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Photo-Oxidation Process of Indole in Aqueous Solution with ZnO Catalyst: Study and Optimization

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Abstract—The photo-oxidation of indole has been investigated using the catalytically active ZnO in aqueous solution, under various physical and chemical conditions. First of all, a structural analysis with X ray diffraction (XRD) shows that ZnO powder crystallizes in wurtzite with a main grain size estimated to be about 270 nm. An increase in catalyst loading greatly enhances the process efficiency until a certain. limit. Indole photodegradation improves with increasing air flow. The effect of the pH on the photo-oxidation efficiency was carried out from 3.88 to 11.16. The activity exhibits its maximal value around the natural pH (6.68). Photocatalytic degradation showed that the activity of ZnO improved with increasing light intensity. This was ascribed to the fact that there was a more efficient generation of electron–hole pairs used in the degradation process.

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Indole is a common product generated by industries for various applications including pharmaceuticals, cosmetics, pesticides, disinfectants, agrochemicals, and dyestuffs [1,2]. This compound is released into the environment and found in aqueous wastes and sediment. Indole and its derivatives form a unique class of toxic and recalcitrant N-heterocyclic compounds that are considered to be environmental pollutants [3]. It also contributes to the unpleasant odor of feces [4]. Chemical disinfection of indole-containing wastewaters with dilute aqueous solution of chlorine, chlorine dioxide, or chloramines leads to the formation of chlorinated aromatic products [5], which are known to be toxic and carcinogenic. The biodegradation of indole which classified in the heterocyclic aromatic compounds has been studied [6, 7].

Elsewhere, other methods are tested for the same goal using inorganic compounds such as semiconductors. These compounds have demonstrated their capacity to degrade a high number of recalcitrant chemicals in gaseous or aqueous systems through relatively inexpensive procedures [8–11]. Among used catalysts, TiO_2 seems to be the most commonly used for a wide range of organic chemical degradation [12–15]. Recently, most interest was devoted to evaluate the potentiality of other metal oxides: zinc oxide appears as a very promising photocatalyst for degradation of organic solutes in aqueous systems. In some cases, ZnO has actually proven more effective than TiO_2 [16, 17].

This paper investigates the kinetic and efficiency parameters of photo-oxidation of indole in aqueous solution under UV illumination. A ZnO-assisted photocatalysis study of indole under UV light irradiation has never been reported.

EXPERIMENTAL

Materials

Indole and zinc oxide were purchased from Aldrich Chemical Company of 99% purity. The ZnO powder was used as received without further purification. Deionized water was used throughout this study. For alteration of pH in the acid and alkaline area, solutions of 0.1 N HC1 and 0.1 N NaOH, respectively, were used. The pH values of the solutions were monitored with multiparameter INOLAB pH-meter, while the reaction temperature was kept constant at 25°C.

Powder X-rays diffraction (XRD) pattern were collected with a Philips PW 1729 diffractometer in a conventional θ–2θ reflection geometry using filtered CuK_α radiation. In Fig. 1, a representative X-ray diffraction profile of the used ZnO powder is reported. A wurtzite structure can be assigned to the used sample by comparing the diffraction peak positions with those

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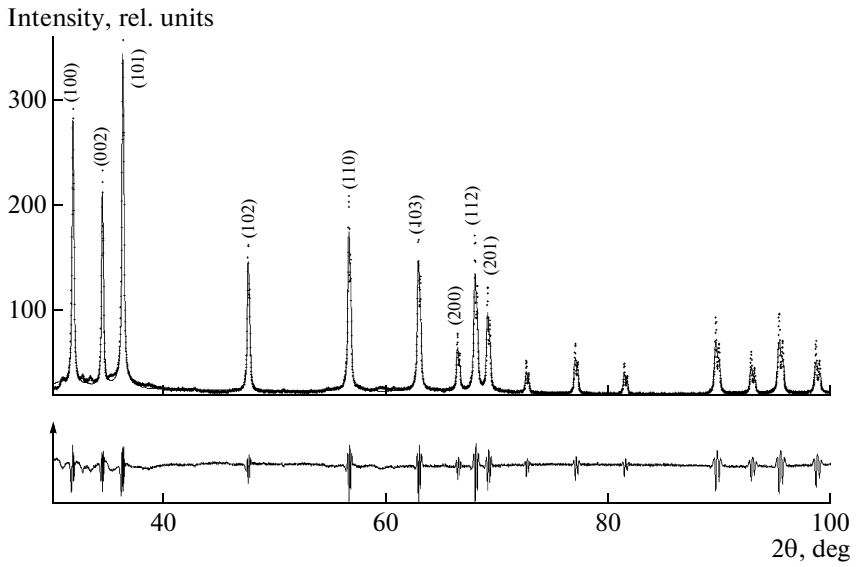

Fig. 1. Typical powder XRD pattern of ZnO catalyst.

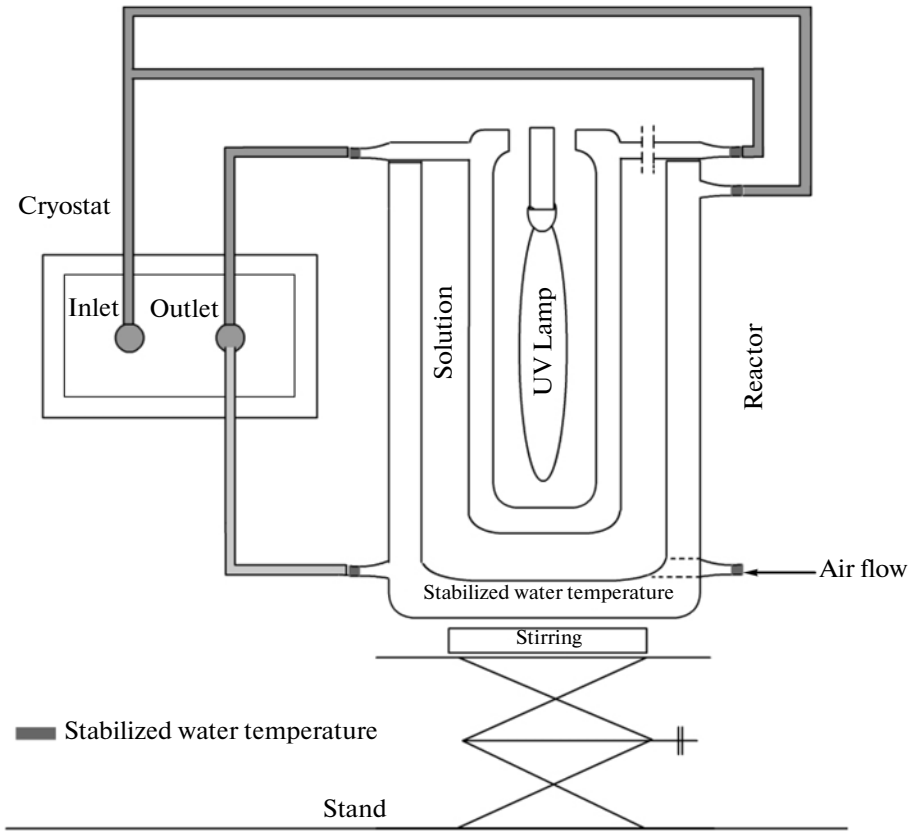

Fig. 2. Scheme of experimental apparatus.

reported in the international crystallographic data table. The average grain size, estimated to be about 270 nm by applying the Debye–Scherrer formula to the (110) reflection line.

Photo-Reactor and Samples Preparation

Photo-oxidation experiments were performed with a photocatalytic reactor system illustrated in Fig. 2. This system consisted of a cylindrical cell with a U let-

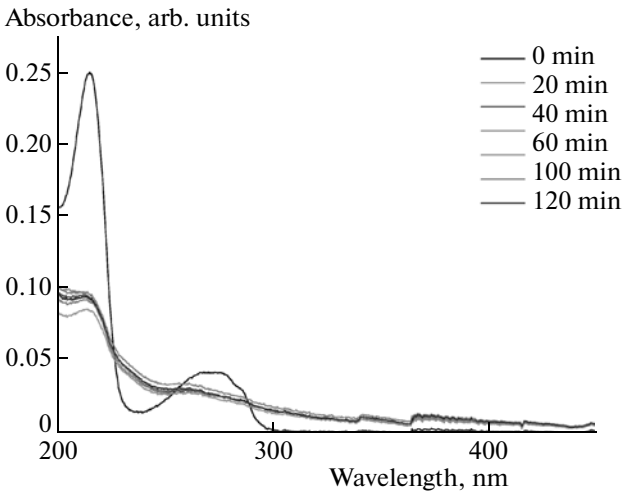

Fig. 3. The UV–Visible spectra of indole in aqueous solution at different irradiation time intervals without air flow at natural pH and ambient temperature (25°C). The ZnO concentration is about 0.5 g/l, lamp power is 9 W, the UV path length is about 5 cm.

ter form. A Philips lamp with 24, 15, or 9 W power is placed in the diameter of a quartz double-jacket tube with one end tightly sealed by a Teflon stopper. The lamp and the tube were immersed in the photoreactor cell with a light path of 5 cm. UV–Vis Spectrophotometer detection (1240 SHIMADZU) was accorded on a wavelength $\lambda = 270$ nm.

The prepared solutions are made by dissolving 10 mg of indole in 1 l of deionised water. Different amounts of ZnO, from 0.5 to 2 g/l, are added forming several samples. In all cases, the suspensions are stirred during 50 min in darkness before UV-irradiation exposition with an air flow (from 0.5 to 2 l/min). Air was bubbled with flow rate 0–2 l/min.

At different time intervals (each 10 min) aliquot was taken out with the help of a syringe, centrifuged and then filtered through Milipore syringe filter of 0.45 μm. The degradation efficiency is estimated by measuring the conversion as $Y = [(C_0 - C_t)/C_0] \times 100$, where C_0 is the initial concentration of indole (mg/l), C_t is indole concentration at t instant.

RESULTS AND DISCUSSION

UV–Visible Spectra

The aqueous solution of indole was unstable under UV irradiation. In Fig. 3, we observe that at initial instant ($t = 0$ min), the indole solution exhibits two characteristic peaks respectively at 220 and 270 nm. Under UV illumination, these absorption bands tend to vanish with increasing irradiation time. In these experiences, the photocatalysis was done without air flow. After 20 min of irradiation time, 66% of indole was photo-degraded.

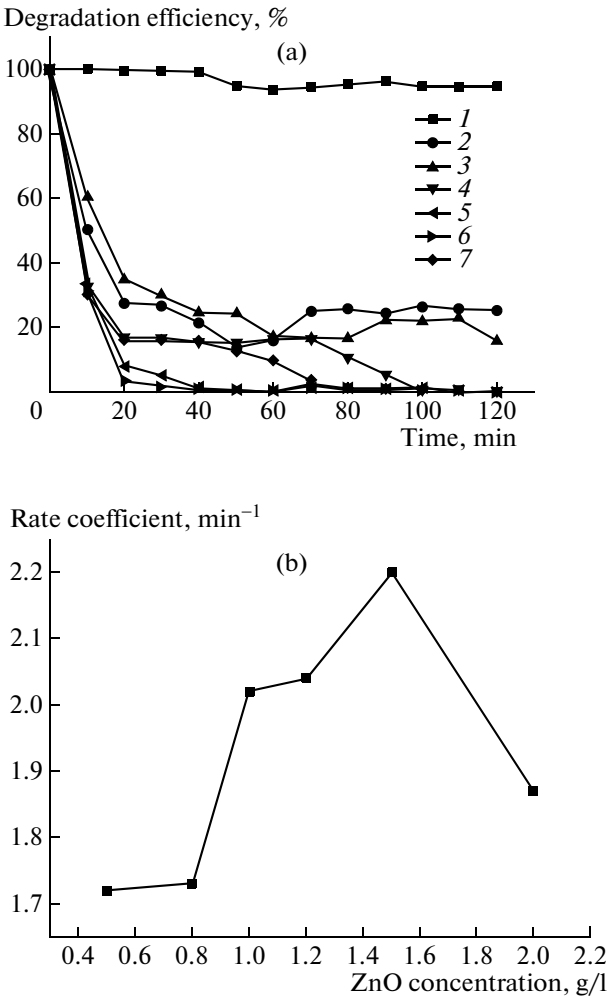

Fig. 4. (a) Relative absorbance vs. time profile during irradiation of indole in aqueous solutions at ambient temperature (25°C) for different amounts of ZnO catalyst, g/l: *1*—0, *2*—0.5, *3*—0.8, *4*—1.0, *5*—1.2, *6*—1.6, *7*—2.0. Lamp power of 9 W, the UV path length is about 5 cm without air flow. (b) Influence of ZnO loading on indole photooxidation first-order rate coefficient. Experimental conditions are given in Fig. 3.

In the absence of the catalyst, indole was photolyzed only up to 3% in 2 h (see Fig. 4a). This little efficiency can be interpreted by the homolytic rupture of the double bond of indole molecule. These observations reveal that both UV light and photocatalyst are needed for effective destruction of indole.

The ability of the semiconductor to act as sensitizer is attributed to its electronic structure which is characterized by filled valence band and an empty conduction band. Under illumination by a light with energy greater than its band gap, electrons and holes are photogenerated:

$$\mathrm{ZnO} + h\nu \longrightarrow \mathrm{ZnO}(e^-_{CB} + h^+_{VB}).$$

These generated species react with oxygen and water molecules to produce strong oxidizing hydroxyl radi-

cals which can promote the oxidation of indole molecule [16, 18, 19]:

$$e^-_{CB} + O_2 \longrightarrow O_2^-,$$

$$h^-_{VB} + H_2O \longrightarrow H^+ + {}^{\bullet}OH.$$

ZnO Catalyst Loading

The amount of photocatalyst is an important parameter that can affects the degradation process kinetics. Hence, to study the relation between photocatalyst loading and rate, the amount of ZnO was varied between 0.5 and 2 g/l in a series of experiments under constant air flow (1.5 l/min) and natural pH 6.68.

In Fig. 4a, we easily see that the reaction follows first order decay, at least until 25 min of catalysis process time. As expected, the reaction rate increases when increasing catalyst amount and it is in a good agreement with recent studies [20]. Summarizing, this phenomenon can be explained by the fact that increasing ZnO amount up to 1.5 g/l leads to an increase of the number of absorbed photons that enhances the photogeneration of hydroxyl radicals [13, 21–26]. After this limit, the rate coefficient decreases which can be simply explained in terms of the decrease of penetration depth of UV light into the suspension [27–30].

Effect of Air Flow

Oxygen required for scavenging electrons generated by UV radiation came from the air bubbled through the liquid. The air flow rate was also sufficient to keep the ZnO particle in suspension. Therefore, it is pertinent and important to study the effect of air flow on the rate of photocatalytic degradation of indole.

This study was carried out at natural pH with the optimized ZnO amount (1.5 g/l). In Fig. 5, we see that the rate coefficient increases with increasing the air flow leading to enhancing photo-oxidation efficiency [17]. By increasing the air flow, the amount of involved oxygen is improved and consequently the conduction band electrons scavenging process rate increases. Therefore, the oxidation of indole is accelerated [16].

Effect of Initial pH

Wastewater containing indole is discharged at different pH. Therefore it is important to study the role of the pH on photo-oxidation of this molecule.

To study the effect of the pH on the photo-oxidation efficiency, experiments were carried out at pH values ranging from 3.88 to 11.16. The pH of the solution is adjusted initially by adding precise amounts of NaOH solution (0.1 N) or HCl (0.1 N) and it is not controlled during the course of the reaction. The rate

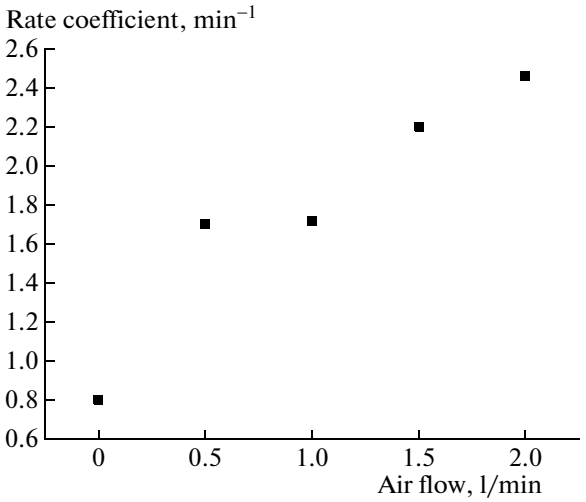

Fig. 5. Rate coefficient vs. air flow for indole oxidation in aqueous solutions with optimized ZnO loading (1.5 g/l) under different air flows at natural pH and ambient temperature.

coefficient is affected very appreciably by varying the pH:

pH	3.88	7.00	6.68 (natural)	9.12	11.16
Rate coefficient, min^{-1}	1.15	1.67	2.41	1.81	1.22

By increasing pH from 3.88 to natural value (6.68), the rate coefficient increases to its maximum value. The process is inversed when the solution becomes basic. Similar situations have been observed in literature [29, 31–33].

The interpretation of pH effects on the efficiency of photocatalytic degradation process is a very hard task [34]. Since the zero point charge of ZnO is 9.0, the surface of the catalyst is positive below pH 9.0. pK_a for indole is around 13, therefore above a pH 13, indole is negatively charged that might result in electrostatic attraction between the nanocatalyst and indole and will increase both adsorption and the degree of photodegradation. But, electrostatic argument seems do not to be the unique explanation of the photocatalytic behavior versus the pH parameter. Camparelli et al. [35] have demonstrated that ZnO can be photocorroded through a self-oxidation and exhibits tendency to dissolve with decreasing the pH [19, 34, 36–39].

Effect of Light Intensity

The influence of light intensity on the degradation efficiency has been examined at constant indole concentration (10 mg/l, pH 6.68) and catalyst loading (1.5 g/l). The light intensity is simply varied by using three different UV lamps with nominal power equal to 9, 15, and 24 W. The spectral distribution of the used lamp is depicted in Fig. 6, where the maximum light

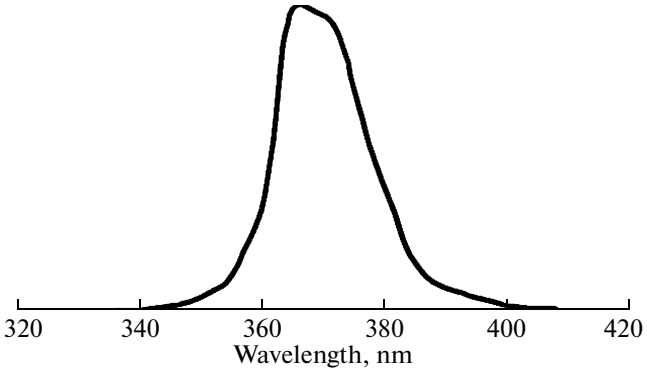

Fig. 6. Emission spectrum of used lamp (Philips PL-L 24W/10/4P).

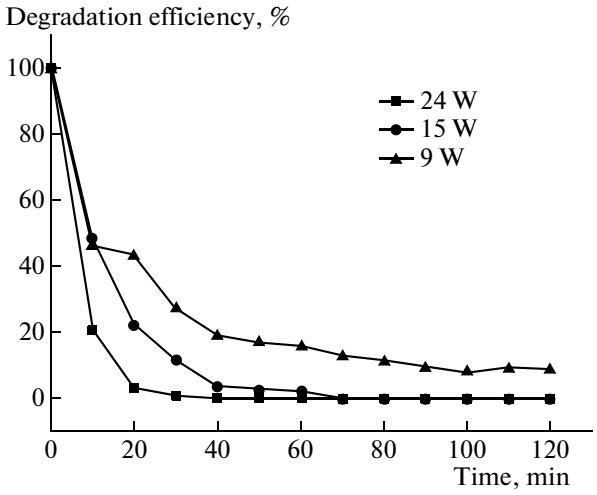

Fig. 7. Effect of lamp power on the photo-oxidation process of indole at natural pH and ambient temperature (25°C) without air flow. The ZnO concentration is about 1.5 g/l.

emission is located at 365 nm. As seen in Fig. 7, the efficiency increases monotonically with increasing light power. UV lamp generates the photons required for the electron transfer from the valence band to the conduction band of ZnO catalyst. This generation process is both related to wavelength and power of the light.

In this study, photo-oxidation of indole has been investigated under various conditions using ZnO powder as active catalyst. Subsequent experiments are conducted with ZnO to investigate its photocatalytic activity under various process conditions. It has been found that:

(1) photocatalytic degradation of indole was negligible when ZnO nanopowder and UV light were used on their own compared when both are used;

(2) the degree of degradation of indole was obviously affected by illumination time, pH and photocatalyst loading;

(3) the efficiency also grows with increasing air flow and increasing light intensity.

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