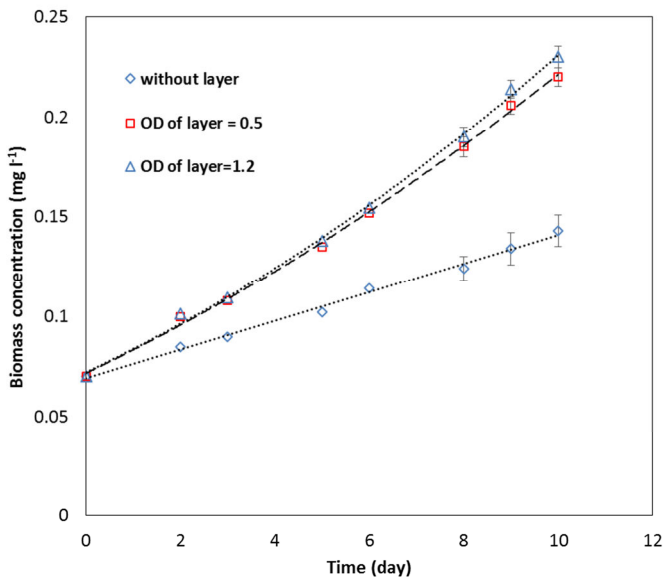

Figure 8: Time course for cell growth of Chlorella sp.

Table 5: Growth parameters of algal samples.

Algal sample	μ_{max} (day^{-1})	P ($Mg\ l^{-1}\ day^{-1}$)
Without layer	0.09	7.00
OD of layer = 0.5	0.17	10.78
OD of layer = 1.2	0.18	11.27
OD of layer = 1.4	0.18	11.90

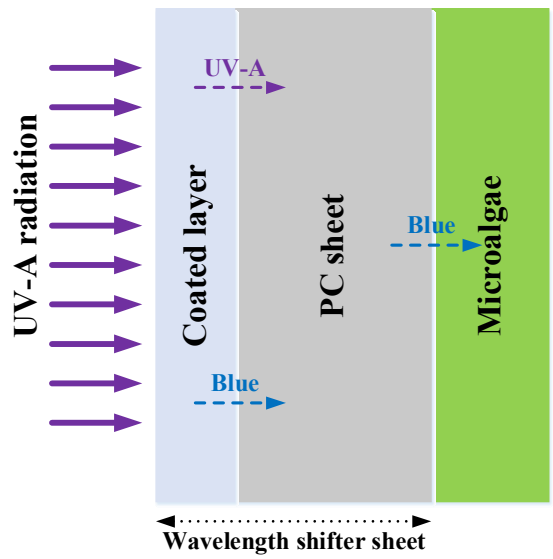

Figure 9: Schematic diagram of light pass in culture flask with coated PC sheet.

4. Conclusion

Increase in surface concentration of OB in coating increased the absorption of coated layer linearly. Also, the emission intensity of the coated plates was increased particularly for higher concentrations. Furthermore, an enhancement in photostability of coating was observed by increasing the weight of deposited layer. The enhancement in biomass productivity of microalga Chlorella sp. using coated layer as wall of culture flask under UV-A radiation was up to 70%. Since OB used in this study is only excited by the UV radiation and is transparent to visible region (400-700 nm), the air spray technique and the drying conditions of the coated layer should be controlled to prevent any translucency or opacity in the region.

Acknowledgment

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