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The Establishment of a Theoretical Model for the Estimation of Some Photo-Physical Processes in Laser Dyes

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Abstract

In this study, a new theoretical method for the estimation of absorption and fluorescence spectra is accomplished. These estimations were established following experimental measurements of absorption and fluorescence spectra for the solutions of fluorescein laser dye mixed with titanium dioxide (TiO_2) nanoparticles in distilled water. The used concentration of fluorescein dye was $1x10^{-5}$ M, whereas the masses of titanium dioxide nanoparticles were 0.0003g, 0.0005g, 0.001g and 0.002g. An absorption spectra improvement was observed upon raising the mass of TiO_2 nanoparticles, which specifies that doping the fluorescein dye with TiO_2 nanoparticles have an essential influence on the dye absorption spectra. On the other side, all fluorescence spectra for the dye quenched as TiO_2 nanoparticles mass was increased, because of the induced electron transfer. The new method of theoretical estimations was based on curve fitting using Logistic Power Peak (LPP) function to estimate theoretical models for the absorption and fluorescence spectra of these samples. The results revealed that these estimated models had exceptional matching shapes with the experimental shapes, so that the estimated models can substitute the experimental measurements.

Keywords: Logistic Power Peak, Fluorescein dye, TiO_2 Nanoparticles, induced electron transfer.

بناء موديلات نظرية لتخمين بعض العمليات الفيزيائية الضوئية للصبغات الليزرية

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الخلاصة

تم تنفيذ طريقة نظرية جديدة لتخمين أطياف الامتصاص والفلورة . تم اجراء هذه التخمينات بعد اجراء تجارب عملية لأطياف الامتصاص والفلورة لمحاليل تحتوي صبغة الفلوريسين الليزرية مع مادة ثنائي اوكسيد التيتانيوم النانوية في الماء المقطر. استخدم تركيز ($1x10^{-5}$ M) لصبغة الفلورسين. بينما كانت كميات مادة ثنائي اوكسيد التيتانيوم النانوية هي (0.0003g، 0.0005g، 0.001g و 0.002g). تم ملاحظة تحسن اطياف الامتصاص مع زيادة الكتل، مما يبين ان التطعيم بجسيمات ثنائي اوكسيد التيتانيوم النانوية له تأثير جوهري على اطياف الامتصاص . من ناحية اخرى، جميع اطياف الفلورة تم كبتها كلما ازدادت كتل جسيمات ثنائي اوكسيد التيتانيوم النانوية نتيجة حدوث انتقال الالكترون المحفز. تعتمد الطريقة النظرية الجديدة للتخمين على عملية مطابقة المنحنيات باستخدام دالة منحني القوة اللوجستي (LPP)، لتخمين الموديلات النظرية

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لاطياف الامتصاص والفلورة لهذه العينات. اظهرت النتائج ان الموديلات النظرية المخمنة تسلك نفس التصرف العملي بشكل ممتاز، بحيث يمكن الاستعاضة عن القياسات التجريبية بالموديلات النظرية المخمنة.

Introduction

Various spectral analyses of the absorption and fluorescence emissions of xanthene dyes (especially fluorescein) were achieved, which included the doping of metal and non-metal nanoparticles in dye liquids. Such analyses were developed due to the essential uses of these dyes in medical and biological applications, including identification and therapy of cancer [1], *in vitro* and *in vivo* bio-imaging [2], imaging of tomography and angiography [3], and other medical applications of nanoparticles (e.g. silver nanoparticles) [4]. Organic laser dyes mixed with nanoparticles are also used for examining the optical properties of scattering media, as in laser action and random lasers [5], [6]. In 2012, Al-Kadhemy *et al.* explored the absorption spectra of styrene-butadiene in toluene, using the TableCurve 2D software [7], which opens the way for using a curve fitting software in the spectral measurements. Fluorescence quenching by electron transfer effects was inspected for nanoparticles with organic dyes by Asiri *et al.* [8], who explained the photodegradation of rhodamine 6G and phenol red by TiO_2 nanoparticles through electron transfer under solar irradiation. Also, Karunakaran *et al.* [9] found that the fluorescence of FPPBI dye was efficiently quenched by TiO_2 nanoparticles, due to electron transfer mechanisms.

In this research, a new method for creating theoretical models in order to estimate the spectral performance of the fluorescein dye with TiO_2 nanoparticles was evaluated. These estimations were performed after experimental measurements of absorption and fluorescence spectra of fluorescein dye with TiO_2 nanoparticles of different masses. The curve fitting process was conducted using the TableCurve 2D software to estimate theoretical models for the spectra of absorption and fluorescence. These estimated models exploited the Logistic Power Peak (LPP) function, which was previously used for various objectives, such as estimating soil properties [10] and light emitted diode (LED) spectral calculations [11]. However, this is the first time to utilize the LPP function to estimate theoretical models of the spectral profiles of the fluorescein dye with TiO_2 nanoparticles.

Materials and Methods

In these tests, the samples consisted of a suspension of 0.0003g, 0.0005g, 0.001g and 0.002g of TiO_2 anatase nanoparticles (Nanoshel LLC, USA) with an average size of 15.7 nm and purity of 99% in fluorescein ($C_{20}H_{12}O_5$, M_W=332.306 g/mol, BDH) with 10 ml of distilled water. The solution of dye samples with a concentration of $1x10^{-5}$ M was prepared using the following equation [12]:

$$m = C\ V\ Mw \quad (1)$$

where m is the weight of the dye needed to obtain the desired concentration, C is the required concentration of the dye, V is the volume of solvent for the dye, and Mw is the molecular weight of the dye. The dye chemical structure is shown in Figure-1.

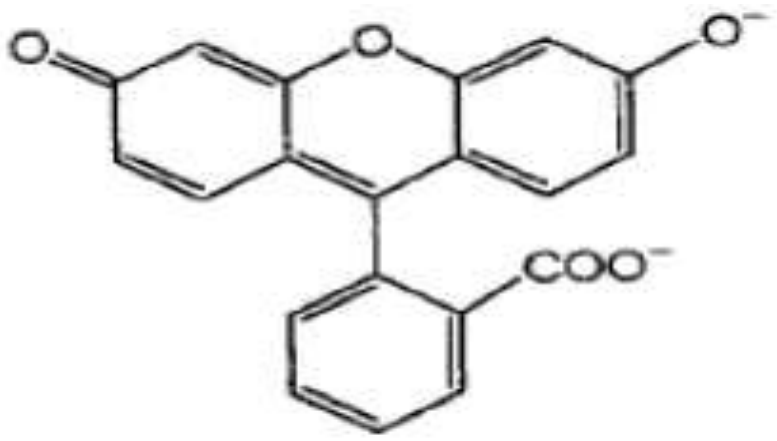


Figure 1- Chemical structure of fluorescein dye [12]**.**

All the used samples were prepared using a hot plate stirrer until the TiO_2 nanoparticles were homogeneously diffused within the fluorescein solution at room temperature (30°C). Fluorescence spectra were determined using a spectrofluorophotometer (SHIMATDZU RF-5301pc).

Results and Discussion

The crystalline structure of TiO_2 nanoparticles was verified by X-ray diffraction (XRD) using SHIMADZU XRD – 6000, Cu Kα, in the 2θ range of 10 to 80°.

The measured XRD pattern of TiO_2 nanoparticles is represented in Figure-2. The pattern reveals that the TiO_2 nanoparticles are crystalline and have a tetragonal crystal system with a lattice constant of a = 3.7850 Å and c = 9.5140 Å. The appearance of strong diffraction peaks at 25° (101), 48° (200), and 37° (004) indicated the presence of TiO_2 in the anatase phase. This finding is consistent with those from other published results [13-15].

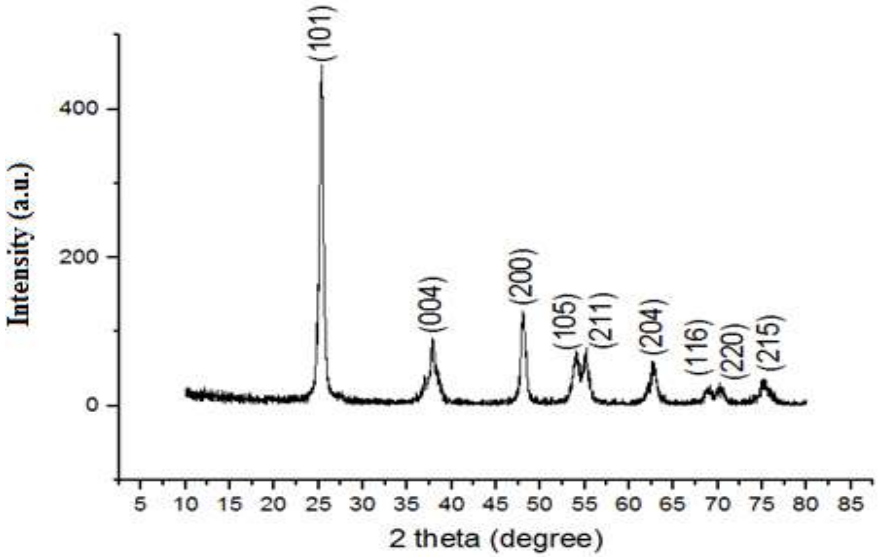


Figure 2- Measured XRD patterns of TiO_2 nanoparticles.

Figure-3 shows the absorption and fluorescence spectra for fluorescein dye with a concentration of $1x10^{-5}$ M, with and without TiO_2 nanoparticles of the tested masses.

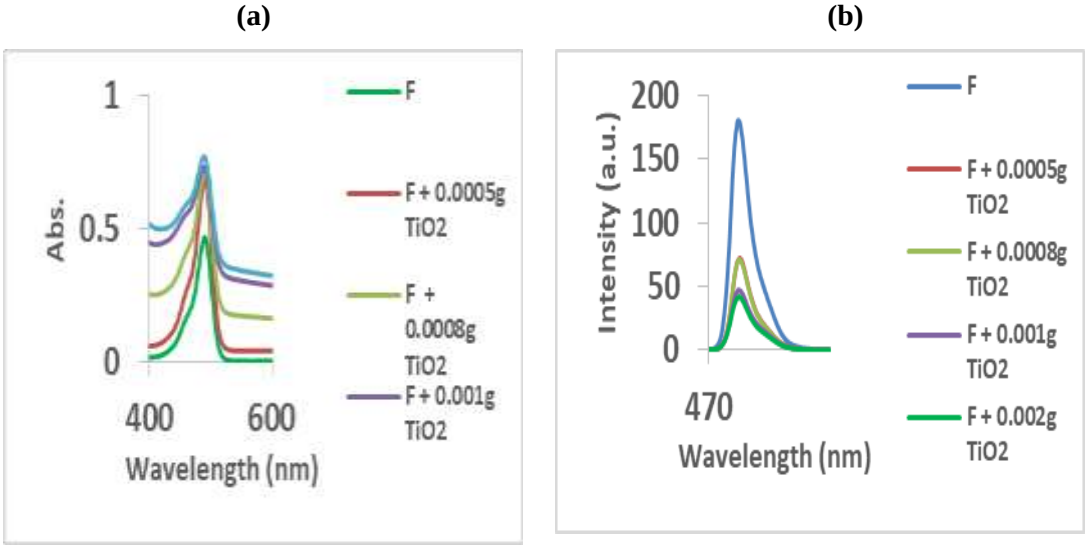


Figure 3- Absorption (a) and fluorescence (b) spectra of fluorescein (F) with different masses of TiO_2 nanoparticles.

The peak maximum spectra of the fluorescein laser dye were λ_e = 490 nm for the absorption and λ_f =514 nm for the fluorescence. The details of these results are presented in Table-1.

Table 1- Absorption and fluorescence spectra of fluorescein dye with different masses of TiO_2 nanoparticles

Dyes	TiO_2 (g)	λ_e (nm)	Absorption Intensity	λ_f (nm)	Fluorescence Intensity
F ($1x10^{-5}$ M)	0	490	0.468	514	180.8
	0.0005	490	0.689	516	72.37
	0.0008	490	0.71	515	71.19
	0.001	490	0.731	514	47.48
	0.002	490	0.771	515	42.11

From Figure-3 and Table-1, it is obvious that increasing the TiO_2 nanoparticle mass resulted in higher absorption spectra, while fluorescence intensities decreased instantly by the quenching process. The electron transfer effect between fluorescein dye and TiO_2 nanoparticle can explain this action. In addition, there was a very slight red shift in the fluorescence intensity with increasing TiO_2 nanoparticle mass, because of the process of re-absorption and re-emission produced by the scattering of the light from TiO_2 nanoparticle.

Table Curve 2D software was used for the theoretical estimation of the experimental absorption and fluorescence spectra of a single concentration of fluorescein dye with changing the mass of TiO_2 nanoparticles. A curve fitting process was achieved for all curves observed in Figure- 3, as shown in Figures- 4 and 6, to discover an appropriate individual curve fitting equation that can be used for all of these spectra.

The used curve fitting equation, in this research, is another type of the Gaussian function which is called the Logistic Power Peak (LPP). A mathematical description of this function is given by Eq. (2):

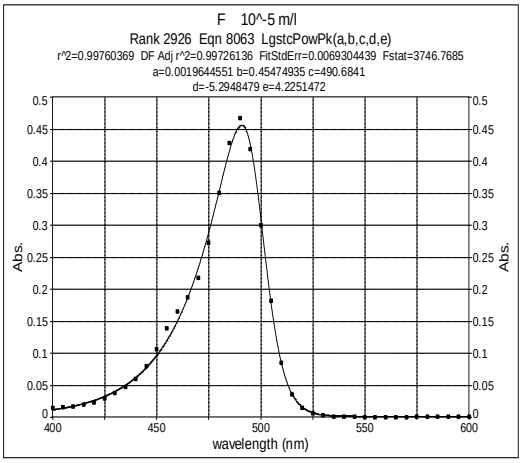
$$Y = (a + b)/e\ (1+ \exp((x + d \ln(e) - c)/d))^{((-e - 1)/e)} \exp((x + d \ln(e) - c)/d)(e + 1)^{((e + 1)/e)} \quad (2)$$

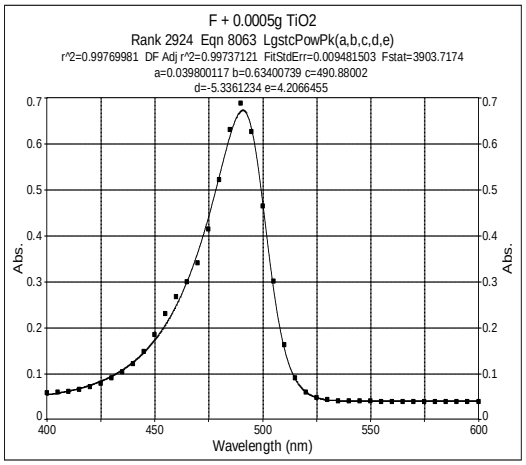
for $e \geq 1$, $d \neq 0$.

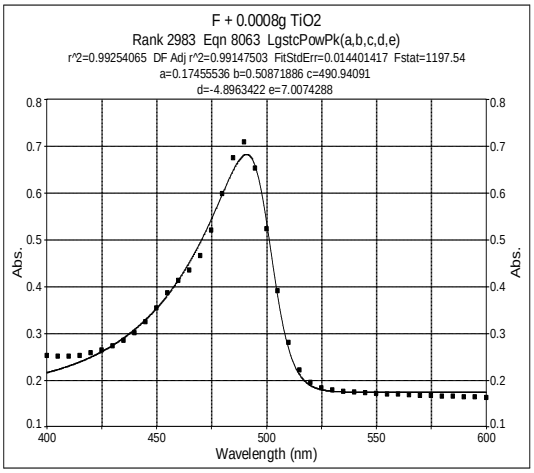
where a and b are the minimum and maximum amplitudes, respectively, d is the width of the spectrum over time, c is position of maximum, and e is the symmetry around the peak (e = 1) or not (e > 1).

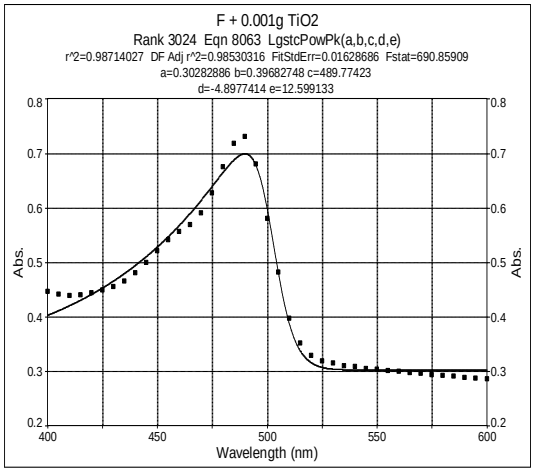
The equation of the theoretical estimation was applied for values of TiO_2 nanoparticles mass, which were not used experimentally, mixed with fluorescein dye solution in distilled water within a concentration of $1x10^{-5}$ M. The theoretical study involves the absorption and fluorescence spectra for the samples.

Figures-(4 and 5) demonstrate the fitting curves and their parameters, respectively, for the experimental absorption spectra, while Figure- 6 and 7 show the fitting curves and their parameters, respectively, for the experimental fluorescence spectra for fluorescein dye solution mixed with TiO_2 nanoparticles.









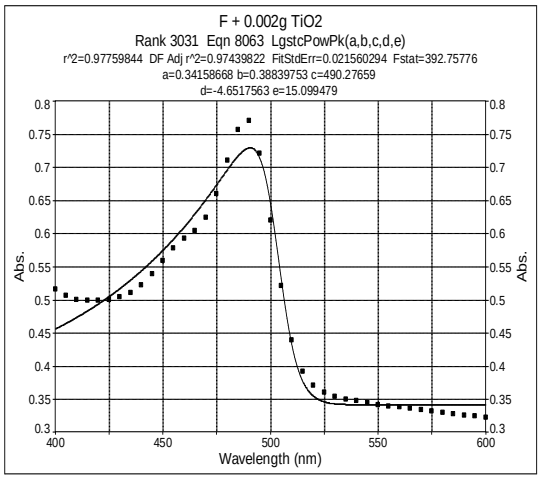
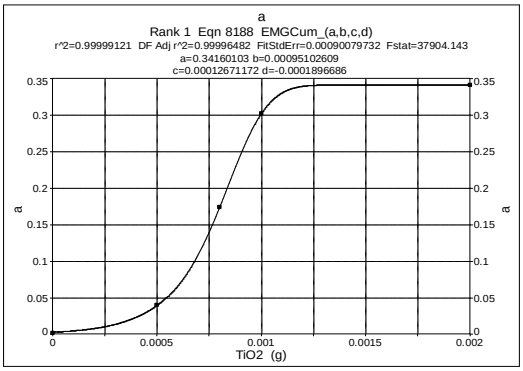
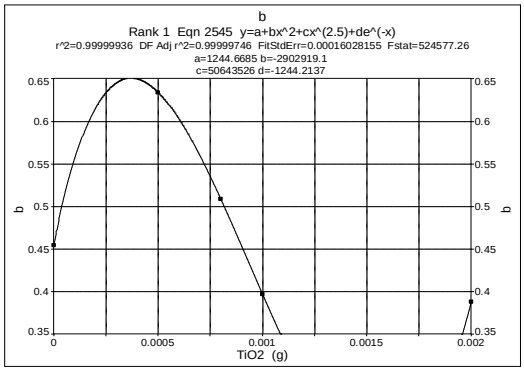
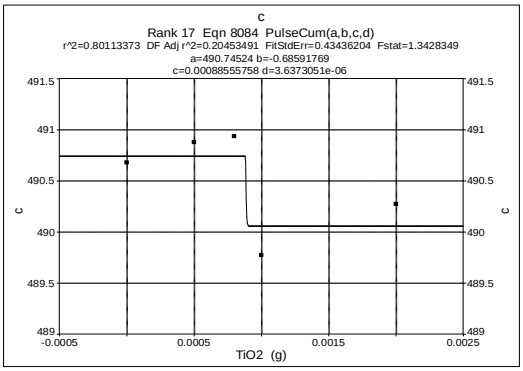
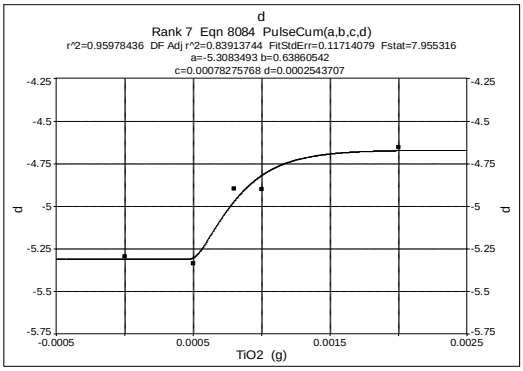


Figure 4- Curve fitting of absorption spectra for fluorescein with TiO_2 nanoparticles.









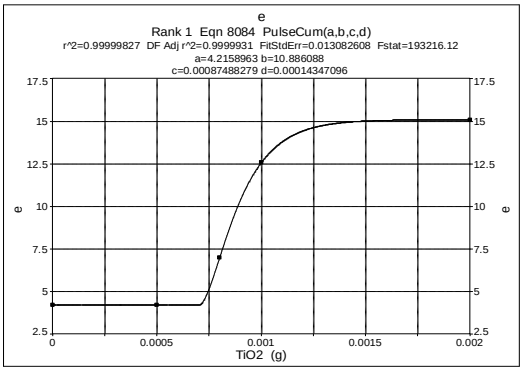
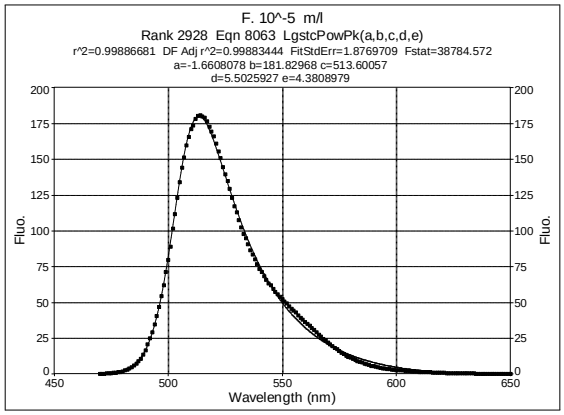
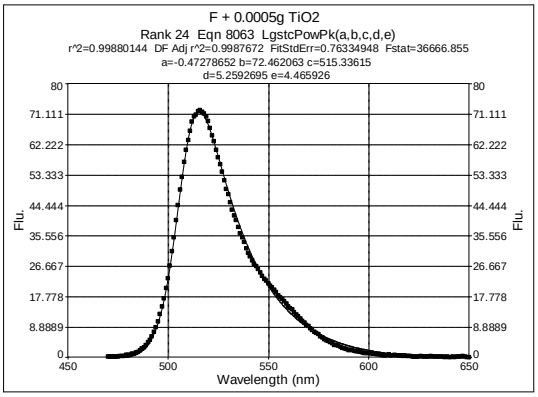
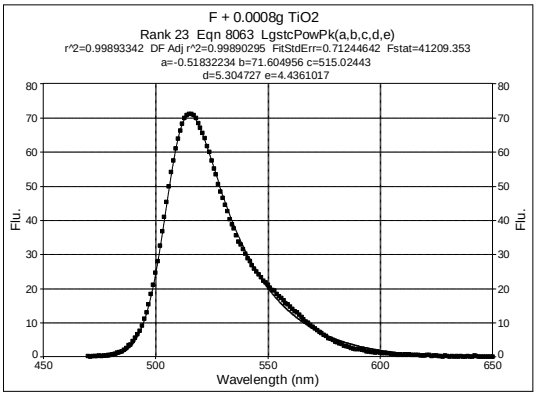
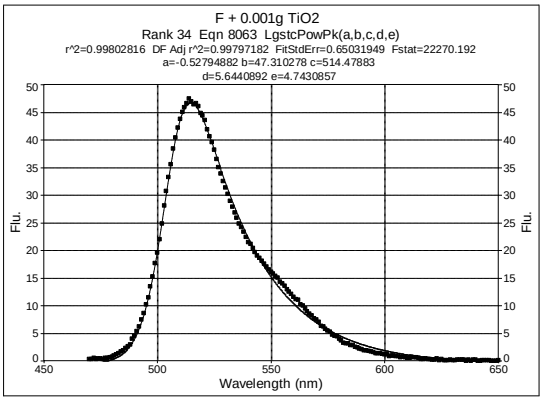


Figure 5- The parameters of fluorescein with TiO_2 nanoparticles for absorption spectra.









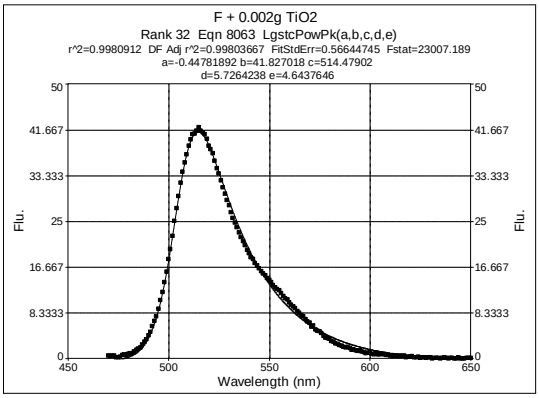


Figure 6- Curve fitting of fluorescence spectra for fluorescein with TiO_2 nanoparticles.

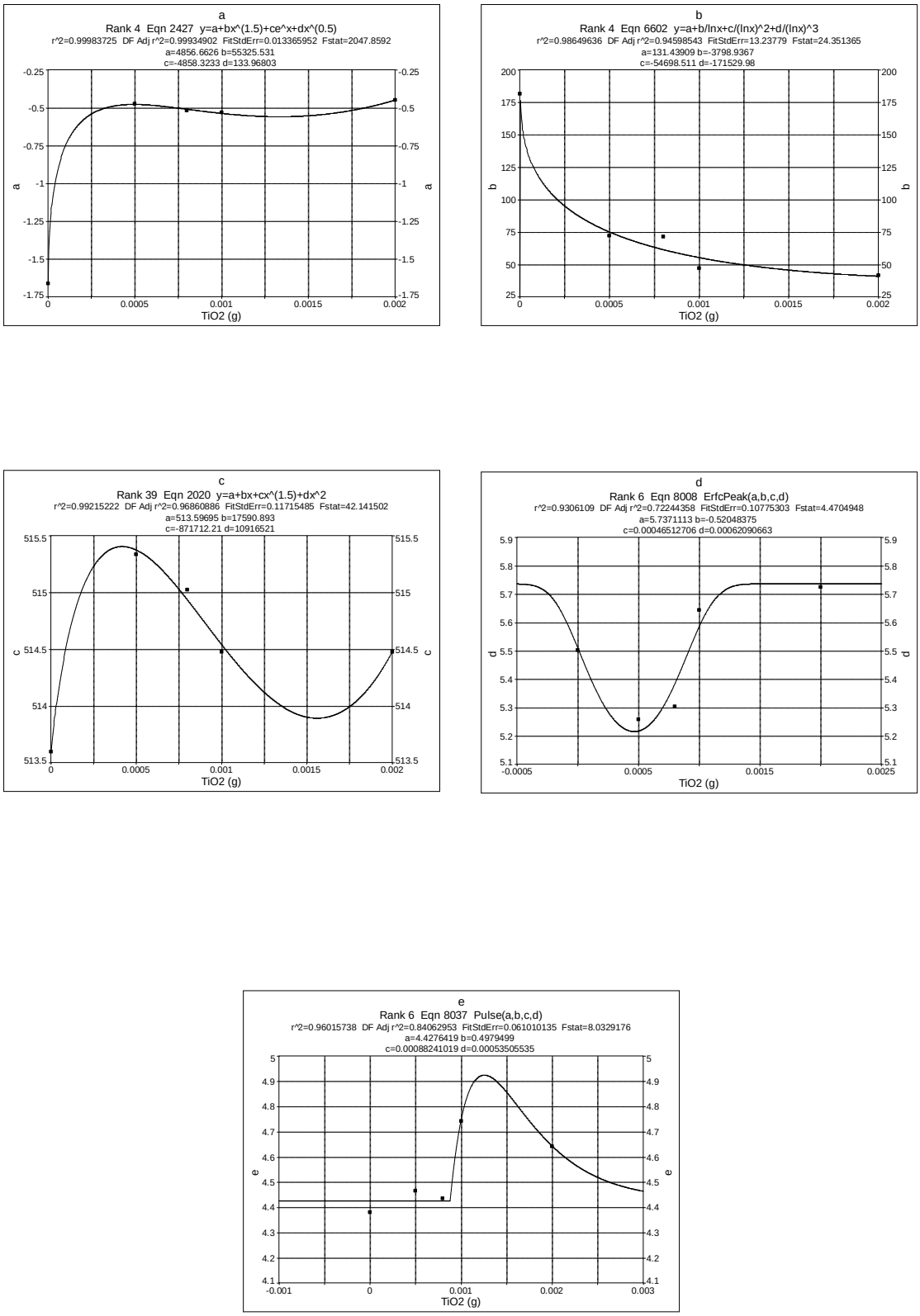


Figure 7- The parameters of fluorescein with TiO_2 nanoparticles for fluorescence spectra.

The curve fitting parameters from Figures-(5 and 7) are presented in Tables- 2 and 3, which contain the absorption and fluorescence parameters, respectively, of both the experimental and theoretical values of the mass of TiO_2 nanoparticles which were mixed with fluorescein dye. The symbol r^2 refers to the correlation coefficient, which was used to measure the strength of a relationship between the two variables (experimental and theoretical data).

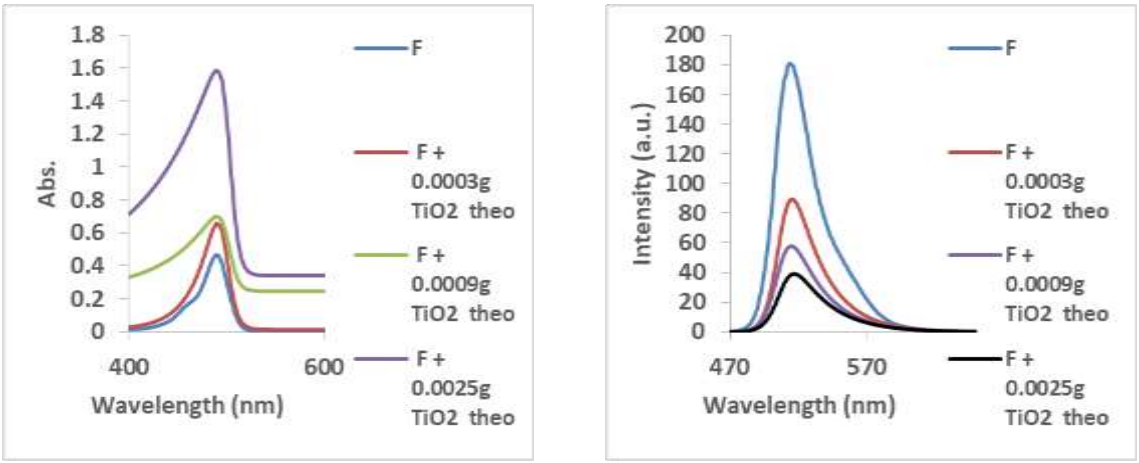
Table 2- Parameters of fluorescein with TiO_2 nanoparticles for absorption spectra

TiO_2 (g)	a	b	c	d	e	r^2
0	0.0019645	0.4547493	490.6841	-5.2948479	4.2251472	0.9976
0.0003 Theo	0.0137	0.6456	490.7452	-5.3083	4.2158	
0.0005	0.0398001	0.6340074	490.88002	-5.3361234	4.2066455	0.9976
0.0008	0.1745554	0.5087189	490.94091	-4.8963422	7.0074288	0.9925
0.0009 Theo	0.2463	0.4533	490.0668	-4.883	10.4072	
0.001	0.3028289	0.3968275	489.77423	-4.8977414	12.599133	0.9871
0.002	0.3415867	0.3883975	490.27659	-4.6517563	15.099479	0.9775
0.0025 Theo	0.3416	1.2442	490.0593	-4.6701	15.1019	

Table 3-Parameters of fluorescein with TiO_2 nanoparticles for fluorescence spectra

TiO_2 (g)	a	b	c	d	e	r^2
0	-1.6608078	181.82968	513.60057	5.5025927	4.3808979	0.9988
0.0003 Theo	-0.5105	89.8488	515.3271	5.258	4.4276	
0.0005	-0.4727865	72.462063	515.33615	5.2592695	4.465926	0.9988
0.0008	-0.5183223	71.604956	515.02443	5.304727	4.4361017	0.9989
0.0009 Theo	-0.5223	58.2915	514.7349	5.4831	4.489	
0.001	-0.5279488	47.310278	514.47883	5.6440892	4.7430857	0.9980
0.002	-0.4478189	41.827018	514.47902	5.7264238	4.6437646	0.9980
0.0025 Theo	-0.2076	39.2809	516.8384	5.7371	4.5198	

For the additional exploration of the theoretical models of the estimated absorption and fluorescence spectra, a profile containing the theoretical values of the mass of TiO_2 nanoparticles that were mixed with fluorescein dye, is provided in Figure-8. The performance of the theoretical absorption and fluorescence spectra was similar to that of the experimental spectra (Figure-3), i.e., the theoretical models based on the used curve fitting equation (Eq. 2) showed a very good matching with the experimental results.



(a) (b)

Figure 8- Theoretical absorption (a) and fluorescence (b) spectra for fluorescein with TiO_2 nanoparticles.

For comparison, all the experimental and theoretical results of TiO_2 nanoparticles mixed with fluorescein dye are presented in Table-4.

Table 4- The spectral behavior of the fluorescein dye mixed with different experimental and theoretical masses of TiO_2 nanoparticles.

	TiO_2 (g)	λ_e (nm)	Absorption Intensity	λ_f (nm)	Fluorescence intensity
F ($1x10^{-5}$ M)	0	490	0.468	514	180.8
	0.0003 Theo	490	0.658	515	89.3
	0.0005	490	0.689	516	72.37
	0.0008	490	0.71	515	71.19
	0.0008 Theo	490	0.674	515	52.611
	0.0009 Theo	490	0.699	515	57.75
	0.001	490	0.731	514	47.48
	0.002	490	0.771	515	42.11
	0.0025 Theo	490	1.585	516	38.99

Conclusions

A new theoretical model for the estimation of the absorption and fluorescence spectra of fluorescein dye, mixed with different TiO_2 nanoparticles masses, was accomplished. The Logistic Power Peak (LPP) equation was found to be the best fitting equation for both absorption and fluorescence spectra of these samples. The performance similarity of the theoretical and practical spectra profiles can make the estimated models an exceptional alternative for the experimental measurements. This alternative would save the time, cost, and overcome the availability of the measuring devices. It also provides a suitable speculation of the overall spectral behavior resulting from mixing TiO_2 nanoparticles with fluorescein laser dye.

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