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Photolytic and photocatalytic decolorization of Lauth's violet using nano-titanium dioxide: A kinetics study

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Abstract

Photolysis and photocatalysis of Lauth's violet using nano-titanium dioxide at various aqueous buffer and non-buffer pHs. The effects of some various operating parameters such as initial dye concentration, medium pH, illumination time and catalyst amount have been investigated in a photoreactor equipped with high pressure mercury lamp. Spectrophotometric methods supported that the dye is almost completely decolorized. The dye decolorization obeyed from a pseudo-first-order kinetics. The observed rate constants (k_{obs}) of direct photolysis and photocatalysis processes were evaluated for all studied pHs. Rate constants of direct photolysis at buffer were evaluated to be 3.7×10^{-3}, 2.5×10^{-2} and 3.0×10^{-2} min^{-1} for pHs of 7, 9 and 11 respectively. The rate constants of dye photolysis at non-buffer pHs were found as 8.8×10^{-2}, 7.4×10^{-2}, 1.1×10^{-1} h^{-1} for pHs of 5, 7 and 9 respectively. Moreover adsorption constant (K_A) and degradation rate (k_r) at surface for photocatalytic process were calculated at acidic, neutral and basic media.

Key words: Kinetic, Lauth's violet, decolorization, nano-photocatalyst

Highlights

- Photolysis of Lauth's violet was performed at various aqueous buffer and non-buffer pHs.
- Photocatalysis of Lauth's violet was performed using nano-titanium dioxide as photocatalyst.

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Introduction

The industrial dyes are known as one of the most important pollutants in wastewaters. They contain heterocyclic moieties that generally induce carcinogenic potential to these compounds and also cause mostly biodegradability resistance of them becoming a notable group of non-pleasant pollution (1). The dyes are detectable even in very low concentration and in some cases removal of them is of interest (2-3). There are many reports for dye removal from wastewaters in the literature. Some of these methods apply chemisorption, biodegradation, ozonation, fluctuation, coagulation and photo-decolorization (4 and 5). Among these methods, photodecolorization is a reasonable technique to elimination of these types of pollutants. Photo-decolorization processes include irradiation produced oxidizing agents that degrades the target pollutants. Heterogeneous photocatalysis using titanium dioxide and zinc oxide have been widely applied for deodorization of wastewaters due to their properties like less expensive, nontoxic and easy availability (6-13).

Lauth's violet is a strongly metachromatic dye that is widely used for biological treatments. Therefore decolorization study and kinetic parameters may be useful for environmental chemists. In continuation of our previous studies (14-17), in this work we wish to report photolytic and photocatalytic decolorization of dye on nano-titanium dioxide at various pHs. The effect of some phsico-chemical parameters and kinetics study of photodecolorization in each pH are presented.

Materials and methods

All chemicals were purchased from Merck and Aldrich and used without further purification. Nano titanium dioxide (anatase 99.5% with particle size 70-100 nm) with analytical grade was used as photocatalyst. The pH of solution was adjusted using diluted aqueous buffers or by addition of sodium hydroxide or hydrogen chloride solution. The buffer solutions were prepared by the chemicals of KH_2PO_4, Na_2HPO_4 (98%), NaOAc (98%), HOAc (99%), $Na_2B_4O_7$ (95%), HCl (36%), H_2SO_4 (98%) and NaOH (99.8%). In all experiments doubly distilled water was used**.** Photochemical reactor equipped by 400W high pressure mercury lamp was used for photocatalytic treatment. UV-VIS spectrophotometer, JASCO-V570, was used for spectral following of dye concentrations. Metrohm -620 model of pH-meter was applied for the test of pH of solution.

Dye concentration measurement

Spectrophotometric method was applied for determination of dye concentration by the aid of calibration curves at λ_{max}=598 nm for non-buffer pHs of 5, 7, 9 and 11 and buffer pHs of 2, 7, 9 and 11.

General photodecolorization process

The photocatalytic or direct photolysis experiments were done by irradiation of 20 ml of 20 ppm aerated and stirred aqueous dye solution in the presence or absence of photocatalyst respectively in a photoreactor cell under 400W high pressure mercury lamp at room temperature. After considered time for photolysis or photocatalysis, dye concentration was measured by UV-visible spectrophotometric method.

Results

Direct photolytic

Direct photolysis of dye was carried out both at buffer and non-buffer pHs of 2, 5, 7, 9 and 11. Fig. 1 (A and B) shows the absorbance-irradiation time plots for dye decolorization at buffer and non-buffer media. As shown in Fig. 1, the dye is degraded after 120, 180 and 900 minutes at buffer while it is decolorized after about 30 hours efficiently. The results show that at non-bufferic pHs, the effective decolorization is carried out after similar times but in buffer media, it seems that the dye is more degradable at pHs of 9 and 11 as compared with pH=7 so that the degradation time at pH of 9 and 11 is very shorter than pH=7.

Fig. 2 (A and B) exhibits the plots of Ln (C_0/C_t) versus irradiation time at buffer and non-buffer pHs. As shown in Fig. 2, the plots are linear suggesting the first order kinetic for photodecolorization and therefore the slopes of the plots can be corresponded to experimental rate constants. Rate constants of photodecolorization at buffer were calculated 3.7×10^{-3}, 2.5×10^{-2} and 3.0×10^{-2} min^{-1} for pHs of 7, 9 and 11 respectively. The rate constants of dye photodegradation at non-buffer pHs were evaluated 8.8×10^{-2}, 7.4×10^{-2}, 1.1×10^{-1} $h^{-1}$for pHs of 5, 7 and 9 respectively. It can be deduced that at buffer and non-buffer media, pHs of 9 and 11 are the best media among the investigated media. On the other hand, it is obvious that at buffer media, the dye is decolorized more efficiently with higher rate constant with respect to non-buffer media. Therefore it can be said, the photodecolorization process is pH-dependent.

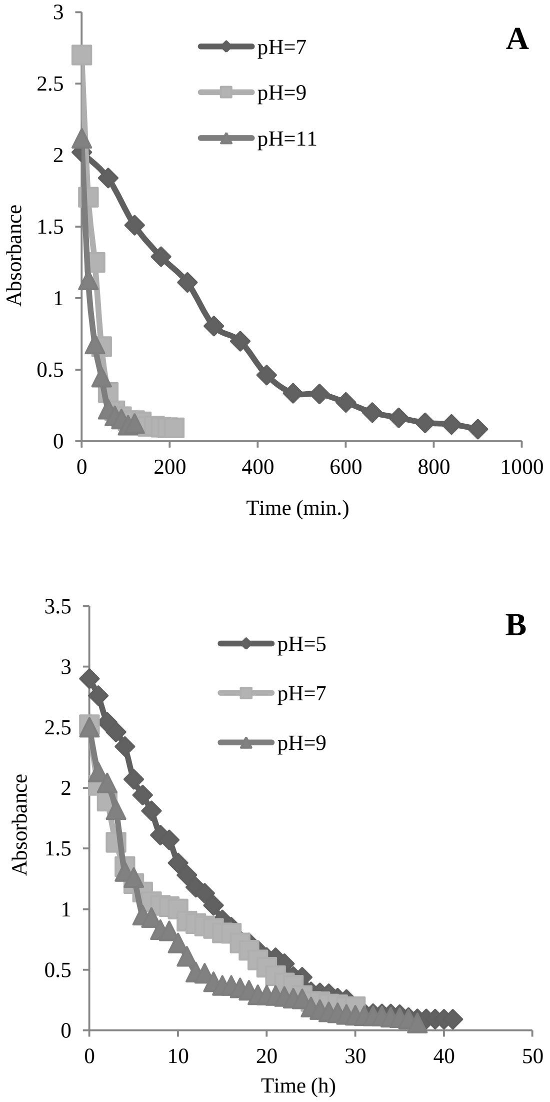

Fig. 1- The absorbance-irradiation time plots at buffer (A) and non-buffer (B) media.

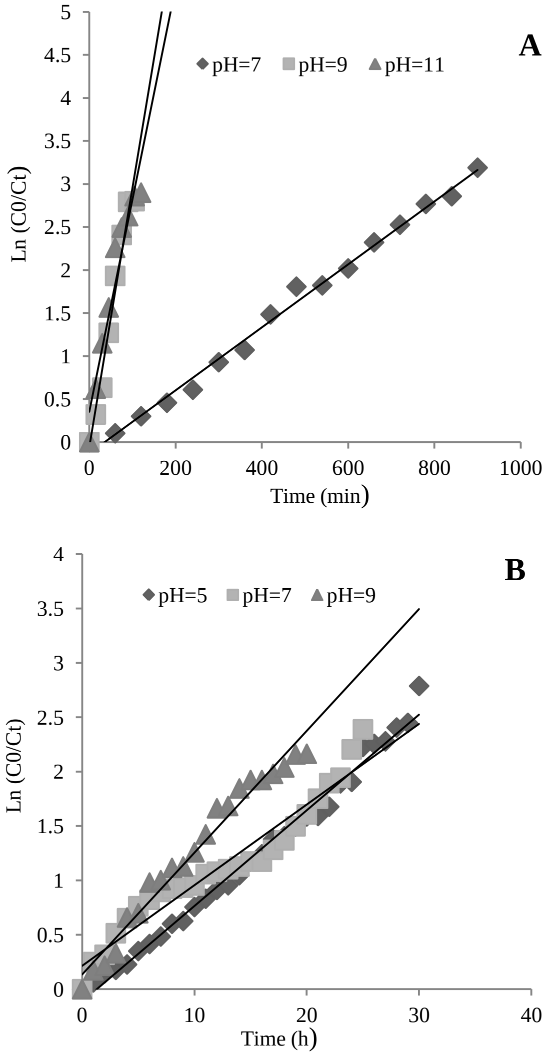

Fig. 2- The Ln (C_0/C_t) versus irradiation time at buffer (A) and non-buffer (B) media.

pH effect on direct photolysis

Fig. 3 (A and B) presents the rate versus initial concentration plot at buffer and non-buffer media. As shown in Fig. 3, the rate-concentration dependence is completely linear so that the photodecolorization rate increases as the initial concentration is increased. It is obvious from Fig. 3 that rate-concentration dependence at pH=11 is more notable than two pHs of 5 and 7 for both buffer and non-buffer media. This observation can be related to notable change in dye structure in basic pH with respect to acidic or neutral pHs. Also, it is to be noted that the rate-concentration dependence at pH=9 in non-buffer media is more important with respect to buffer media.

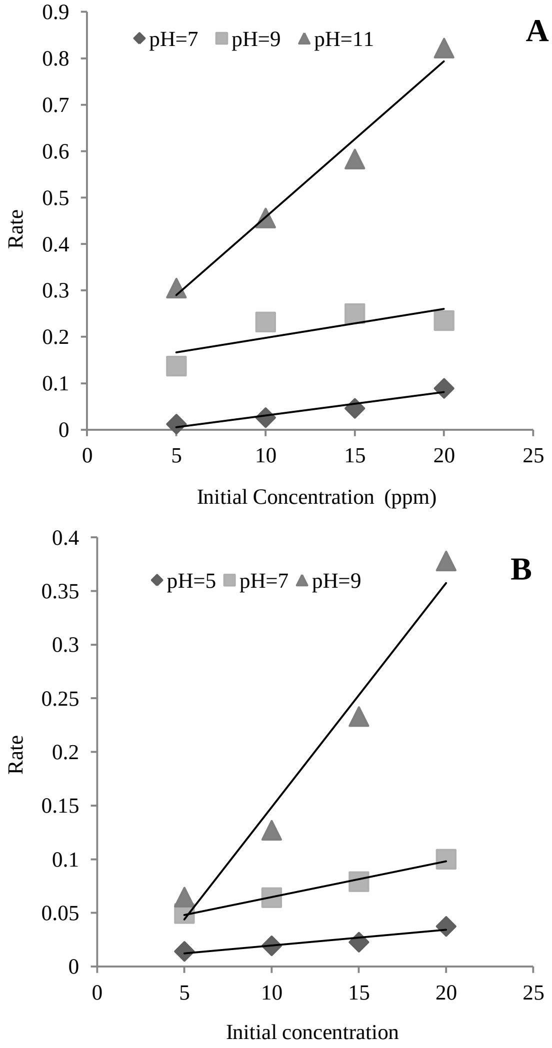

Fig. 3- The rate versus initial concentration at buffer (A) and non-buffer (B) media.

Photocatalytic decolorization

Photocatalytic removal of dye in the presence of nano-titanium dioxide as photocatalyst under UV-illumination is depicted in Fig. 4. It is suggested that excitation of one electron from the valence band of the TiO_2 to its conduction band leading to electron/hole (e^-/h^+) pairs generation under UV radiation (Scheme 1). The e^-/h^+ pairs can produce various oxidizing agents such as hydroxyl radicals, superoxide anion radicals and hydrogen peroxide. These oxidant agents are responsible for any dye decolorization in the considered media.

$$TiO_2 + h\nu \rightarrow e^- + h^+$$

$$h^+ + H_2O(TiO_2) \rightarrow {}^\bullet OH(TiO_2) + H^+$$

$$h^+ + OH(TiO_2)^- \rightarrow {}^\bullet OH(TiO_2)$$

$$e^- + O_2 \rightarrow O_2^{\bullet -}$$

$$O_2^{\bullet -} + HO_2^\bullet + H^+ \rightarrow H_2O_2 + O_2$$

$$^\bullet OH(TiO_2) + D \rightarrow \text{intermediates} \rightarrow P$$

Scheme 1

After direct photolysis of dye at buffer and non-buffer pHs, we decided to study photocatalytic degradation of dye at non-buffer media. Therefore optimization of some parameters such as irradiation time, photocatalyst amount and initial concentration was done.

Catalyst loading effect

Fig. 4 shows the absorbance of residual dye concentration versus catalyst amount at non-buffer pHs. As seen in the Fig. 4, the amount of 10, 20 and 25 mg were found to be optimum amounts of photocatalyst at pHs of 5, 7 and 9 respectively for efficient dye degradation and in the presence of higher amount of catalyst, the dye degradation was suppressed, probably due to UV-light scattering and therefore reduction of light penetration into the bulk solution leading to low efficiency in dye photodecolorization (8, 18-20).

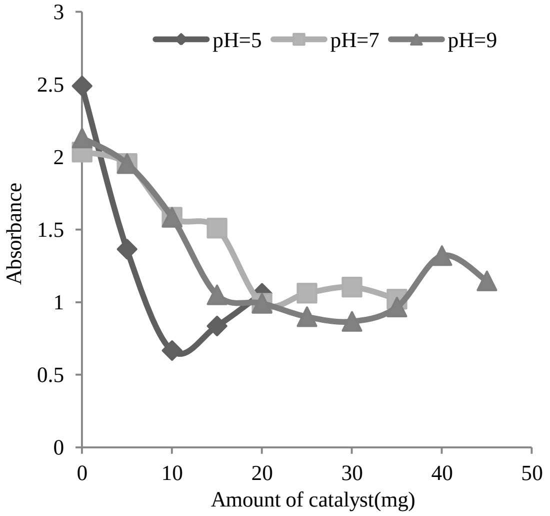

Fig. 4- The absorbance of residual concentration versus catalyst amount at non-buffer pHs after 1h.

Kinetic study

Fig. 5 depicts the irradiation time dependence of dye decolorization in the presence of optimum amount of catalyst at each pH. The exponentially decrease of dye residual absorbance suggests that the decolorization process obey from first order kinetics.

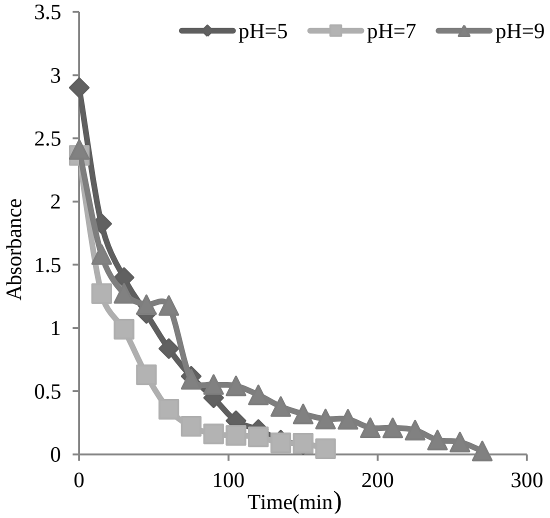

Fig. 5- The absorbance of residual dye versus irradiation time.

Therefore if the LnC_0/C_t is sketched versus the irradiation time and being a linear form, the slope of the plot will be equal to pseudo-rate constant for decolorization process. These mentioned plots are shown in Fig. 6 for pHs of 5, 7 and 9. Based on the plots in Fig. 6, the photodecolorization rate constants were evaluated 2.37×10^{-2}, 2.24×10^{-2} and 1.13×10^{-2} min^{-1} for pHs of 5, 7 and 9 respectively. It seems that the rate constants at two pHs of 5 and 7 are similar and are about twice with respect to pH of 7.

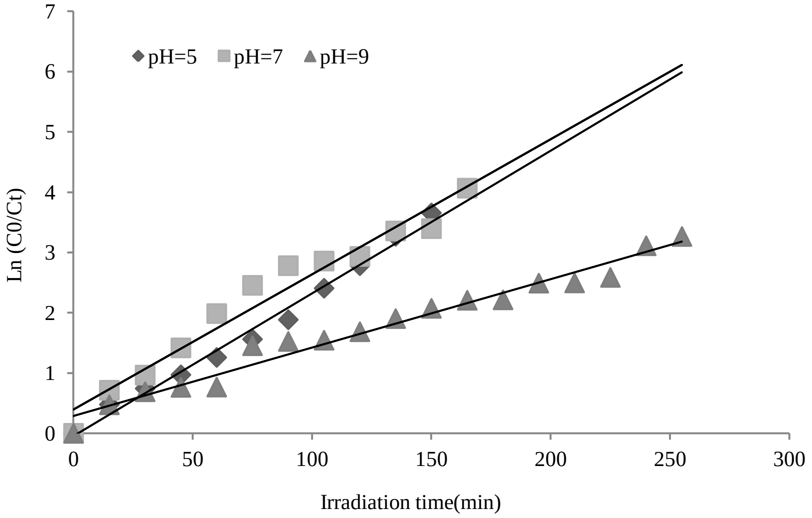

Fig. 6- The Ln (C_0/C_t) versus irradiation time at non-buffer media.

The dye adsorption on photocatalyst surface is described by modified Langmuir-Hinshelwood (L-H) kinetic model (21-23). In L-H model the reaction rate is proportional to the surface coverage θ:

$$\theta = \frac{KC_0}{1 + KC_0 + K_s C_s}$$

Where *K* is the adsorption coefficient for target molecules; *Ks* is the adsorption coefficient of solvent; C_0 and C_s are the initial concentration of substrate and solvent concentration respectively. The photocatalytic degradation rate constant at photocatalyst surface can be derived from a single-component L-H kinetic rate expression as formulated in below:

$$Rate = R = \frac{-dc}{dt} = k_r \theta = k_r \frac{KC_0}{1 + KC_0 + K_s C_s}$$

Where k_r is decolorization rate constant at surface. If K_A is defined as:

$$K_A = \frac{K}{1 + K_s C_s}$$

The rate expression will be as:

$$Rate = R = \frac{-dc}{dt} = k_r \theta = k_r \frac{K_A C_0}{1 + K_A C_0}$$

This equation can be rearranged to another form as it follows:

$$\frac{1}{R} = \frac{1}{k_r K_A C_0} + \frac{1}{k_r}$$

The linear plots of $1/R_{L\text{-}H}$ *versus* $1/C_0$ for dye at pHs of 5, 7 and 9 have been depicted at Fig. 7 that shows plots with good linearity character indicating L-H model behavior at above pHs.

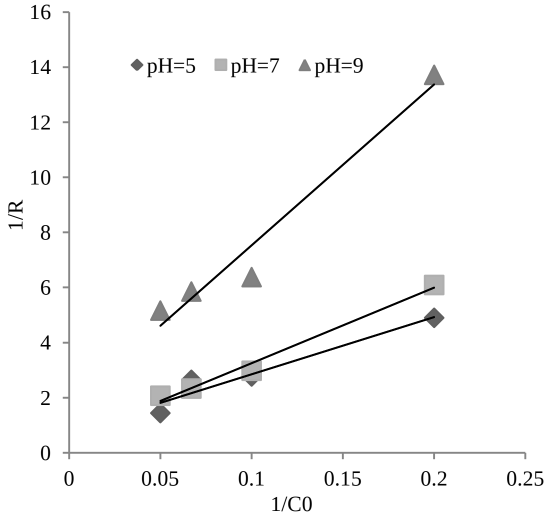

Fig. 7- The plots of 1/R vs. 1/C_0 at various pHs after 1h (Langmuir-Hinshelwood kinetics model)

The observed rate constant of photocatalytic decolorization, k_{obs} and dye decolorization, half-life, $t_{1/2}$, adsorption constant, K_A, and the L-H rate constant and the apparent reaction rate constant k_r for dye on photocatalyst at various pH are presented in Table 1.

Table 1- Kinetic and thermodynamic parameters in photocatalytic decolorization of dye at various pH at room temperature.

Dye	pH=5	pH=7	pH=9
k_{obs} (min^{-1})	2.37×10^{-2}	2.24×10^{-2}	1.13×10^{-2}
$t_{1/2}$ (min)	29.24	30.94	61.33
K_A (L. mg^{-1})	3.64×10^{-2}	1.38×10^{-2}	2.90×10^{-2}
k_r (mg. min^{-1}. L^{-1})	1.29	1.98	0.59

As seen in table1, observed photodegradation rate constant, k_{obs}, apparent reaction rate constant (k_r) and degradation half time, $t_{1/2}$ are similar at pHs of 5 and 7 and are higher than the ones at pH=9. The maximum and minimum values of K_A are related to pH=5 and 7 respectively.

Discussion and conclusion

In this work we presented direct photodecolorization and photocatalytic decolorization of Lauth's violet at various buffer and non-buffer pHs with regard to some physicochemical factors such as irradiation time, concentration and photocatalyst amounts. In direct photolysis, buffer media were found to be more suitable for photodecolorization than non-buffer media. The best pH was 5 for direct photocatalysis process in our conditions. In photocatalytic decolorization, the pHs of 5 and 7 were found to be similar for photocatalytic removal. After optimization of physicochemical parameters, rate constants, adsorption constants and degradation rates at surface were calculated for all media. Rate constants of direct photolysis at buffer media were evaluated as 3.7×10^{-3}, 2.5×10^{-2} and 3.0×10^{-2} min^{-1} for pHs of 7, 9 and 11 respectively. Also the rate constants of dye photolysis at non-buffer pHs were found as 8.8×10^{-2}, 7.4×10^{-2}, 1.1×10^{-1} $h^{-1}$for pHs of 5, 7 and 9 respectively.

Acknowledgement

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رنگ زدایی نورکافتی و نورکافتی کاتالیزوری رنگ لاتز ویولت با استفاده از نانو تیتانیم دی اکسید: یک مطالعه سینتیکی

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چکیده

نور کافتی و نورکافت کاتالیزوری با استفاده از نانو تیتانیوم دی اکسید برای تخریب رنگ لاتز ویولت در محیط‌های با اسیدیته بافری و غیر بافری اجرا شد. اثر شاخص‌های مؤثر مانند غلظت اولیه رنگ، اسیدیته، زمان تابش و مقدار کاتالیزور در یک سیستم فوتوراکتور مجهز به لامپ پرفشار جیوه بررسی شدند. روش اسپکتروفوتومتری تخریب کمابیش کامل رنگ را نشان دادند. رنگ زدایی از سینتیک شبه درجه یک پیروی کرد. ثابت‌های سرعت مشاهده شده (k_{obs}) نورکافت مستقیم و نورکافت فوتوکاتالیزوری در همه اسیدیته‌ها مورد نظر ارزیابی شدند. ثابت‌های سرعت رنگ زدایی در محیط بافری به مقدارهای $۳/۷ \times ۱۰^{-۳}$، $۲/۵ \times ۱۰^{-۲}$ و $۳/۰ \times ۱۰^{-۲}$ بر دقیقه در اسیدیته‌های ۷، ۹ و ۱۱ و در محیط غیربافری به مقدارهای $۸/۸ \times ۱۰^{-۲}$، $۷/۴ \times ۱۰^{-۲}$ و $۱/۱ \times ۱۰^{-۱}$ بر دقیقه در اسیدیته‌های ۵، ۷ و ۹ ارزیابی شدند. همچنین، ثابت‌های سرعت رنگ زدایی کاتالیزوری در محیط غیر بافری در اسیدیته‌های اسیدی، خنثی و بازی به دست آورده شد. علاوه بر این، ثابت‌های جذب (K_A) و سرعت‌های تخریب در سطح(k_r) در اسیدیته‌های مختلف محاسبه شدند.

واژه‌های کلیدی: سینتیک، لاتز ویولت، رنگ زدایی، نانو فوتوکاتالیزور

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[*] نویسنده مسؤول مکاتبات

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