

Photodecomposition of direct red 81 (5-solamin) by using nano sized zinc oxide deposited on glass beads in neutral and alkaline pH and various atmospheres

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Abstract

This research describes photo degradation of direct red 81(5-solamin) in the presence of zinc oxide nano-sized catalyst supported on granule glass under UV light irradiation. The effects of some parameters such as various pH and different atmosphere on photo degradation efficiency were studied. After various experiments it was revealed that among various atmospheres, at neutral medium, oxygen and air and at alkaline medium nitrogen and oxygen were found as the best atmosphere for photo-degradation. The rate constants of 0.007, 0.004, 0.001 and 0.001 mg/L.min were evaluated for air, oxygen, nitrogen, and argon atmospheres respectively at neutral while the rate constant values of 0.005, 0.004, 0.001 and 0.001 mg/L.min were found for alkaline conditions in the presence of nitrogen, oxygen, air, and argon atmospheres respectively.

Key words: Direct red 81(5-solamin), Photo degradation efficiency, UV light, Nano ZnO

Highlights

- Photodecomposition study of direct red 81 (5-solamin) in alkaline pH and various atmospheres were performed.
- Evaluation of pseudo first order rate constants of photodecomposition of direct red 81(5-solamin) in neutral pH and various atmospheres was carried out.
- Calculation of pseudo first order rate constants of photodecomposition of direct red 81 (5-solamin) in alkaline pH and various atmospheres was carried out.

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Introduction

The serious environmental impact of pollutants and the low efficiency of current remediation processes, conduct the environmentally friendly researchers for removal of these pollutants (1). Heterogeneous photo catalysis has attracted many attentions for presenting new approaches for purifying wastewaters. TiO₂ and ZnO have been extensively used as heterogeneous photo catalysts, mainly because of their high capacity for degradation of toxic and pollutant species via a simple procedure. The applications of the photo catalytic process, mostly involving TiO₂, have been extensively documented. Nowadays, thin films of photo catalysts containing high photocatalytic activity, high stability, and convenient reusability; have received more and more attention in industrially point of view (2-7).

ZnO is of especial interest, because of possibility for modification and control of size particles (8). ZnO thin films are prepared by different techniques such as

metal organic chemical vapor deposition, sol-gel, thermal evaporation, oxidation and anodizing (9). Sol-gel method is the most effective way for preparation of ZnO thin films (10), because this method is low-cost for deposition of homogeneous thin films with desired thickness.

The aim of this work is to prepare zinc oxide thin film on the surface of granule glass by sol-gel coating method. A commercial granule glass was successfully used as support for preparing nano-sized zinc oxide thin film on its surface. Then the supported zinc oxide thin films were employed as photo-catalyst in photocatalytic decolorization of direct red 81 (5-solamin) in aqueous solutions.

Direct red 8 (15-solamin) is a commercially pollutant dye that exist in wastewaters. This dye can effect on environment so that it is necessary to be removed from the wastewaters. The molecular structure of the titled dye is found in Fig. 1.

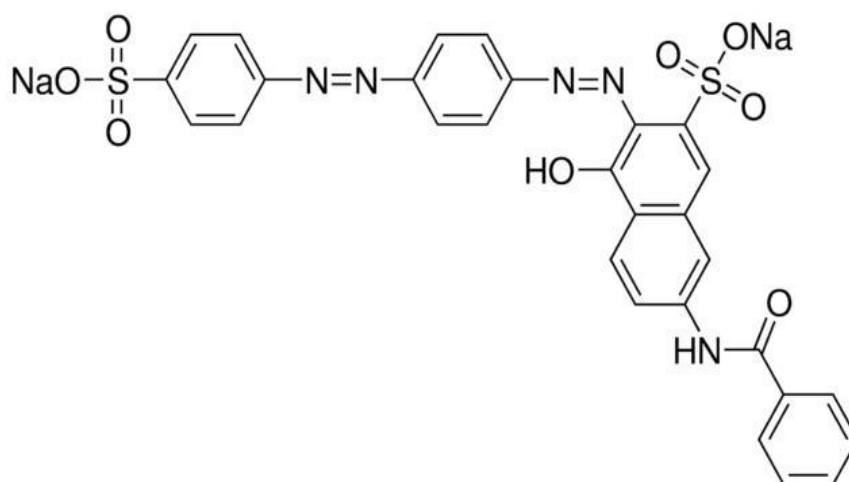


Fig. 1- Molecular structure of direct red 81(5-solamin)

Materials and methods

Materials and instruments

All chemicals were provided from Merck. To control pH, 0.01 M NaOH and HCl solutions were used. In all experiments doubly distilled water was used. Photochemical reactor equipped by four 8 w UV lamps was applied for photo decolorization experiments. UV-Visible spectrophotometer, Perkin Elmer Lambda25, was applied for spectral monitoring of dye concentrations. Metrohm -620 model of pH-meter was used for controlling solution pHs. Bruker D8 advanced X-ray diffractometer; Cu α radiation was used for XRD analyses. A Philips XL30 instrument was applied for Scanning electron microscopy (SEM) record.

Film deposition

Nanosized zinc oxide thin film was deposited on glass beads (diameter 3mm) by a method as following: Glass beads were pretreated with dilute hydrofluoric acid (5% v/v) for 24 h and washed thoroughly with distilled water, making a rough surface for better contact of zinc oxide thin film on its surface. Zinc oxide binary sol was added to the glass beads placed in a funnel and the excess of it was removed. The treated glass beads were subsequently placed in the furnace and pre-heated at 275 °C for 10 min and then post-heated at 450 °C for 1 hour. The deposition was repeated for 5 times to obtain films with different thickness (11).

Photolysis process

The photo catalytic decolorization experiments were performed in a simple photocell reactor, placed in a 25 °C water

bath. 5 g of granule glass supported with 5-layers of zinc oxide thin films was placed in 25 mL of 25 ppm dyes solution and then was illuminated with four 8W lamp (Philips; 365nm) placed at 5 cm far from the reaction mixture. At each desired times; the solution was separated and dye concentration was measured by spectrophotometer by the aid of calibration curves at those conditions.

Results

Characterization techniques for thin films

The structure and crystalline size of photo-catalyst were determined by XRD diffraction according to our previous report (10). X-ray diffraction showed zinc oxide structure with c-axis orientation (002). The surface of the films was observed by scanning electron microscopy as reported previously (11).

The SEM image showed homogeneity of deposited zinc oxide on glass beads. After these investigations, in continuation of other applications of this photocatalyst, it was used for degradation of titled dye at neutral and alkaline pHs in current research.

Photocatalytic activity

As shown in Fig. 2 (pH=7), in neutral medium, the dye was decolorized under oxygen and nitrogen atmospheres faster than air and argon atmospheres. It is suggested the dye is degraded oxidatively under oxygen and air while it is only decomposed under argon and nitrogen atmospheres. In Fig. 3 (pH=10), at alkaline medium, the dye is degraded more rapid under nitrogen and air atmospheres than air oxygen and argon atmospheres.

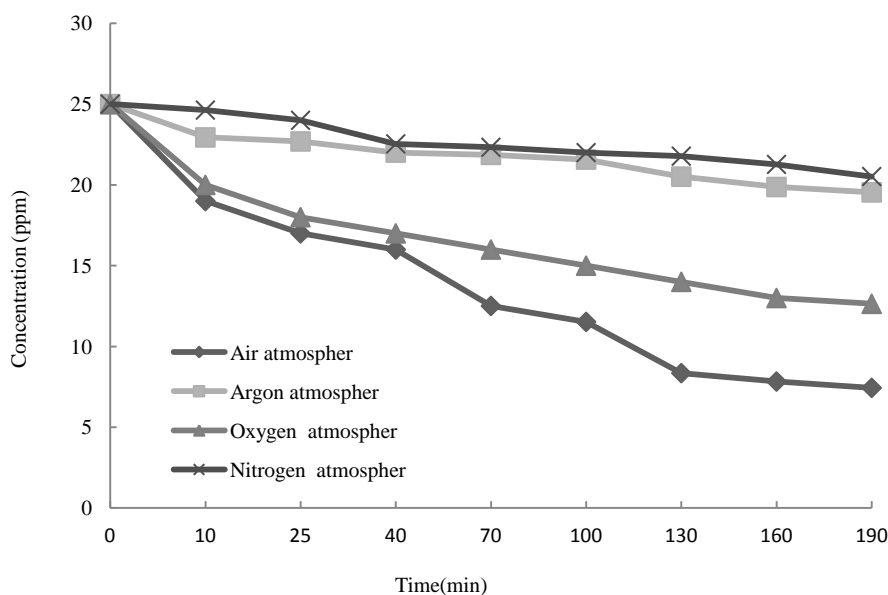


Fig. 2- Residual concentration of direct red 81(5-solamin) (25 ppm), in de-ionized water after photo catalytic decolorization under UV irradiation in neutral (pH=7) medium under various atmosphere

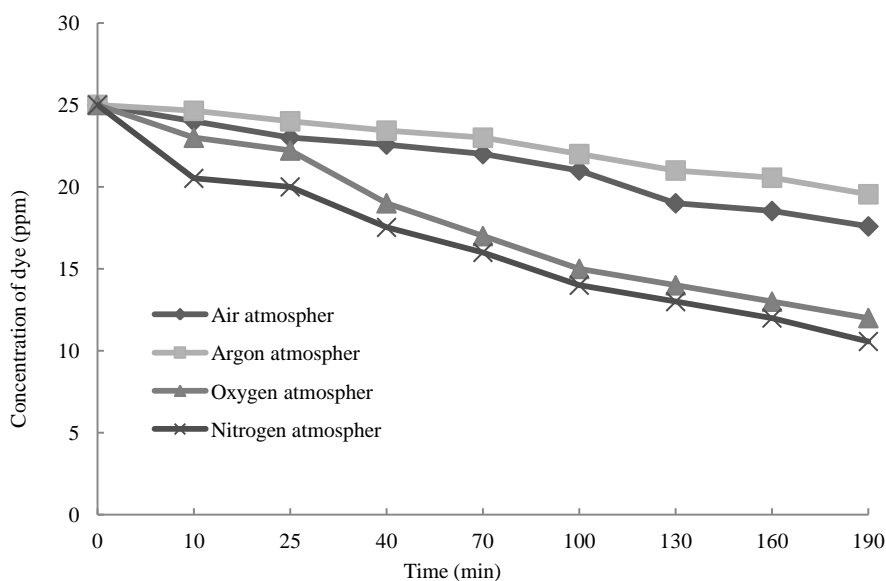


Fig. 3- Residual concentration of direct red 81(5-solamin) (25 ppm), in de-ionized water after photo catalytic decolorization under UV irradiation in alkaline (pH=10) medium under various atmosphere

For evaluation of the photodegradation rate constant under above conditions, the kinetic investigations were carried out based on the concentration-time plots in Fig. 2 and 3. Generally photo degradation of dyes are obeyed from first order kinetics if the plots of $\ln(C_0/C_t)$ versus time are shown as straightforward lines. For this

mean for two above considered pHs, the plots of $\ln(C_0/C_t)$ versus time was sketched that the related plots are illustrated in Fig. 4 and 5. The plots at all conditions were found to be linear after notable initial decrease (after 10 min.) that may be due to adsorption of dye on catalyst surface.

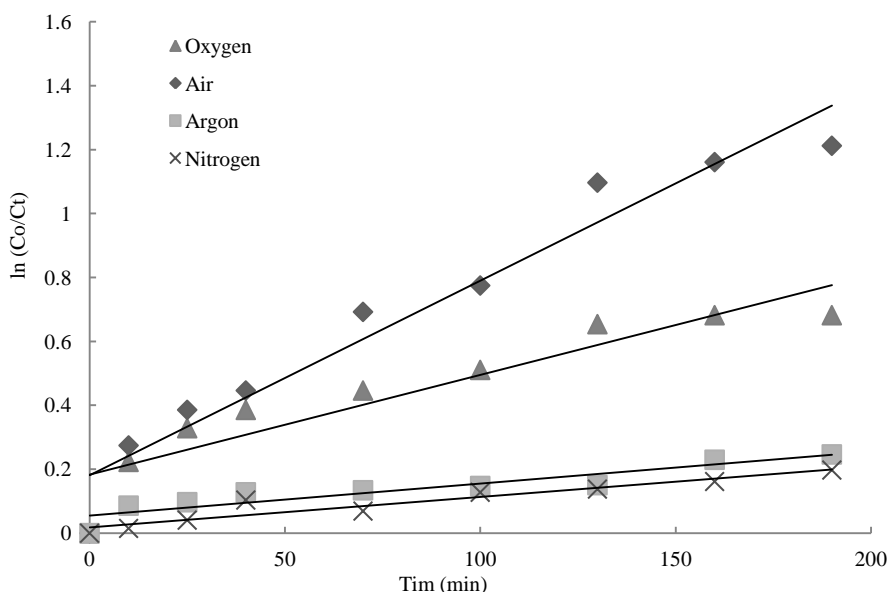


Fig. 4- $\ln(C_0/C_t)$ versus time (min.) for photo catalytic decolorization of direct red 81(5-solamin) under UV irradiation in neutral (pH=7) medium under various atmosphere

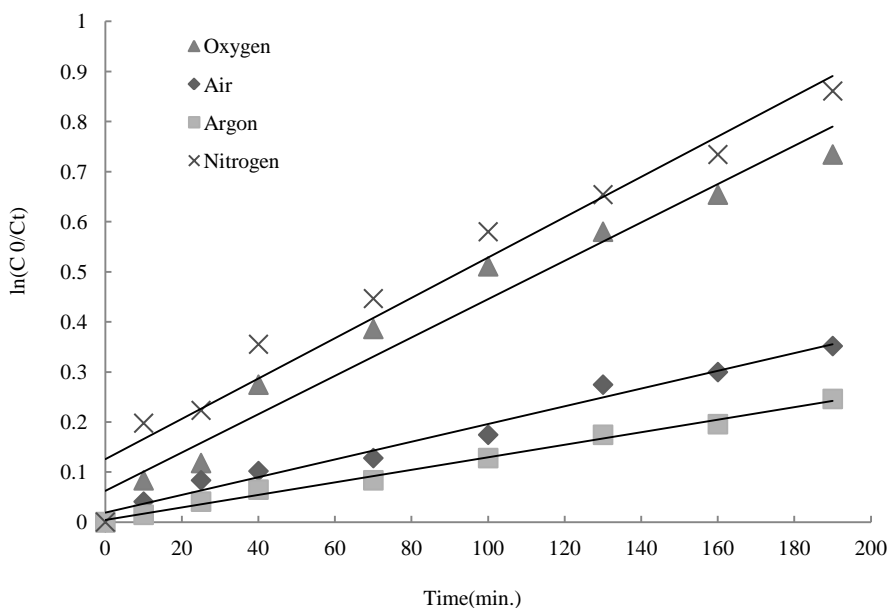


Fig. 5- $\ln(C_0/C_t)$ versus time (min.) for photo catalytic decolorization of direct red 81(5-solamin) under UV irradiation in alkaline (pH=10) medium under various atmosphere

The rate constants derived for neutral pH (Fig. 4) were evaluated to be 0.007, 0.004, 0.001 and 0.001 mg/L.min under air, oxygen, nitrogen, and argon atmosphere respectively. These values suggest that more degradation is occurred under air and oxygen atmosphere with respect to other

atmospheres. The rate constants evaluated for alkaline medium (Fig. 5), were found as 0.005, 0.004, 0.001 and 0.001 mg/L.min for nitrogen, oxygen, air, and argon atmospheres indicating more decolorization under nitrogen and oxygen atmospheres as compared with other ones.

Discussion and conclusion

In this work, we reported photo degradation of direct red 81(5-solamin) by nano-sized zinc oxide thin film supported on glass beads, at various atmospheres and different pHs. The titled dye was decolorized efficiently by using this photocatalytic system. Under considered atmospheres, pseudo first order was found as kinetic model. The rate constants of 0.007, 0.004, 0.001 and 0.001 mg/L.min. were evaluated for air, oxygen, nitrogen, and argon atmospheres respectively at neutral while the rate constant values of 0.005, 0.004, 0.001 and 0.001 mg/L.min were calculated under alkaline conditions for nitrogen, oxygen, air, and argon atmospheres respectively. Easy preparation, handling and separation of photocatalyst from solution are some advantages of this system. Improvement of photocatalytic activity of this system by doping of some metal on catalyst surface is under investigation in our library.

Acknowledgement

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رنگ زدایی نور کافتی رنگ دیرکت رد ۸۱ (۵-سولامین) با استفاده از روی اکسید نانو اندازه قرار داده شده روی بستر شیشه‌ای در اسیدپتته خنثی، قلیایی و اتمسفرهای مختلف

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چکیده

هدف از این پژوهش، تخریب نور کافتی توسط کاتالیزور روی اکسید نانو اندازه رنگ ۵-سولامین بر روی گلوله‌های شیشه‌ای تحت پرتودهی نور UV است. در این پژوهش، تخریب نور کافتی رنگ دیرکت رد ۸۱ (۵-سولامین) به عنوان یک آلاینده فاضلاب مطالعه شده است. همچنین، اثر متغیرهای اسیدپتته و اتمسفرهای مختلف روی کارایی تخریب نور کافتی مطالعه شد. اثر متغیرهای مختلف مانند اسیدپتته و اتمسفرهای مختلف در یک فوتوراکتور مجهز به چهار لامپ ۸ وات مطالعه شد. پیشرفت واکنش تخریب با اندازه گیری میزان جذب نمونه‌ها در طول موج حداکثر جذب دنبال شد. حداکثر جذب برای رنگ ۵-سولامین در طول موج ۵۱۰ نانومتر انجام می‌شود. آزمایش‌ها در دو محیط خنثی و قلیایی انجام گرفت. هر یک از این دو محیط تحت اتمسفرهای هوا، آرگون، نیتروژن و اکسیژن بررسی شد. پس از این بررسی‌ها مشخص شد که اتمسفرهای اکسیژن و هوا در محیط خنثی بهترین عملکرد و نیتروژن و اکسیژن در محیط قلیایی بهترین عملکرد را در بین چهار اتمسفر نشان می‌دهند. در پایان، مشخص شد که تخریب نور کافتی با استفاده از روی اکسید نانو اندازه لایه نشانی شده روی شیشه، گزینه جدیدی برای از بین بردن کارآمد فاضلاب است. نتایج نشان داد که رنگ یاد شده تحت اتمسفر و اسیدپتته‌های مختلف با سرعت‌های مختلف تخریب می‌شود.

واژه‌های کلیدی: رنگ دیرکت رد ۸۱ (۵-سولامین)، تخریب نورتایی کارآمد، پرتو UV، نانو ZnO

* نویسنده مسؤول مکاتبات