
Kinetics of dye removal using Fe₃O₄ nanoparticles and pulsed white-LED illumination

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Received: 01.10.2019

Abstract. Removal of dyes with the aid of photocatalytic nanomaterials illuminated with continuous-light sources has been given substantial attention in the recent years. In the present work we study the efficiency of dye degradation using some alternative photocatalytic nanoparticles under condition of pulsed illumination. Our specific purpose is to investigate the removal of rhodamine 6G dye basing on suspended Fe₃O₄ solution. The experiments are carried out in the batch mode when the effect of the exposition time (ranging from 30 to 150 min) on the dye removal is examined under both continuous and pulsed white-LED illuminations. Different pulsed-light frequencies and duty cycles are tested. We estimate the concentration of rhodamine 6G in the mixed solution following from its absorption spectrum measured with a UV-Vis spectrometer and determine in this manner the percentage of dye removal. Our main conclusion is that Fe₃O₄ nanoparticles enable removing efficiently the rhodamine 6G dye under pulsed white-LED illumination. In particular, more than 90% of the dye is removed when the duty cycle is equal to 25% and the frequency to 30 kHz. The equilibrium state of this process is achieved in about 60 min.

Keywords: adsorption, dyes, photocatalysts, magnetic nanoparticles.

UDC: 535.34+535.8

1. Introduction

Nowadays dyes are widely used in many industries associated with textiles, paints, rubber plastics, paper, cosmetics etc. They are considered as one of the key factors that affect environmental problems globally. In this regard, numerous types of eco-friendly and acceptable approaches have been developed to remove such dye effluents as, e.g., adsorption, coagulation/precipitation and aerobic/anaerobic processes [1, 2]. Although target pollutants are eliminated well by these methods, it is still possible that they are partly transferred from one to another phase. As a consequence, further treatments are necessary whenever by-product or some other types of contaminants are additionally generated. In order to complete oxidation of organic compounds to harmless products such as carbon dioxide and water molecules, such advanced light-induced oxidation processes as a one-stop system are more economically efficient than many traditional systems [3–10]. The mechanism of these processes can be briefly explained as follows. As incident light falls on a surface of adsorbent catalyst, the electrons in the valence band are excited and move up into the conduction band, leaving the holes there. The holes interact continuously with water molecules as donors, thus generating free hydroxyl radicals which have a strong oxidizing power responsible for degradation of pollutants. The oxidative reactions of these free radicals with

the present organic dyes finally yield in biodegradable intermediates and a mineralization process. As an example, sulphide-based photocatalysts have been selected for the advanced oxidation process. Mehrizad et al. have reported a reduction of rhodamine 6G, using different nanocomposites such as ZnS/C or ZnS/polyaniline under UV irradiation [11]. The mechanism of photocatalytic degradation has been explained well by a Langmuir–Hinshelwood kinetics model [11, 12]. Furthermore, removal of rhodamine 6G with Ag/ZnS/C under visible light has been reported [13]. A specific mechanism of the photocatalytic degradation has been attributed to photosensitizing and surface plasmonic effects of carbon nanotubes and Ag nanoparticles.

In addition to sulphide-based photocatalysts, photocatalysts based on oxygen are also considered as a real alternative for the advanced oxidation processes known from the literature. For instance, the removal of dyes with TiO₂ nanoparticles under continuous illumination by various light sources such as UV, visible or sunlight has been considered [7–10]. Although continuous illumination can indeed be beneficial in the photocatalytic reactions, the efficiency of dye degradation under pulsed illumination, which is based on the alternative photocatalytic nanoparticles, has not yet been reported.

In the present study, we select magnetic Fe₃O₄ nanoparticles, instead of TiO₂ ones. They can eliminate dye contaminants basing upon advanced oxidation processes [5, 6] and, moreover, magnetic dye-adsorbent catalysts can be easily removed from the treated water through external magnetic-separation processes, thus making their recycling possible. We select a basic rhodamine 6G dye widely used in textile industry, instead of methylene blue or rhodamine B. The reason is that rhodamine 6G reveals strong adsorption onto solid matters and is soluble in water. Below we discuss the efficiency of pulsed white-LED light, as opposed to continuous white-LED radiation, in the process of removing rhodamine 6G from industrial effluents with the magnetic Fe₃O₄ nanoparticles.

2. Materials and methods

Rhodamine 6G dye agent and magnetic Fe₃O₄ nanoparticles (with the diameters 50–100 nm) were purchased from Sigma Aldrich, USA. A stock solution of 0.1 mM rhodamine 6G was prepared by dissolving the appropriate amount of dye in deionized water. 10 mg of Fe₃O₄ nanoparticles were dispersed in 100 mL of deionized water to obtain the concentration 100 mg/L. The studies of photocatalytic degradation were carried out by mixing 1 mL of rhodamine 6G solution with 99 mL of Fe₃O₄ solution at the room temperature (26°C), as shown in Fig. 1. The mixed solution was stirred under the constant stirring speed 4000 rpm. A white-LED light source was taken to illuminate a sample in both pulsed and continuous modes. Under the pulsed illumination, the frequencies were equal to 0.5–30 kHz, whereas the duty cycles varied from 0 to 100%.

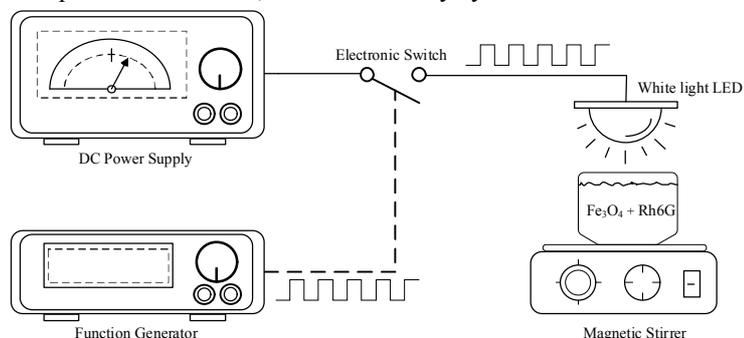


Fig. 1. Schematic illustration of stirring a sample and illuminating it by white-LED light.

For each of specified intervals of exposition time, every mixed sample was centrifuged at 4000 rpm for 15 min. The supernatant was then characterized using its absorption spectrum measured with a UV–Vis spectrophotometer (AvaSpec-2048, USA), as shown in Fig. 2.

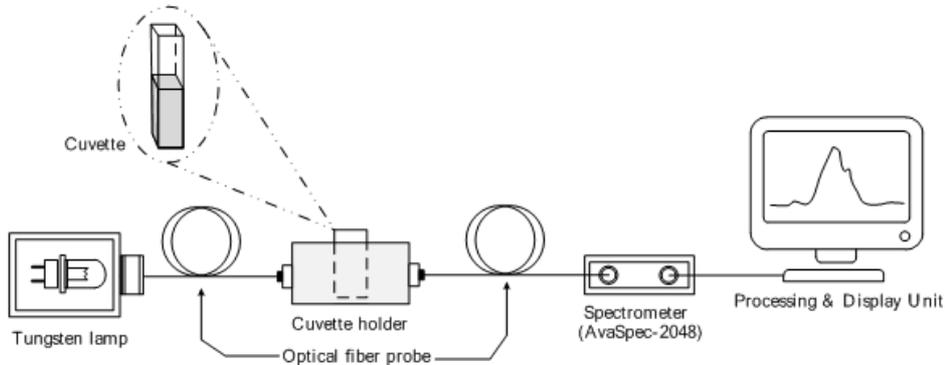


Fig. 2. A scheme of investigation of supernatant of a mixed sample at different exposition times, using a UV-Vis spectrophotometer.

The peak absorbance detected in each spectrum at the wavelength 530 nm was used for determining the initial and final concentrations of rhodamine 6G. This was done with the aid of calibration curve described as $A = 79289C - 0.0032$. Here A and C are the absorbance and the concentration of rhodamine 6G, respectively. The UV-Vis spectra for all the samples were reported in Ref. [14]. We calculated the percentage of dye removal, using the relation

$$\%Dye\ removal = \frac{C_0 - C_e}{C_0} \times 100, \quad (1)$$

where C_0 and C_e denote respectively the initial and final concentrations of rhodamine 6G at the equilibrium state.

In order to manipulate a 3 W white-LED in its pulsed mode, a driver circuit was employed (see Fig. 3). The circuit was designed for converting a logic-level pulse (0–5 V) to a higher-voltage pulse (0–12 V) to turn on a high-power LED. A function generator provided square-wave pulses to an NPN transistor (Part number: BC337). A 12 V DC power supply was applied to a source terminal of a p-channel MOSFET (Part number: IRF9540N). Finally, the output signal from a drain terminal was fed to a high-power LED.

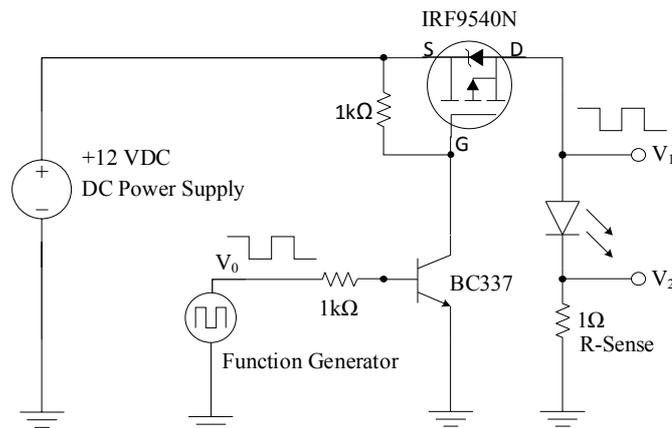


Fig. 3. Design of our home-made electronic-pulse circuit attached to a white-LED light source.

The duty cycle of the optical pulse was determined as follows:

$$Duty\ cycle = \frac{\tau}{T} \times 100\% , \quad (2)$$

where τ and T are respectively the optical pulse width and the “on”-period of the LED. In order to investigate the effect of duty cycle of the white-LED light on the dye removal, we exposed the samples to this light operated at five different duty cycles: 0, 25, 50, 75 and 100%. The exposition times were equal to 0, 30, 60, 90, 120 and 150 min, while the frequency of the white-LED light was fixed at 1 kHz. To study the effect of frequency of the white-LED on the dye removal, we used four different frequencies: 0.5, 1, 10 and 30 kHz. The exposition times were the same as above and the duty cycle was fixed at 25%. Finally, in order to obtain reliable results, we used three duplicate experimental runs under each experimental condition. The relevant error for each of experimental series was less than 5%.

3. Results and discussion

Since the absorption is the main characteristics that evaluates the photocatalytic performance of the magnetic Fe₃O₄ nanoparticles mixed with rhodamine 6G under the white-LED illumination, we measure the absorption spectra for the mixed-solution samples, using the UV-Vis spectrometer as reported earlier [11]. In brief, the absorption band of the Fe₃O₄ nanoparticles mixed with rhodamine 6G is found at 450–650 nm and a narrow peak absorbance is seen at the central wavelength 530 nm. This corresponds to the bandgap 2.34 eV. The above value indicates high enough photocatalytic performance of the Fe₃O₄ nanoparticles.

We have also shown that the transformation of magnetic dye-adsorbent catalyst to magnetic photocatalyst under the white-LED illumination is accompanied by changing mechanism for the dye removal from the aqueous solution – from the surface adsorption to the photocatalytic degradation. Basing on this mechanism of photocatalyst behaviour, the white-LED light that acts upon the magnetic Fe₃O₄ nanoparticles has a supra-bandgap energy, resulting in strong association of photo-generated electron–hole pairs. Further on, these pairs spread towards the surface where the electrons adsorb hydroxide and the holes adsorb oxygen molecules, to form free radicals before the holes and the electrons become involved into recombination process with a significant probability. Therefore, as the Fe₃O₄ nanoparticles are illuminated by the white-LED light with the photon energy comparable to their bandgap energy, they are able to generate highly active oxidizing and reducing sites, which can potentially oxidize a large amount of rhodamine 6G.

Fig. 4 compares the photocatalytic-degradation tests performed for the magnetic Fe₃O₄ nanoparticles mixed with rhodamine 6G at different duty cycles and a constant frequency (1 kHz). We find that the removal kinetics is dependent of both the duty cycle and the exposition time. At first, the percentage of dye removal increases with increasing exposition time and then it tends to remain constant at longer exposition times. Under pulsed white-LED illumination with the duty cycles 25, 50 and 75%, the photocatalytic performance of the Fe₃O₄ nanoparticles reaches its equilibrium state at 120 min, although the equilibrium is reached earlier (at 60 min) in the case of continuous white-LED illumination (the duty cycle 100%). At a certain exposition time (e.g., 60 min), the percentage of dye removal achieved with the continuous white-LED exposure (95.99%) is still higher than that obtained under pulsed white-LED exposure (85.64%). The percentage of dye removal decreases when the duty cycle is reduced, because the less photon numbers constrain the process of formation of electron–hole pairs and so hinder production of hydroxyl and superoxide.

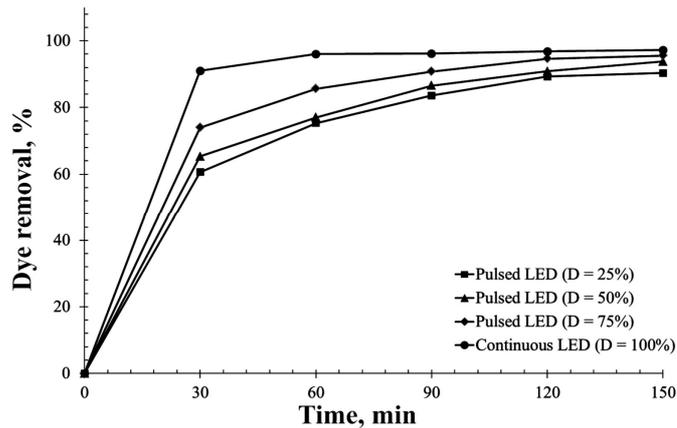


Fig. 4. Kinetics of dye removal by magnetic Fe_3O_4 nanoparticles mixed with rhodamine 6G in a solution formed under pulsed white-LED illumination at a constant frequency (1 kHz) and different duty cycles D (25, 50, 75 and 100%).

We have varied the frequency of pulsed white-LED exposure (0.5, 1, 10 and 30 kHz) in case of the duty cycle 25%. The aim is to examine whether the optimal conditions might result in the percentage of dye removal close to that observed under continuous white-LED exposure in the equilibrium state (60 min). The dye-removal kinetics achieved at four different frequencies of the pulsed white-LED exposure ranging from 0.5 to 30 kHz are displayed in Fig. 5. Here the duty cycle remains constant, being equal to 25%. We have found that the kinetics depends on both the operating frequency and the exposition time. The percentage of dye removal increases with increasing exposition time and then remains invariable. Furthermore, the dye removal is firmly influenced by the frequency of the pulsed white LED. Namely, the dye-removal percentage increases with increasing frequency and increasing exposition time. Interestingly, the kinetics observed under the pulsed white-LED illumination at the frequency 30 kHz is quite similar to that detected at the continuous white-LED illumination. In other words, the highest percentage of dye removal reaches its equilibrium at 60 min. The dye-removal percentage under this pulsed white-LED exposure is 92.25%, while the dye removal under the continuous white-LED exposure is only slightly higher, 95.99%. Therefore, we conclude that the pulsed white-LED illumination performed at the frequency 30 kHz and a constant duty cycle (25%) provides a shortened time of

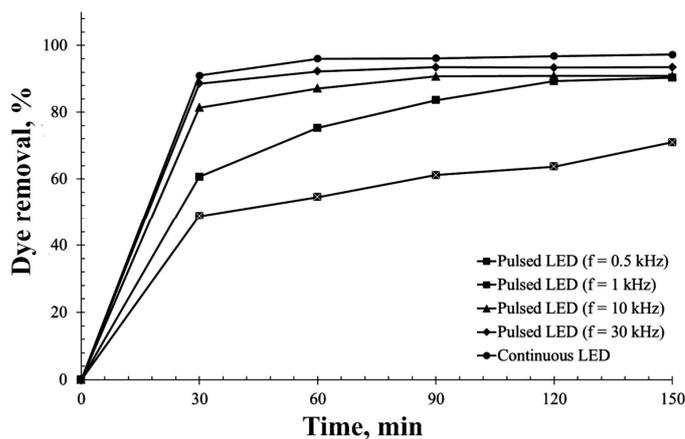


Fig. 5. Kinetics of dye removal by magnetic Fe_3O_4 nanoparticles mixed with rhodamine 6G in a solution formed under continuous and pulsed white-LED exposures at different frequencies f (0.5, 1, 10 and 30 kHz) and a constant duty cycle (25%).

reaching the equilibrium (near 60 min). This corresponds to the condition optimal for the highest percentage of dye removal achieved with the magnetic Fe₃O₄ nanoparticles. The reason is that, under this condition, there still remain a sufficient number of adsorption sites for unsaturated magnetic Fe₃O₄ nanoparticles during the adsorption process.

4. Conclusion

In the present work we report on removal of the rhodamine 6G dye using the magnetic Fe₃O₄ nanoparticles. The corresponding mechanisms are the surface adsorption and the photocatalytic degradation occurring at the continuous and pulsed white-LED illuminations. The concentration of rhodamine 6G in the mixed solution, which is necessary for determining the percentage of dye removal, has been estimated from the absorption spectrum detected using the UV-Vis spectrometer. It has been found that the dye-removal kinetics depends on the operating frequency, the duty cycle and the exposition time. In particular, the percentages of dye removal higher than 90% can be achieved from the pulsed white-LED illumination at the times of the order of 60 min, which are shorter than those typical for the continuous white-LED illumination. The optimal conditions for the pulsed white-LED illumination, which ensure the highest percentages of dye removal, are the operating frequency 30 kHz and the duty cycle 25%.

Acknowledgement

This research has been funded by the King Mongkut's Institute of Technology Ladkrabang.

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Pattareeya Damrongsak, Bhanupol Klongratog, Sirichai Hoomsuk and Kitsakorn Locharoenrat. 2019. Kinetics of dye removal using Fe₃O₄ nanoparticles and pulsed white-LED illumination. *Ukr.J.Phys.Opt.* **20**: 168 – 174. doi: 10.3116/16091833/20/4/168/2019

***Анотація.** В останні роки надається значна увага видаленню барвників за допомогою фотокаталітичних наноматеріалів, освітлених джерелами неперервного світла. У цій праці вивчено ефективність деградації барвника з використанням альтернативних фотокаталітичних наночастинок за умови імпульсного освітлення. Наша конкретна мета – вивчити видалення барвника родаміну 6G за допомогою суспендованого розчину Fe₃O₄. Експерименти проводилися в пакетному режимі, коли вплив часу експозиції (в межах від 30 до 150 хв) на видалення барвника досліджують і при неперервному, і при імпульсному світлодіодному освітленні. Тестувалися різні частоти імпульсів світла та різні параметри прогальності. Концентрацію родаміну 6G у змішаному розчині було оцінено, виходячи з його спектра поглинання, виміряного спектрометром ультрафіолетового та видимого випромінювання, і так визначено відсоток видалення барвника. Основний висновок полягає в тому, що наночастилки Fe₃O₄ дають змогу ефективно видаляти барвник родаміну 6G під дією імпульсного освітлення білим світлодіодом. Зокрема, більше ніж 90% барвника видаляється за умов, коли прогальність дорівнює 25%, а частота – 30 кГц. Стан рівноваги цього процесу досягають приблизно за 60 хв.*