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COMPUTATIONAL SIMULATION MODEL FOR DYE ADSORPTION IN NANO TiO_2 FILM FOR THE APPLICATIONS IN DYE SENSITIZED SOLAR CELLS

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Abstract

The theoretical and computational studies of dye sensitized solar cells (DSSCs) can contribute to a deeper understanding of these types of solar cells. The DSSCs are the novel design of solar cells which could be used as power producing windows or skylights. They represent a particular promising approach to a direct conversion of sunlight into electrical energy at low cost and with high efficiency. The light adsorption occurs in dye molecules adsorbed on a highly porous structure of TiO_2 film. Despite the progress in the efficiency and stability of these solar cells, there is still a room of research on some of their operational aspects that are still not understood. One process, for which there is limited information, is the time taken to upload the dye on the TiO_2 nanoporous film. The processes followed experimentally for dye uptake is by dipping the TiO_2 semiconductor electrode into the dye solution for periods of several hours to several days. However, such long dipping times are not economical for industrial production of DSSCs. The factors controlling this process are not yet fully investigated. We propose a simple model based on the Langmuir isotherms to study and understand the diffusion and adsorption of the dye molecules in TiO_2 films. Our computational modelling results show that the adsorption of dye into the TiO_2 nanotubes film is controlled by the diffusion coefficient, the adsorption-desorption ratio and the initial dye concentration. Our results show that the initial dye concentration plays an important role on the surface coverage. It is also noted that for a higher concentration shorter immersion time is needed for the sufficient surface coverage. Furthermore, it is observed that for the large values of the adsorption-desorption ratio there is a delay in the diffusion of dye molecules on the surface.

Keywords: dye, dye sensitized, Langmuir, solar cells, surface coverage

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1. Introduction

The solution to the growing demand of environmentally sustainable energy supply to the world might lie in the ability to the use of renewable energy technologies (Anselmi et al., 2012; Ciubota-Rosie et al., 2008). The infinite supply of solar radiation from the sun makes the conversion of solar light into electricity or other energy substances the most promising alternative for future global energy system (Johansson et al., 2014). In a developing country like South Africa (SA), the use and utilization of renewable energy technologies for a sustainable energy supply can contribute in solving the ESKOM and country problem of electricity load shedding. A low cost photovoltaic technology, such as DSSCs is

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*Author to whom all correspondence should be addressed: e-mail: Eric.Maluta@univen.ac.za one of the promising approaches for a system which can be used with high conversion efficiency (Chang et al., 2012; De Angelis et al., 2010). The use of PV power plants, powered by DSSCs solar systems which have high energy conversion efficiency and of low cost, can be of added advantages to the rural areas of SA where there are no national grid lines.

Recently, there has been a growing interest in improving the efficiency of dye sensitized solar cells (Chang et al., 2012; Gianotti et al., 2014; Qin and Peng, 2012; Völker et al., 2012). The dye sensitizer absorbs the photon and transfer the photoexcited electron to a wide band gap TiO_2 semiconductor electrode. The charge hole which is created in the dye after excitation state is then transferred to a redox couple electrolyte (Hug et al., 2014; Idígoras et al., 2015; Zhang et al., 2013). Thus there are many factors involved from photon absorption by the dye sensitizer to electron transport on the TiO_2 working electrode. One of the factors which have recently attracted more researchers is the amount of dye adsorbed on the surface of the TiO_2 nano-film (Chou et al., 2007; Chang et al., 2012; Gianotti et al., 2014; Idígoras et al., 2015) with the general target of increasing the surface coverage and shifting the dye adsorption towards the near IR region and eventually achieving higher conversion efficiency.

In order to improve the efficiency of dye sensitized solar cells, it is important to adsorb the dye molecules uniformly within TiO_2 film electrode material which is used. The dye sensitized solar cell typical components are two electrodes and a redox electrolyte. The light absorption takes place on the photo-electrode interface, where a sensitizer, dye molecule is attached to a semiconductor substrate. The dye molecules adsorbed on the TiO_2 semiconductor as a working electrode are of importance during the photon adsorption and the overall efficiency of the solar cells. The experimental procedure used for the dye adsorption on the surface of the TiO_2 is by immersion in the solution of dye molecules, generally, the ruthenium complex dye. This experiment is sometimes done in several hours or days (Chou et al., 2007; Ghicov et al., 2009; Yuasa et al., 2012]. The optimum adsorption time is extremely one of the important factors during the experiment. It is well known that the time taken during the dye uptake experiment has an impact on the efficiency of the solar cells. Fig. 1, elaborates the difference between the high and low surface coverage of the TiO_2 film. It is understood that a high surface coverage of the TiO_2 film will give rise to a higher probability of electron injection and hence improves the overall efficiency of the solar cells. Insufficient surface coverage will result in the reduction of the number of photon absorbed, i.e., reduces the short circuit current and the overall conversion efficiency (Chou et al., 2007).

In this study we intend to show a simple model for the computational study of the dye uptake on TiO_2 film. Our aim is to understand the factors affecting the dye adsorption and the optimum time needed for this process.

2. Theory

The diffusion process has recently attracted many scientists. Adsorption processes from liquid phase to solid surface are of immense importance in science and technology research. Hence, the diffusion of a substance may occur in all three phases, i.e., gas, solid and liquid. Adsorption is one of the most common methods used in waste water treatment, dye sensitized solar cell, because it is economical, effective and simple in design (Bhugun and Anson 1997; Nestle and Kimmich 1996; Shaheed et al., 2014; Sahin 2005). However, in DSSCs, the adsorption process is influenced by the nature of the dye molecules and the active layer of the working TiO_2 electrode. The surface coverage and the time taken during the process of dye adsorption in dye sensitized solar cell are the important characteristics for the efficiency of the solar cells (Chang et al., 2012; Chou et al., 2007). In this study the Langmuir adsorption isotherms has been used to understand the dye adsorption on TiO_2 nano film and factors contributing to this process. The present model is intended for a general case in which the dye molecules are adsorbed on the surface of TiO_2 film to form a monolayer. The model is based on the Langmuir adsorption isotherm, which uses active site concept in adsorption expression in order to address the reduction of its rate relative to the coverage of the wall.

The model assumes that (Holliman et al., 2008; Lionello et al., 2005; Desta, 2013):

(a) adsorption of dye molecules is controlled by transient diffusion along the film,

(b) the dye molecules to the surface of the film and only a monolayer is formed and

(c) the number of molecules remain constant even after the adsorption.

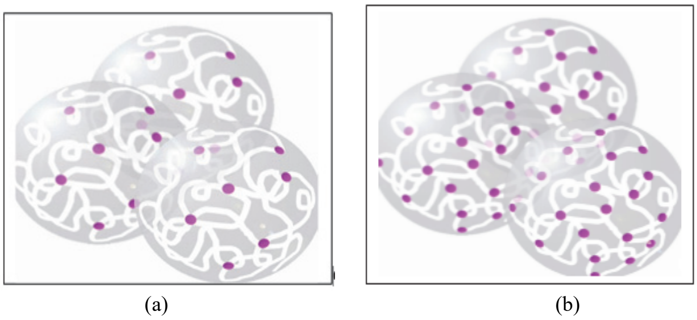

(a) (b)

Fig. 1. Illustration of the difference between a low and high surface coverage: (a) low coverage; (b) high coverage

We solved one dimensional diffusion equation for dye molecules concentration c(x, t), where x is the distance from the second end of the TiO_2 working electrode given by (Kankare and Vinokurov 1999; Lionello et al., 2005; Lovrić et al., 2010; Nestle and Kimmich 1996; Porciuncula et al., 2013; Yüksek et al., 2009), Eq. 1:

$$\frac{\partial c(x,t)}{\partial t} = D\nabla^2 c(x,t) \tag{1}$$

Nestle and Kimmich, developed a model based on the assumption that the concentration (c_b) of bound molecules in the sorbent material is proportional to the concentration (c) on the unbound sorbate in the same material (Nestle and Kimmich 1996). They modified the diffusion coefficient and defined the concentration dependent diffusion coefficient (D_{eff}), which was also used in the current study and given by (Nestle and Kimmich 1996), Eq. 2:

$$D_{eff} = \frac{D_0}{1+K} \tag{1}$$

where D_0 is the diffusion coefficient in the absence of any absorption reaction and K is the material sticking

To find the net flux of dye molecules $J(x, t)$ moving towards the pore surfaces Eq. 3,

$$J = -\frac{\partial c(x,t)}{\partial t} \tag{2}$$

we consider the molecules flowing onto the surface and being adsorbed onto it less the desorbed molecules to give the fractional surface coverage given by (Kankare and Vinokurov 1999; Lionello et al., 2005) Eq. 4:

$$\theta(x,t) = \frac{\Gamma(x,t)}{\Gamma_{\max}} \tag{3}$$

where $\Gamma(x,t)$ is the surface coverage which is a distance x from the bulk dye concentration.

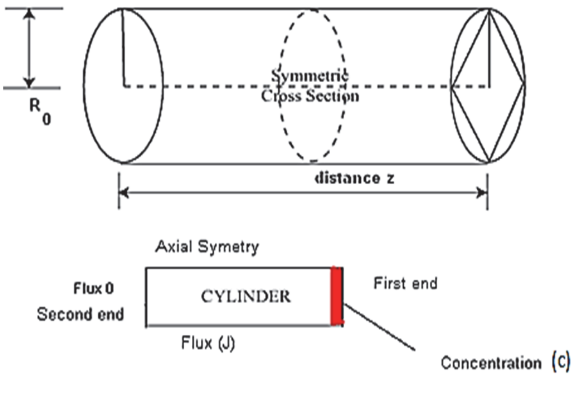


Fig. 2. Illustration for model setup and boundary conditions

The equation for the overall dye uptake rate which consider the length of dye molecule, can be idealized using the Langmuir kinetic model (Fil et al., 2018; Lionello et al., 2005; Lovrić et al., 2010; Sahin 2005), Eq. 5:

$$\Gamma_{\max}\frac{\partial c(x,t)}{\partial t} = k_{ads}\cdot l_{mol}\cdot c(x,t)\left(1-\theta(x,t)\right) - k_{des}\Gamma\left(x,t\right) \tag{5}$$

Langmuir visualized the dynamic equilibrium between adsorbate dye molecules and the adsorbed molecules in the surface layer by the fraction of the sites covered given by θ. The number of dye molecules impinging on the adsorbate surface per unit area in a unit time is proportional to the concentration inside the film. The rate of adsorption is proportional to $c(x,t)\left(1-\theta(x,t)\right)$ and the rate of desorption is proportional to $\theta(x,t)$ only. At equilibrium, these two rates are equal, so that, Eq. 6:

$$k_{ads}\cdot l_{mol}\cdot c\left(x,t\right)(1-\theta(x,t)) = k_{des}\cdot\Gamma_{\max}\cdot\theta(x,t) \tag{4}$$

where k_{ads} and k_{des} are the rate constants for adsorption and desorption respectively. If we define K as the ratio of k_{ads} and k_{des}, the surface coverage can be given by Eq. 7.

$$\theta(x,t) = \frac{c(x,t)/c_{con}}{1+c(x,t)/c_{con}} \tag{5}$$

where $c_{con} = \frac{\Gamma_{\max}}{kl_{mol}}$ and $K = \frac{k_{ads}}{k_{des}}$ are called the material sticking coefficient.

The total number of dye molecules given by $N = N_{sol} + N_{surf}$ is constant and the number of dye molecules in the solution is given as Eq. 8:

$$N_{sol} = 2\pi\int_0^d dx\int_0^{R_0} c(\mathrm{r},x,t)rdr \tag{8}$$

and the number of dye molecules on the surface, Eq. 9:

$$N_{surf} = 2\pi R_0\Gamma_{\max}\int_0^t \theta(x,t)dx \tag{6}$$

A simple model of concentration dependent diffusion equation was solved by MATLAB software. The problem is set as a transient conversion diffusion problem for the dye molecules flux and adsorption in one dimensional geometry. The boundary conditions are of conversion diffusion type. To mimic the real dye sensitized solar cell, we have used the following parameters in the model: length of the TiO_2 film (L) = $13x10^{-6}$ m, initial dye diffusion coefficient (D_0) =

$5\text{x}10^{-6}$ m^2s^{-1}, maximum surface coverage (Γ_{max})= $5\text{x}10^{19}$ m^{-2}, length of dye molecule (l_{mol}) = $0.5\text{x}10^{-9}$m.

At the beginning of the simulation the film is empty. A finite difference scheme for equation (1) was developed, guided by the following initial and boundary conditions, Eqs.10-12:

$$c(x,t) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2} \tag{7}$$

$$c(0,t) = c_b \tag{8}$$

$$\frac{\partial c(L,t)}{\partial x} = 0 \tag{9}$$

For the initial condition we have used the Gaussian function with mean ($\mu = 0.5$) and standard deviation ($\sigma = 0.05$).

3. Results and discussion

The dye concentration and adsorption time play an important role on the surface coverage of the pore and the overall light conversion efficiency of the solar cell. They also have a great influence on the dye adsorption onto the pore. The simulation and analysis of dye adsorption into the TiO_2 pore surfaces was performed for various dye concentrations (c), to compare the amount of dye molecules on the pore. As shown in the Fig. 3, it was found that the adsorption time depends on the amount of dye concentration used. It can be observed from the figure that for the higher dye concentration the time needed for the dye uploading will be shorter compared to the time needed for lower concentration.

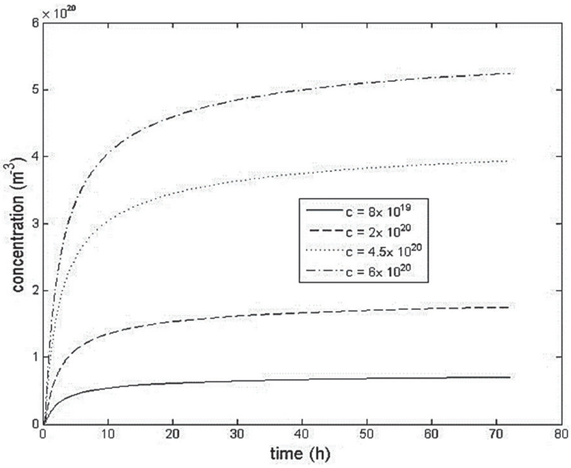


Fig. 3. Dependency of the surface concentration on the different values of the initial dye concentration (c), the value used for the calculations are k = $2\text{x}10^3$, D_0 = $5\text{x}10^{-9}$ m^2s^{-1}, l_{mol} = $0.5\text{x}10^{-9}$m, Γ_{max} = $5\text{x}10^{19}$ m^{-2} and d = 13μm is the length of the film

This shows that at high concentrations a shorter time is needed for the dye molecules to be adsorbed into the pore and at lower concentration a longer time is needed, so that at the end of the process we have sufficient surface coverage. These results are in agreement with the experimental results reported by Choe et al. (2007) and by Giovannetti et al. (2014). Their results also show that at higher concentration shorter immersion time is needed to obtain highest overall energy conversion efficiency while for a lower dye concentration, a longer immersion time is needed. The most important factor is that an insufficient surface coverage of dye molecules on the surface of the TiO_2 nanotube film or nanoparticle film working as the semiconductor in this type of solar cells would results in the reduction of the number of electron during the photon absorption. Hence this will lead to a lower value of the short circuit current density and the overall efficiency of the solar cells.

The importance of the time scale to upload the dye can be observed from Figs. 3-7. These figures illustrate the concentration flowing on the film and the dye molecules attached on the surface of the film. It can be observed from Figs. 3 and 4 that initially about 12 hours and lower there is low dye concentration in the film and we also have a lower surface coverage.

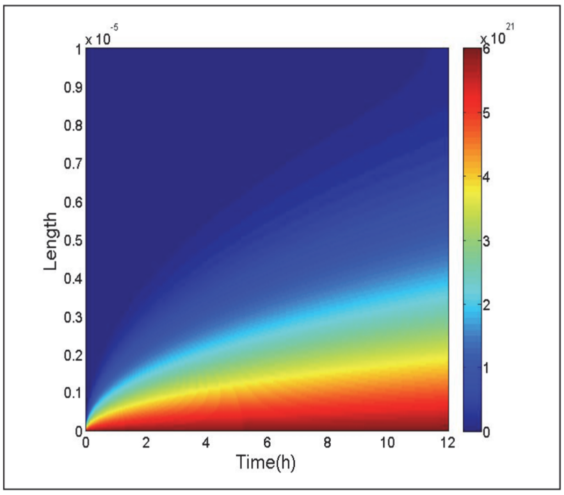


Fig. 4. Illustration of the dye flowing (along) in the film for initial time of 12 hours

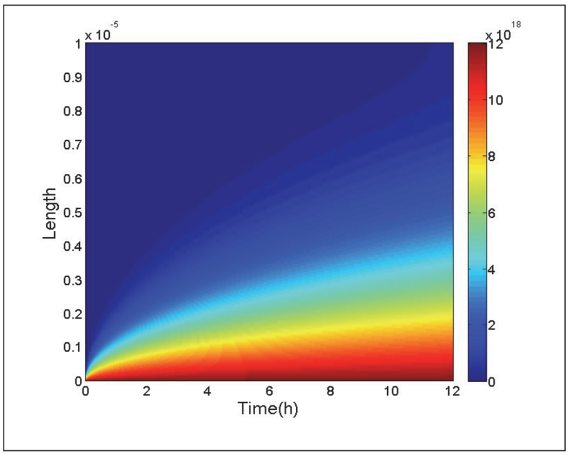
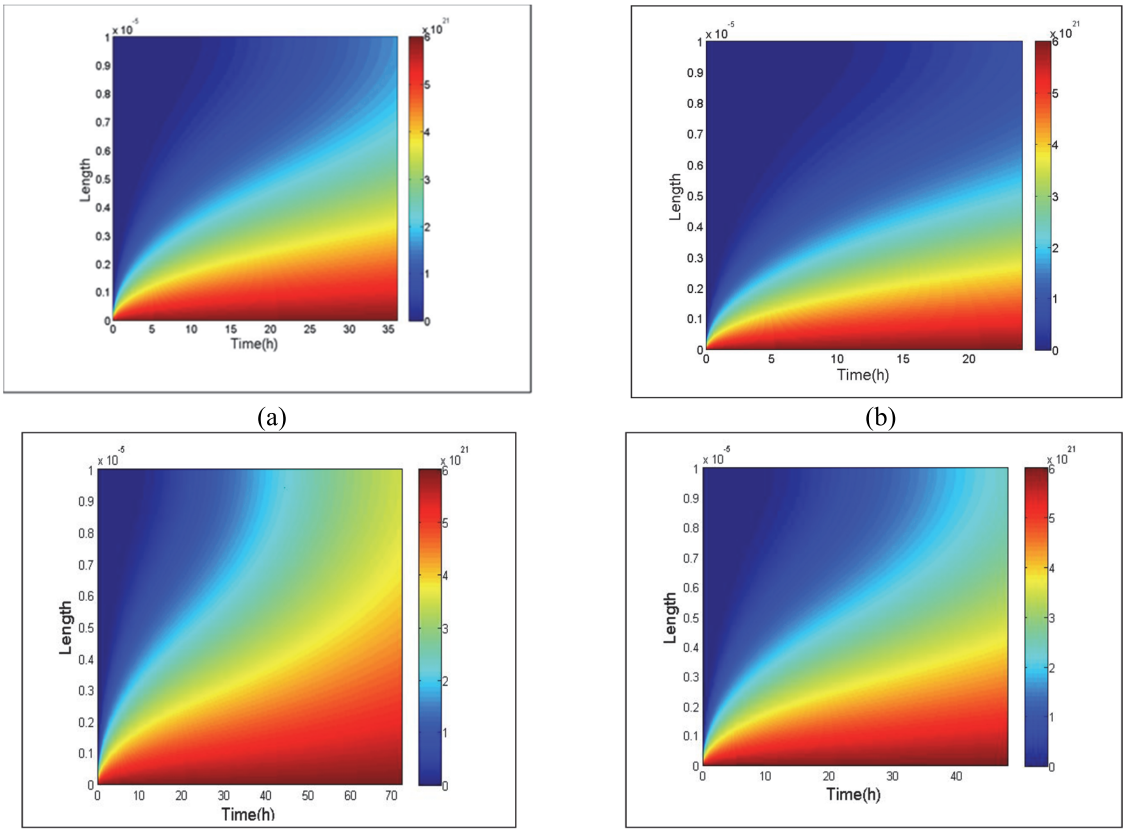


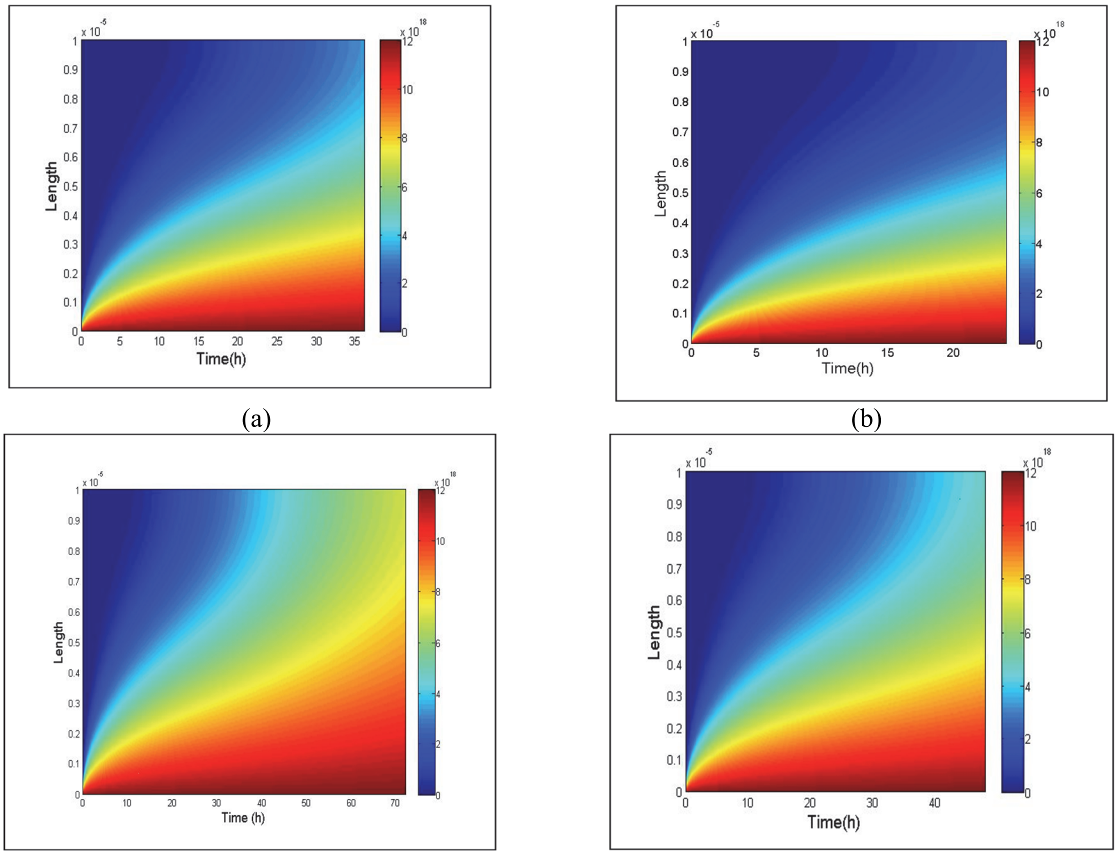
Fig. 5. Illustration of the dye adsorbed (along) in the film for initial time of 12 hours



(a) (b)

(c) (d)

Fig. 6. Illustration of the dye spreading inside the film during different time scale as illustrated on the figure: (a) 24 hours, (b) 36 hours, (c) 48 hours, (d) 72 hours



(a) (b)

(c) (d)

Fig. 7. Illustration of the dye adsorbed on the surface of the film during different time scale as illustrated on the figure: (a) 24 hours, (b) 36 hours, (c) 48 hours, (d) 72 hours

As we increase the time we observe more concentration of the dye molecules in the film and an increase on the surface coverage. The time scale is also important as reported from experimental studies by Chou et al., when they indicated that a longer immersion time affect the overall conversion efficiency. Ghicov et al. (2014) reported that the short circuit photocurrent increases up to 4 days of dye loading and for longer absorption time like 7 days the short circuit photo current decreases due to aggregation of dye on the surface. This process leads the dye molecules to form a micro-cluster of dye molecules on the surface of the TiO_2 semiconductor, which reduce the efficiency of electron injection. Thus, an optimum time is needed for dye uptake to prevent the dye aggregation and a shorter uploading time will be effective for industrial production of these solar cells.

The adsorption process is a complex phenomenon which comprises of the different steps like diffusion of dye molecules and adsorption of the molecules on the surface of the pore. This involves the interaction between the dye molecules and active sites of the surface. Fig. 8 shows the time variation due to the diffusion coefficient. It is clear that the time variation depends on the diffusion coefficient. But if we scale our graph by the characteristic time, Eq.13:

$$t_z = \frac{d^2}{D_0} \tag{10}$$

where *d* is the length of the film, the variation of dye uptake on the pore surface at the end is the same. An experimental result for diffusion effect was reported by Paulose et al. (2007), where they have reported an experimental results of the diffusion of Phenol Red on the TiO_2 nanotubes. They reported that using a diffusion coefficient of $D = 2.84 \times 10^{-10}$ m^2s^{-1} with an initial concentration of $c = 6 \times 10^{21} m^{-3}$, it takes about 5 hours (Paulose et al. 2007). It can be observed also in the current study that the diffusion coefficient plays an important role on the uploading time.

Our computational results agree very well with the experimental data reported by Holliman et al. (2008), and Desta (2013). All these data show a very fast dye uptake for the first few hours and then as the active layer of the film decreases, there is a decrease on the rate of dye adsorption (Fig. 3). In the current study as we have represented the TiO_2 film by a cylinder, the flow pattern of the dye molecules unto the pore, on both directions can be explained by the fact that the concentration diffuses first in the radial direction and then along the pore. Thus, the concentration fills the pore in the radial direction (r-axis) and the process of adsorption and desorption takes place along the pore surface (z-axis). Hence, diffusion along the pore radius is very fast compared to the diffusion along the pore surface as expected. The diffusion along the pore is slowed down by adsorption of dye molecules at the pore surface.

The adsorbed molecules are removed from the solution, so more dye molecules have to diffuse into the pore, from pore entrance at z = d to replace them. This delay is seen more clearly for much larger values of *K* as illustrated on Fig. 9. In this case almost all molecules landing on the surface are attached. The upload time depends on the value of *K*, as for smaller value of *K* it takes less time for the dye molecules to be adsorbed on the pore wall. This shows that the optimization of the duration of the dye loading on the TiO_2 film is an important subject for research in DSSCs and there is a need to optimize the dye uploading for a better performance of the solar cell and industrial production. The meaning of the diffusion coefficient (D_0) and material sticking coefficient (*K*) need to be understood so that an optimum time and sufficient coverage of the film can be achieved.

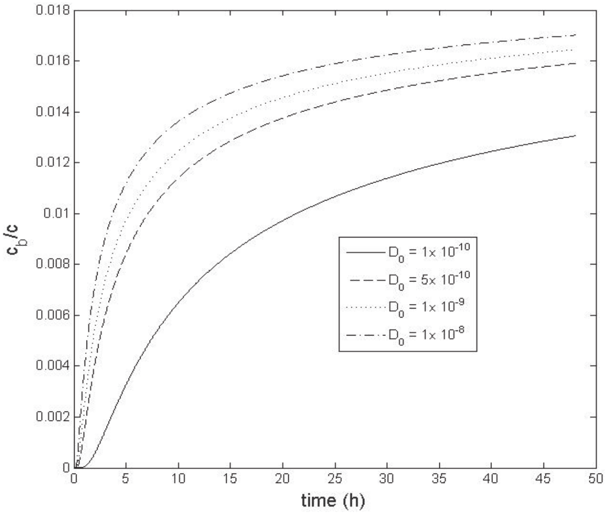


Fig. 8. Dependency of the surface dye concentration on the different values of the diffusion coefficient (D_0), the value used for the calculations are $K = 2 \times 10^3$, $c = 6 \times 10^{21}$ m^2s^{-1}, $l_{mol} = 0.5 \times 10^{-9}$m, $\Gamma_{max} = 5 \times 10^{19}$ m^{-2} and d = 13μm

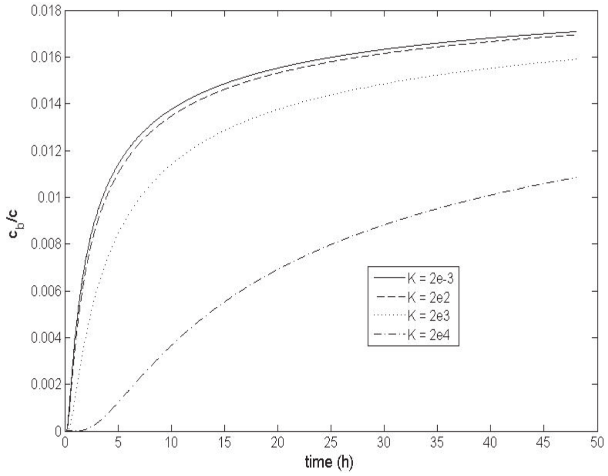


Fig. 9. Dependency of the surface dye concentration on the different values of the sticking coefficient (*K*), the value used for the calculations are $D_0 = 2 \times 10^3$, $c = 6 \times 10^{21}$ m^2s^{-1}, $l_{mol} = 0.5 \times 10^{-9}$m, $\Gamma_{max} = 5 \times 10^{19}$ m^{-2} and d = 13μm

4. Conclusions

In this work we developed a simple model for dye uptake on DSSCs. The model presented shows that it can take few hours for dye molecules to be absorbed into a nano-porous TiO_2 film in DSSCs. The model shows that the time depends on the ratio of the adsorption to desorption rates K and this will vary for different film materials.

The time scale for diffusion along the pore radius is given by a simple expression for t_z. Our results also show that the diffusion coefficient and the initial dye concentration play an important role on the time needed for dye uptake on DSCCs.

For a higher initial dye concentration, a shorter immersion time is needed for the sufficient surface coverage, which is in line with some previously reported experimental data. Experimentally the longer immersion time affects the efficiency of the solar cells. We have observed that the large values of the adsorption-desorption ratio show a delay in the diffusion of dye molecules. In addition to that, at large values, we expect all dye molecules which reach the surface will eventually stick to the surface.

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