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Box–Behnken experimental design for optimization of ammonia photocatalytic degradation by ZnO/Oak charcoal composite

N. Tafreshi[a], S. Sharifnia[b,*], S. Moradi Dehaghi[a]

[a] Department of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran
[b] Catalyst Research Center, Department of Chemical Engineering, Razi University, Kermanshah 67149-67246, Iran

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ABSTRACT

Box–Behnken experimental design method was used to optimize the experimental conditions of photocatalytic removal of ammonia from synthetic wastewater by ZnO/Oak charcoal photocatalyst. The hybrid photocatalyst was synthesized by impregnation method and characterized by XRD, FTIR and FESEM analyses. The results of analyses showed the suitable dispersion of ZnO over the support surface. Also, the FESEM analysis confirmed the good features of the Oak charcoal as either support or adsorbent. pH (4–12), catalyst dosage (0.5–2 g/L) and initial ammonia concentration (85–850 mg/L) were the main parameters affecting the ammonia removal. The results of experiments were modeled by a second-order polynomial equation. The high value of the determination coefficient (R^2 = 99.6 and adjusted R^2 = 98.9%) revealed that the experimental data fitted well with the proposed model. The maximum efficiency of ammonia removal was obtained about 80% at optimum conditions of initial ammonia concentration of 153.9 mg/L, catalyst dosage of 1.59 g/L and solution pH 10.5. Based on the results of analysis of variance, the significance order of the independent parameters was as follows: initial ammonia concentration > catalyst dosage > solution pH.

1. Introduction

Nowadays, ammonia is known as an important water contaminant. The excessive amount of ammonia in the environment damages natural nutrient cycle between living world, soil, water, and atmosphere. The main sources of ammonia are the microbial decomposition of nitrogen containing organic substances at very low oxygen concentrations, or decomposition of urea and nitrogen compounds in wastewater treatment processes (Leyva-Ramos et al., 2010; Balci, 2004). As this hazardous compound causes undesirable odors, several diseases and environmental problems, there is an urgent need to control and remove ammonia pollutant from ground and surface water sources.

Photocatalytic degradation of ammonia has been regarded as a suitable method for treating wastewater (Shavisi et al., 2014a). ZnO is a known semiconductor with the band gap energy of 3.37 eV which can be effectively applied for wastewater treatment, due to its potential in water splitting and production of $^{\bullet}OH$ (Jasso-Salcedo et al., 2014). Hydroxyl radicals play a major role in the decomposition of NH_3 molecule into N_2, NO_2^-, and NO_3^- (Zendehzaban et al., 2013). Hydroxyl radical can be formed by either direct oxidation of OH^- or decomposition of hydrogen peroxide, as shown in Eqs. (1)–(6) (Hirakawa et al., 2007; Augugliaro et al., 2012).

$$OH^- + h^+ \rightarrow {}^{\bullet}OH \quad (1)$$

$$O_2 + e^- \rightarrow {}^{\bullet}O^-{}_2 \quad (2)$$

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad (3)$$

$$^{\bullet}O_2{}^- + {}^{\bullet}O_2{}^- + 2H^+ \rightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^- \quad (5)$$

$$H_2O_2 + {}^{\bullet}O_2{}^- \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad (6)$$

* *Corresponding author*. Fax: +98 83 34274542.
E-mail addresses: sharif@razi.ac.ir, ssharif_99@yahoo.com (S. Sharifnia).

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Table 1 – Factors and their levels in full factorial design.

Factor	Coded levels		
	Low (−1.000)	Medium (0.000)	High (1.000)
Initial concentration (mg/L) (X_1)	85	467.5	850
pH (X_2)	4	8	12
Catalyst dosage (g/L) (X_3)	0.5	1.25	2

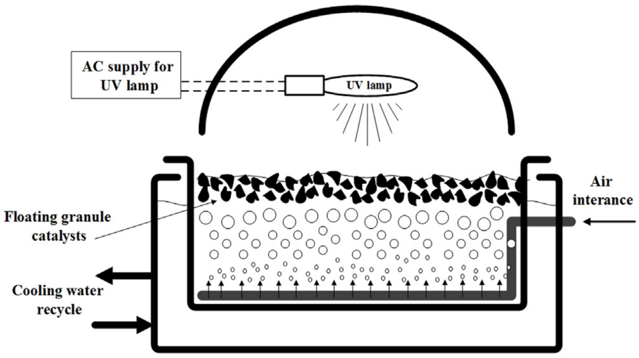

Fig. 1 – The image of the photocatalytic reactor set-up for the removal of aqueous ammonia.

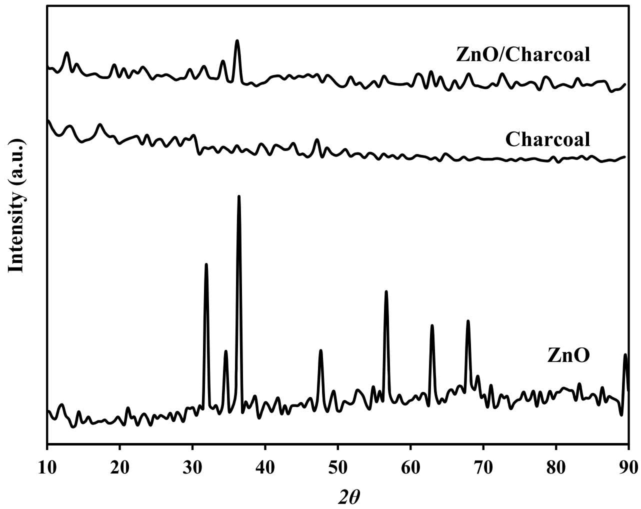

Fig. 2 – X-ray diffraction patterns of the photocatalyst, support, and their composite.

Considering the nano sized ZnO particles, immobilization of the photocatalyst on a suitable, floating, and inert support can facilitate the separation process and irradiation to ZnO. So far, the different types of supports have been applied, for example, zeolite (Wang et al., 2011), glass (Lv et al., 2011), stainless steel (Torabi Merajina et al., 2013), LECA (Shavisi et al., 2014b) and perlite (Shavisi et al., 2014a). Charcoal is a good choice for loading ZnO due to its large specific surface area and pore volume, which result in excellent adsorption capacity for both the catalyst particles and pollutants (Zhang et al., 2014; Luo et al., 2015).

Experimental design methods have been employed for optimization of biological and chemical processes (Petrovic et al., 2015; Chen et al., 2012; Bitara et al., 2015). These methods offer the optimum conditions for achievement of the best response through a relatively small number of experiments (Cuellar et al., 2016). Box–Behnken design (BBD) is a suitable and up-to-date optimization method which is classified as a rotatable or nearly rotatable second-order design based on three-level incomplete factorial designs. The number of experiments (N) required for the development of BBD is defined as $N = 2k(k-1) + C_o$, where k and C_o are the factor number and the number of central points, respectively (Niazi et al., 2015).

In this paper, by means of the so-called synergistic effects of adsorption and photocatalysis of ZnO/Oak charcoal, the removal of ammonia from synthetic wastewater was examined. Box–Behnken response surface design was used to optimize and investigate the influence of the key process variables such as initial pH and concentration, and catalyst dosage on the efficiency of ammonia removal. The surface properties of the photocatalyst were characterized by XRD, FTIR, and FESEM analyses. Also, a mechanistic study has been presented to identify the photocatalysis pathway of ammonia decomposition to nitrogen, nitrate and nitrite.

2. Experimental

2.1. *Material*

ZnO (99.99%) powder (wurtzite hexagonal structure) and all chemicals such as ammonia (32%), ethanol (99.5%), nitric acid (65%), and NaOH (99%) were purchased from Merck Co. The Oak charcoal was prepared by carbonization of Oak from Oak trees in Kermanshah's forests, Iran. All experiments were carried out by double distilled water produced in our laboratory.

2.2. *Photocatalyst preparation and characterization*

The Oak wood was cut into shredded pieces with average dimensions of 6 mm × 4 mm × 2 mm, and soaked in 2 mol/L HNO_3 at 60 °C, in order to eliminate metal ions. Then, to remove the pigments in the tissues of the Oak wood, it was immersed in absolute alcohol and deionized water with volume ratio of 1:1 at 60 °C for 12 h. This process was repeated twice and the wood pieces were dried at 60 °C for 12 h. The carbonization process of the Oak wood was carried out at 450 °C and 1 h. Zinc oxide powder was dispersed in ethanol as a base medium of slurry. Then, dilute nitric acid with a pH 3.5 was added to the slurry. After sonication of the slurry for 30 min and separation of the flocculated ZnO powders, a more uniform slurry was obtained. The hybrid photocatalyst was prepared by impregnation method. The dried Oak charcoal was added to the slurry. After full adsorption of ZnO by the Oak charcoal pieces, the suspension was filtered and the filtrate was dried at 120 °C for 12 h. Then, the calcination was performed at 450 °C for 2 h by a nitrogen gas furnace. Finally, the hybrid catalyst with 0.1 g ZnO/g Oak charcoal was obtained.

The morphological and elemental characteristic of the Oak charcoal, and the hybrid photocatalyst was identified by XRD (XRD, PHILIPS PW1140), FTIR (FTIR, MB160 ABB BomemInc Canada) and FESEM (FESEM, MIRA3-TESCAN) analyses. The XRD analysis was taken at 40 kV and 200 mA with monochromic CuKα (λ = 1.5418 Å). The FTIR spectra was recorded in the range 400–4000 cm^{-1} at a resolution of 4 cm^{-1}. Samples of 1–2 mg were mixed with 100 mg KBr and pressed into translucent disks at room temperature.

2.3. *Photoreactor tests*

A Pyrex glass vessel reactor with the inner volume of 1.5 L was used for photocatalytic degradation of ammonia by