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Short Communication

Synthesize of ZnO/NPs and Investigation of Its Effect in Reduction of Electrochemical Charge Transfer Resistance; Application of It for Photodecomposition of Calcon (C.I.15705) Dye in Various Media

Kiumars Ghowsi [1], Hamid Reza Ebrahimi[1,], Fahimeh Kazemipour-Baravati[2] and Hasan Bagheri[3]*

[1] Department of Chemistry, Majlesi Branch, Islamic Azad University, Isfahan, Iran
[2] Department of Physics, Khayyam Higher Education Center, Mashhad, Iran
[3] Department of Chemistry, Takestan Branch, Islamic Azad University, Takestan, Iran
[*]E-mail: hebrahimi2010@gmail.com

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In this study, in the first step we describe synthesis of ZnO/NPs. The effect of ZnO particles size on charge transfer resistance (R_{ct}) investigated using electrochemical impedance spectroscopy method in the presence of 1 mM $K_4[Fe(CN)_6]$ at a surface of carbon paste electrode. In continuous, we describe photocatalic decomposition of calcon dye as a pollutant in wastewaters samples. The photodegradation was investigated in water in neutral, alkaline and acidic media under external UV light irradiation by zinc oxide nano-sized catalysts on granule glass. The effect of four type atmospheres including air, nitrogen, oxygen and argon was investigated. Finally it was found that photodecomposition using ZnO nano-sized 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.

Keywords: Electrochemical impedance spectroscopy, Calcon dye, **Z**inc oxide nanoparticle, Photocatalyst, Wastewater

1. INTRODUCTION

Nanoscience represent new and enabling platforms that promise to provide a broad range of novel uses and improved technologies for pharmaceutical, environmental, biological, and other scientific applications [1-8]. Materials in nanosize have been the subject of extensive research because of their unique physical and chemical properties [9-15]. Development of new nanomaterials with metal nanoparticles (Zn, Ti, Ag, Au, etc.) deposited on oxide surfaces, embedded within pores or encapsulated in its matrices have gained much attention in material science because of expanding applications of such composites in optics, medical diagnostics, analytical chemistry, catalysis, photocatalysis etc. The most widely used catalyst is ZnO. [16-21]. Zinc oxide nanopasrticle (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 the specific chemical, surface and microstructural properties of this material [22-26].

Electrochemical impedance spectroscopy is a powerful and very informative technique for probing charge transfer properties at the electrode–solution interface [27-36]. One of the important advantages of EIS over other electrochemical techniques is the small amplitude perturbation from steady state, which makes it possible to treat the response theoretically by linearised or otherwise simplified current–potential characteristics [37-46]

With increasing revolution in science and technology, there was a greater demand for newer chemicals which could be used in various industrial activities. Organic dyes are one such of the many new chemicals which could be used in many industrial processes including fabric, woven, leather, textile, pulp and paper, tanneries, cosmetic, pharmaceuticals and food processing. 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 the heterogeneous photocatalysis involving zinc oxide (ZnO) emerges as a promising new route for water purification process [47].

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) [48]. 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 [49].

Various physical, chemical and biological treatments have been widely used to handle the dye removal from wastewaters in order to comply with the environmental regulations, which are becoming more stringent these days. Physical and biological treatments have been successfully applied till 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 anaerobic treatment method does not lower down the pollutant contents to a satisfactory level. Activated charcoal adsorption and air stripping methods are non-destructive, since they simply transfer the pollutants from water to another phase. They either transfer it 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 [50].

Among AOPs, heterogeneous photocatalysis seems to be an attractive method as it has been successfully employed for the degradation of various families of organic pollutants, including the dyes. Heterogeneous photocatalysis is a process in which the degradation of organic pollutants is governed by the combined actions of a semiconductor catalyst, an emitted light and an oxidizing agent. The semiconductor catalysts usually are oxides that can be more appealing than the conventional chemical oxidation methods because semiconductors are low cost, nontoxic and capable of extended use without substantial loss of photocatalytic activity [51, 52].

As part of our goal 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 nano-sized zinc oxide thin film. The binary zinc oxide /Glass films have been employed in photocatalytic decolorization of calcon in aqueous solutions. Decolorization of dye is measured by spectrophotometer (Perkin Elmer, Lambda25).

2. EXPERIMENTAL

2.1. General

All the chemicals were analytic grade reagents without further purification and purchased for Merck Company. The coating substrate (granule glass) was pre-heated 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. Electrochemical investigation

Impedance spectroscopy (EIS) was performed in an analytical system, Autolab with PGSTAT 302N (Eco Chemie, the Netherlands). A frequency range of 100 kHz to 1.0 Hz was employed. The AC voltage amplitude used was 5 mV, and the equilibrium time was 20 min. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl (KCl_{sat}) electrode as a reference electrode were used. The working electrode was either an unmodified carbon paste electrode (CPE) or a ZnO/CNTs carbon paste electrode ZnO/CNTs/CPE. To prepare the modified electrode 0.1 g of ZnO/NPs was hand mixed with 0.9 g of graphite powder in a mortar and pestle. Using a syringe, 15 drops of paraffin were added to the mixture and mixed well for 50 min until a uniformly wetted paste was obtained. The paste was then packed into a glass tube. Pushing a copper wire down the glass tube into the back of the mixture made electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper.

2.3. Film deposition and nanoparticles:

Nanosized zinc oxide thin film was supported on glass beads (diameter 3mm) by the method as follows. 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 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

[53]. For obtained nanoparticles in electrochemical investigation we use sol-gel method above procedure without presence of glass beads.

2.4. 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-layer that placed in 25 mL 25 ppm dyes solution and was irradiated with four 8W lamp (Philips; 365nm) placed 5 cm above the solutions. For pH adjustment 0.01 M NaOH and HCl solution was used to reach desired pH. Concentration was measured by spectrophotometer (Perkin Elmer, Lambda25). In all experiments 25 mL of 25 ppm dyes solution were used with stirring during the irradiation.

3. RESULTS AND DISCUSSION

3.1. Electrochemical impedance spectroscopy

Elecrochemical methods are very powerful techniques for investigation of nanoparticle changing at a conductive body [54-73]. Between electrochemical techniques electrochemical impedance spectroscopy is very specific for investigation charge resistance of a nanaoparticle or nanocompostie at a surface of electrode [74-76]. So, we selected EIS for more investigation. Electrochemical impedance spectroscopy was also employed to investigate the preparation of ZnO nanoparicle.

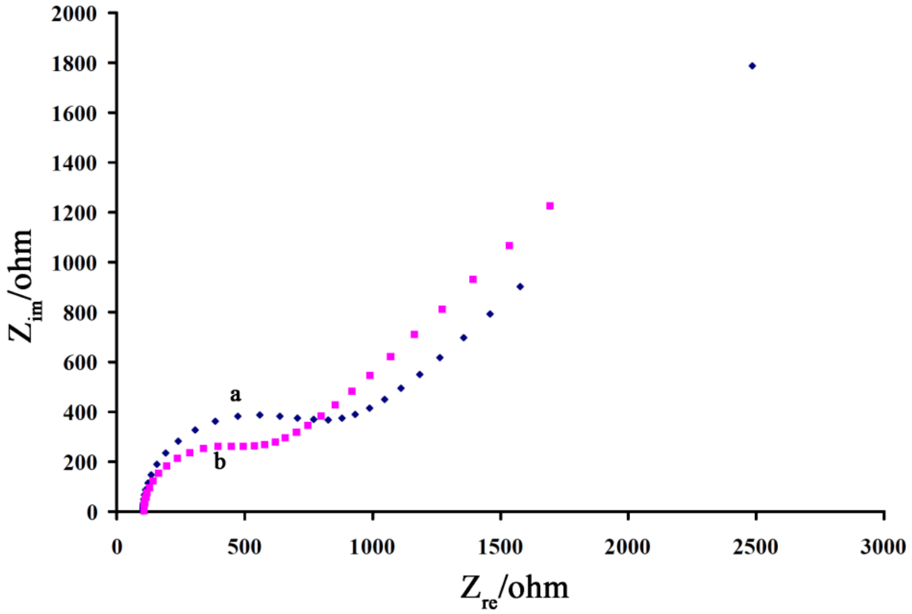

Figure 1. Nyquist diagrams of 1 mM $K_4[Fe(CN)_6]$. (a) at a surface of carbon paste electrode (b) at a surface of carbon paste electrode modified with ZnO nanoparticles.

Fig. 1 presents Nyquist diagrams of the imaginary impedance (Z_{im}) versus the real impedance (Z_{re}) of the EIS obtained at the recorded at a surface of carbon paste electrode (a) and carbon paste electrode modified with ZnO nanoparticle in the presence of 1 mM $K_4[Fe(CN)_6]$. In the presence of the 1 mM $K_4[Fe(CN)_6]$, the Nyquist diagram comprises a depressed semicircle at high frequencies which may be related to the combination of charge transfer resistance for electro oxidation of this compounds and the double-layer capacitance (C_d), is generally a function of potential.

Also, Z_w (Warburg impedance) related to the semi-infinite linear diffusion. The semicircle diameters of Nyquist plot reflect the electron transfer resistance (R_{ct}), which is from the electron transfer of the solution. Result shows at a surface of carbon paste electrode modified with ZnO the semicircle a diameter is lower than of carbon paste electrode. This result suggest the electrical conductivity this nanoparticle at a surface of electrode [77-82].

3.2. 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). The surface of the films was observed by scanning electron microscopy (SEM) with a Philips XL30 [83].

3.3. Photocatalytic activity

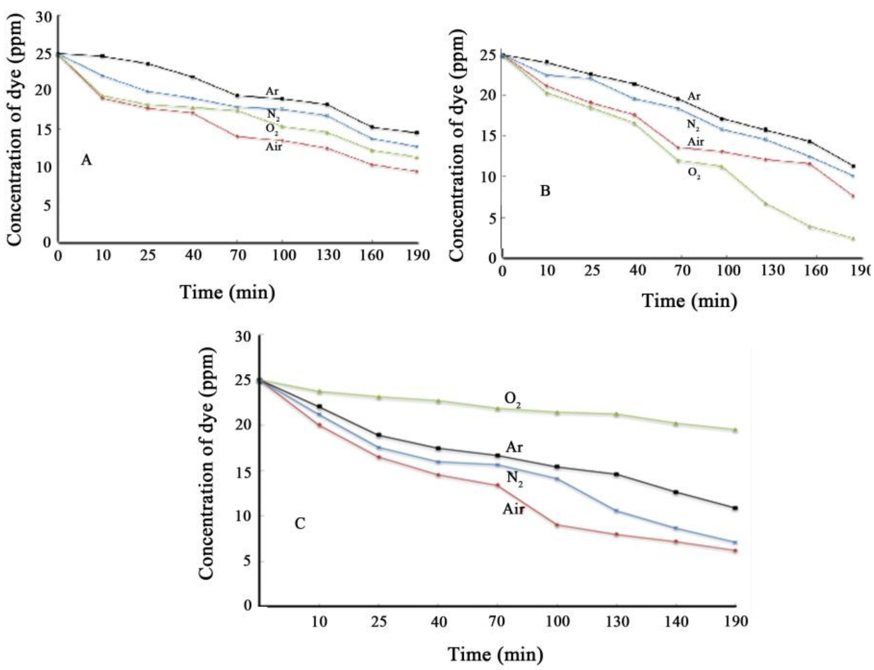

Figure 2. Residual concentration of Calcon (25ppm), in de-ionized water after photocatalyticdecolorization under UV irradiation in acidic (pH=5) (A), neutral (pH=7) (B) and alkaline (pH=10) medium (C) under various atmosphere.

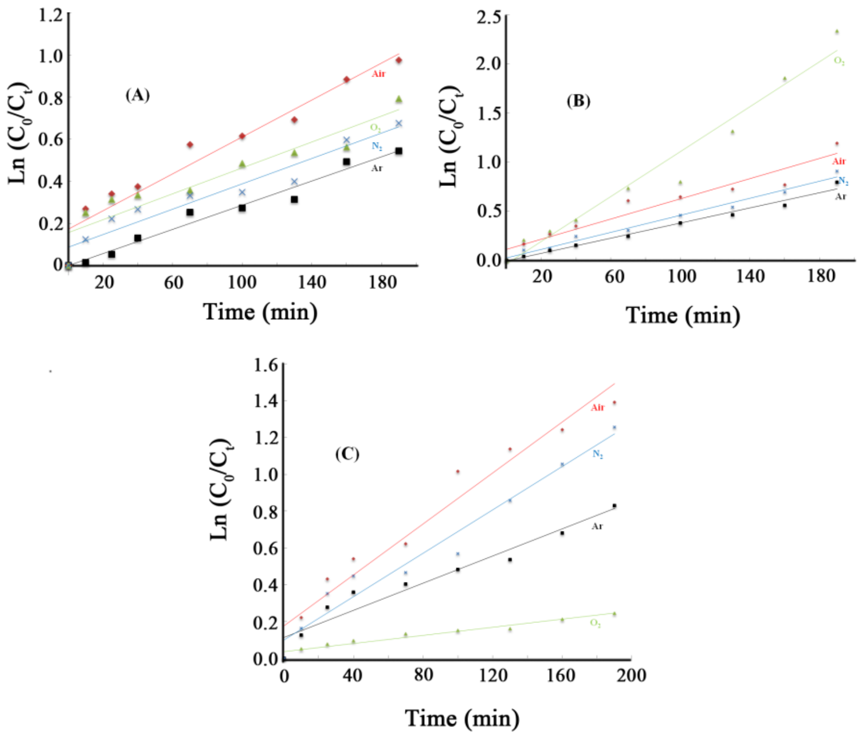

Figure 3. ln(C_0/C_t) versus time(min.) for photocatalytic decolorization under UV irradiation in neutral (pH=7) medium (A), alkaline (pH=10) (B) and acidic (pH=5) (C) under various atmosphere.

Evaluation of the granule glass coated with nano-sized zinc oxide as potential photocatalyst for water pollutant purification was based on the decolorization of a dye. Figure 2 show the decolorization of calcon (25 ppm) under UV irradiation (365nm) on granule glass coated with nano-sized zinc oxide with 5-layers at neutral (A), alkaline (B) and acidic (C) pH respectively.

As shown in figure 2 in alkaline pH(A), the decolorization rate is decreased in order of air, oxygen, nitrogen and argon respectively while in neutral pH(B), the order of decolorization rates is oxygen, air, nitrogen, and argon respectively. In alkaline pH(C), the order of decolorization rates is air, nitrogen, argon and oxygen, respectively. For evaluation of decolorization rate constant, the ln(C_0/C_t) versus time were sketched as seen in Figure 3A, 3B and 3C.

As shown in figure 2, in all media the dye is decolorized in argon and nitrogen than air and oxygen. It is suggested in spite of aerobic and oxygenated atmosphere, the dye is oxidized although slow but the titled dye is degraded non-oxidative faster under argon and nitrogen. For evaluating the photodegradation rate under above conditions, the kinetic investigation was performed based on the concentration- time data in figure 2.

Generally photodegradation of dyes are obey from first order reactions if the plots of ln(C_0/C_t) versus time are straightforward lines. For this mean for three above pHs, the plots of ln(C_0/C_t) versus time was sketched and have been illustrated in figure 3. The behaviors of plots at all conditions were found linear after notable initial decrease (after 10 min.) that may be due to adsorption of dye on catalyst surface. The decrease in concentration after 10 min. may be attributed to photodegradation. The rate constants derived for natural pH (Figure 3A) are 0.172, 0.156, 0.087 and 0.001 mg/L.min. for air, oxygen, nitrogen, and argon respectively. These values suggest more degradation in argon and nitrogen. The rate constants evaluated for alkaline media (Figure 3B), were found 0.510 mg/L.min for oxygen and 0.1 mg/L.min for air, nitrogen and argon. That indicates more decolorization for atmosphere of oxygen in respect of other atmospheres. Finally the rate constant values of acidic media (Figure 3C) were found 0.1 mg/L, for air and nitrogen, and 0.058 and 0.015 mg/L.min, for argon and oxygen.

4. CONCLUSION

In this work, we reported preparation of nano-sized zinc oxide thin film on glass beads and ZnO/NPs. In the first step we study effect of ZnO/NPs incorporated in carbon paste matrix for reduction of charge transfer resistant in electrochemical systems. In continuous, photocatalytic activity of it, at various atmospheres: air, nitrogen, oxygen and argon, was investigated. The titled dye was decolorized efficiently by use of this photocatalytic system. Among considered atmospheres, orders of kinetics were found that to be pseudo first order at nitrogen and oxygen. Kinetics of decolorizaton was investigated and pseudo-first order kinetic was found under O_2 and N_2 atmosphere. Easily 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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