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Research Article

Photocatalytic Decomposition of Methyl Red Dye by Using Nanosized Zinc Oxide Deposited on Glass Beads in Various pH and Various Atmosphere

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Photocatalytic decomposition of methyl red (MR) as a pollutant in wastewater samples is investigated in this study. This photodegradation was investigated in water in neutral, alkaline, and acidic media under external UV light irradiation by zinc oxide nanosized catalysts on granule glass. The effect of four atmosphere types including air, nitrogen, oxygen, and argon was investigated. Finally, it was found that photodecomposition using nanosized ZnO layered on glass is a new alternative route for efficient wastewater treatment. The results showed that the titled dye is degraded by various rate under different atmosphere and pH.

1. Introduction

Nanotechnologies represent new and enabling platforms that promise to provide a broad range of novel uses and improved technologies for electrochemical, pharmaceutical, environmental, biological, and other scientific applications [1–5]. One of the reasons behind the intense interest is that nanotechnology permits the controlled synthesis of materials where at least one dimension of the structure is less than 100 nm. Newly, nanostructured materials have also been incorporated into sensor preparation for biological and pharmaceutical analyses [5–13]. Nanomaterials exhibit many advantages such as a large ratio of surface area to volume and high activity, and they have become one of the most promising materials [14–20]. In between, Zinc oxide (ZnO) is an important multifunctional material with applications such as varistors, gas sensors, SAW devices, transparent electrodes, and catalysts. The various applications of ZnO are due to its specific chemical, surface, and microstructural properties of [21–24].

With the increasing revolution in science and technology, there was a greater demand for newer chemicals which could be used in various industrial activities [25]. Organic dyes are one of the such many new chemicals which could be used in many industrial processes including fabric, woven, leather, textile, pulp and paper, tanneries, cosmetic, pharmaceuticals, and food processings [26]. Owing to the potential toxicity of the dyes and their visibility in surface waters, removal and degradation of them have attracted considerable attention worldwide. A wide range of approaches have been developed, amongst which is the heterogeneous photocatalysis involving zinc oxide (ZnO) that emerges as a promising new route for water purification process. Photocatalytic decolorization by semiconductors is a new, effective, and rapid technique for the removal of pollutants from water [27].

Dyes and their intermediates can undergo reductive processes and result in the formation of potentially carcinogenic or mutagenic compounds and detrimental impact towards the survival of microorganisms, aquatic life, and environmental matrix (water and soil) [28]. The ingestion of such contaminated water in the human body may also be susceptible to a broad spectrum of immune-suppression, respiratory, central nervous, neurobehavioral disorders presage as allergy, tissue necrosis, eye (or skin) infections and irritation, and even lung edema [29].

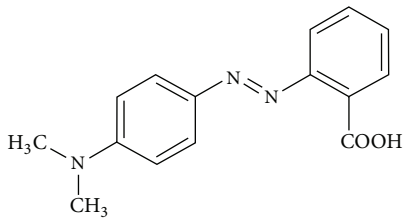

Figure 1: Schematic structure of methyl red.

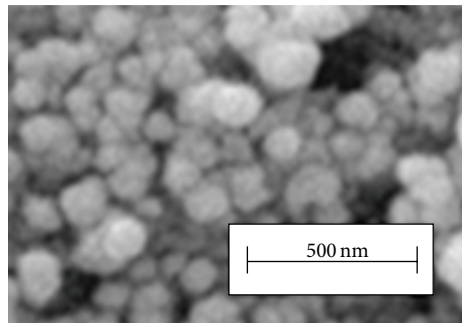

Figure 2: SEM image of ZnO nanoparticles.

Physical and biological treatments have been successfully applied until now, but these methods have their own drawbacks. The aerobic treatment process is associated with the formation and disposal of large amounts of biological sludge, while wastewater treated by the anaerobic treatment method does not lower down the pollutant contents to a satisfactory level. Activated charcoal adsorption and air-stripping methods are nondestructive, since they simply transfer the pollutants from water to another phase. They transfer it either to the atmosphere, which causes air pollution, or to a solid which is often disposed off in landfills or must be needed to regularly regenerate the adsorbent materials [30]. According to the above points, attention to wastewaters analysis increases in scientific researches [31–39].

As part of our aim is to produce zinc oxide thin film on granule glass by sol-gel coating method, in this paper, a commercial granule glass was successfully used as substrate to prepare nanosized zinc oxide thin film. The zinc oxide thin films have been employed in photocatalytic decolorization of MR in aqueous solutions. The schematic structure of methyl red is presented in Figure 1.

2. Experimental

2.1. General. All of the chemicals were analytical grade reagents without further purification and were purchased from Merck Company. The coating substrate (granule glass) was preheated at 275°C for 10 min in air after each coating. The sol-gel coating was made usually a day after the sol solution was prepared.

2.2. Film Deposition. Nanosized zinc oxide thin film was supported on glass beads (diameter of 3 mm) by the following method. 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 it. Zinc oxide binary sol was added to the glass beads placed in a funnel, and the excess of it was removed. They were subsequently placed in the furnace preheated at 275°C for 10 min, and then postheated at 450°C for 1 hour. The deposition was repeated for 5 times to obtain films with different thickness [39]. Figure 2 shows SEM image of ZnO nanoparticle.

2.3. Photocatalytic Measurement. The photocatalytic decolorization experiments were carried out in a simple oxidation reactor, placed in a 25°C water bath; 5 g of granule glass with 5 layers was placed in 25 mL 25 ppm dyes solution and was irradiated with four 8 W lamps (Philips; 365 nm) placed 5 cm above the solutions. For pH adjustment, 0.01 M NaOH and HCl solution was used to reach the desired pH. Concentration was measured by spectrophotometer (Perkin Elmer, Lambda 25). In all experiments, 25 mL of 25 ppm dyes solution was used with stirring during the irradiation.

3. Results and Discussion

3.1. Characterization Techniques for Thin Films. The structure and crystalline size were determined by XRD diffraction (Bruker D8 advanced X-ray diffractometer: Cu Kα radiation). X-ray diffraction shows zinc oxide structure with *c*-axis orientation (002) [40]. The surface of the films was observed by scanning electron microscopy (SEM) with a Philips XL30 [40].

3.2. Photocatalytic Activity. As shown in Figure 3(a), in neutral media, the dye is decolorized in oxygen and nitrogen better than air and argon. In Figure 3(b), in alkaline media, the dye is decolorized in nitrogen and air better than oxygen and argon. And finally in Figure 3(c), in acidic media, the dye is decolorized in argon and air better than oxygen and nitrogen.

For evaluating the photodegradation rate under the above conditions, the kinetic investigation was performed based on the concentration-time data in Figure 4. Generally, photodegradation of dyes obeyed first-order reactions if the plots of $\ln(C_0/C_t)$ versus time are straightforward lines. For this mean for the three above pHs, the plots of $\ln(C_0/C_t)$ versus time were sketched and have been illustrated in Figure 4. The behaviors of plots at all conditions were found linear after the notable initial decrease (after 10 min) that may be due to adsorption of dye on catalyst surface.

The rate constants derived for neutral pH (Figure 4(a)) are 0.116, 0.099, 0.075, and 0.068 mg/L·min for oxygen, nitrogen, air, and argon respectively. These values suggest more degradation in oxygen and nitrogen. The rate constants evaluated for alkaline media (Figure 4(b)) were found to be 0.081, 0.069, 0.053, and 0.034 mg/L·min for nitrogen, air, oxygen, and argon. That again indicates more decolorization for atmospheres of nitrogen, and air, respectively. Finally, the rate constant values of acidic media (Figure 4(c)) are

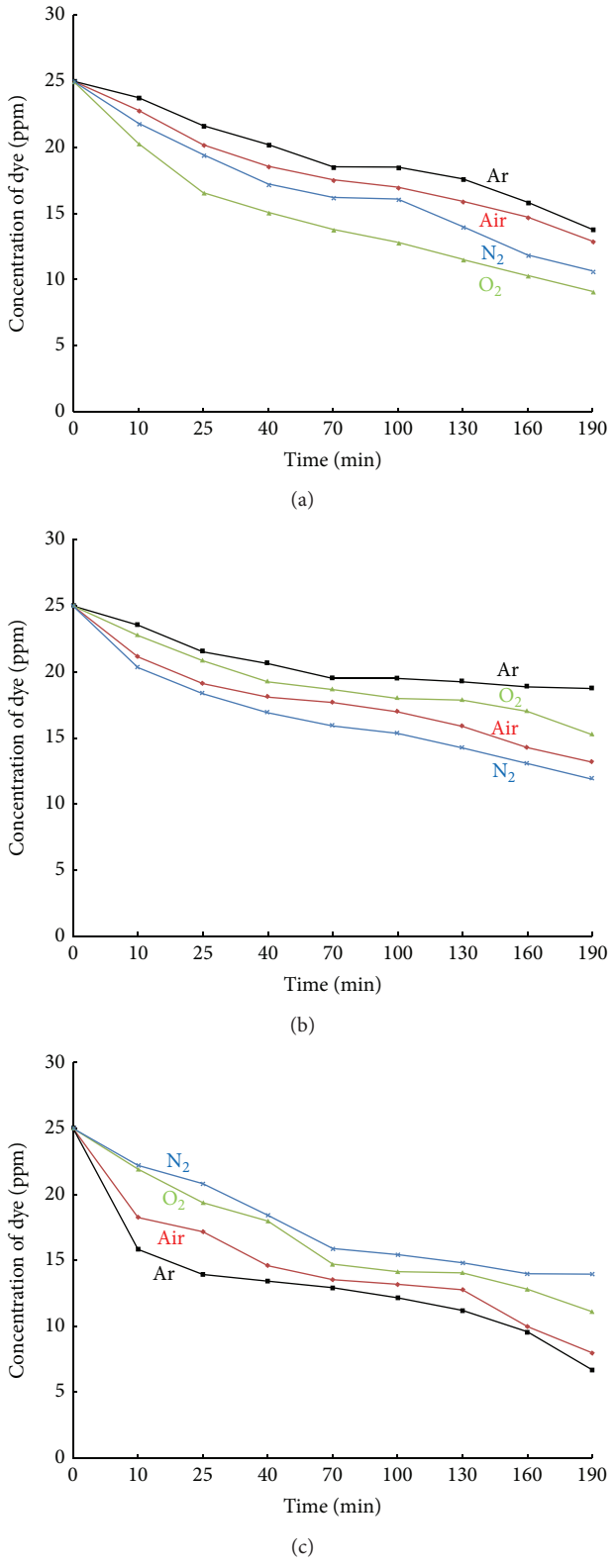

FIGURE 3: Residual concentration of MR (25 ppm) in deionized water after photocatalytic decolorization under UV irradiation in neutral (pH = 7) medium (a), alkaline (pH = 10) medium (b), and acidic (pH = 5) medium (c) under various atmosphere.

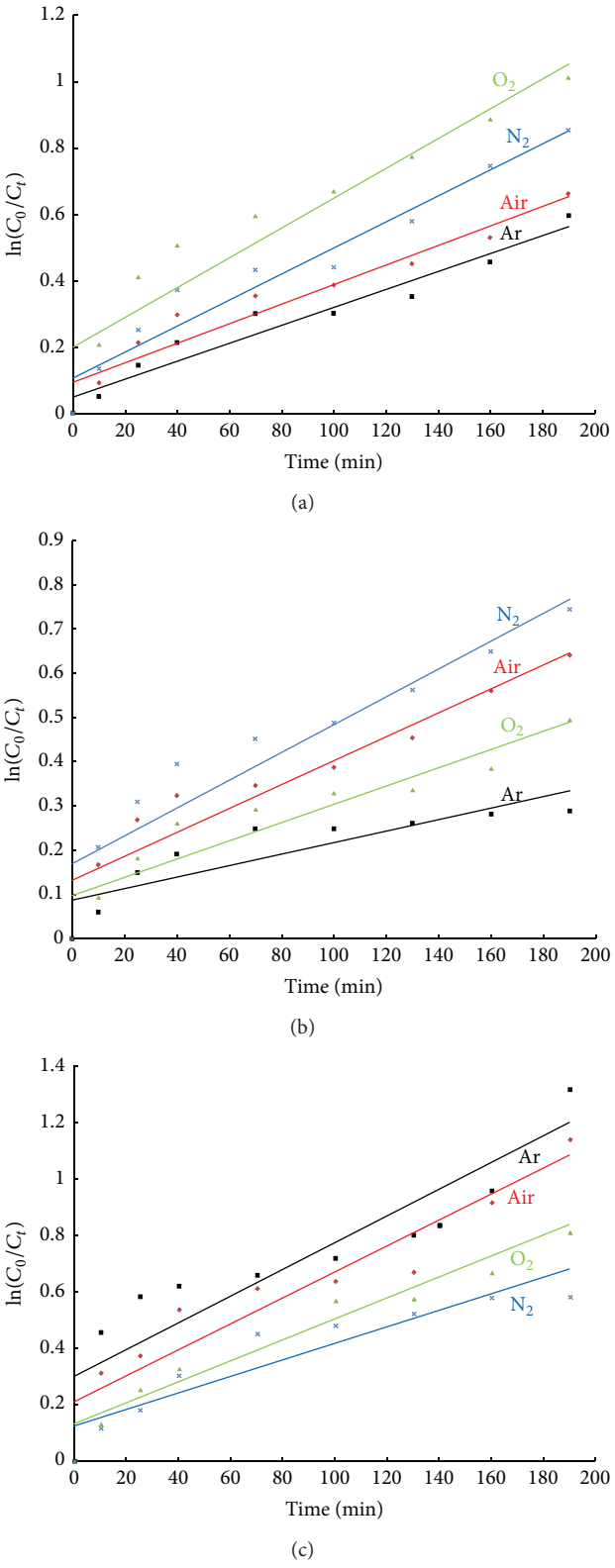

FIGURE 4: $\ln(C_0/C_t)$ versus time (min) for photocatalytic decolorization under UV irradiation in neutral (pH = 7) medium (a), alkaline (pH = 10) medium (b), and acidic (pH = 5) medium (c) under various atmosphere.

obtained as 0.121, 0.117, 0.095, and 0.076 mg/L·min for argon, air, oxygen, and nitrogen, respectively. which indicate more decolorization for atmospheres of argon and air.

4. Conclusion

In this work, we reported photocatalytic activity of nanosized zinc oxide thin film at various atmospheres: air, nitrogen, oxygen, and argon, and in different media. The titled dye was decolorized efficiently by use of this photocatalytic system. Among the considered atmospheres, orders of kinetics were found to be pseudo first order at nitrogen and oxygen. Kinetics of decolorization was investigated and was found to be pseudo-first order in various atmospheres. According to our experiments in neutral, alkaline and acidic media, oxygen, nitrogen, and argon, respectively, have the best efficiency for decolorization. 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.

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