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Modeling and optimization of phenol degradation over copper-doped titanium dioxide photocatalyst using response surface methodology

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ABSTRACT

In this research paper, Box–Behnken design (BBD) combined with response surface methodology (RSM) has been applied to optimize phenol photocatalytic degradation. In this process, nano-structured copper-doped titanium dioxide was used as the photocatalyst. The experiments were conducted in the presence of H_2O_2 and under the UV irradiation. The operational factors were initial phenol concentration, reaction time, and Cu/TiO_2 dosage. The effects of process variables as well as their binary interactions were modeled. High values of the determined R^2 coefficients of the model (>0.99) confirm that the proposed equation fits the experimental data accurately. The fundamental objective of this work was to determine the most important parameter of the mentioned process. The ANOVA results enunciated that the significance of the parameters is as follows (the most to the least significant): Cu/TiO_2 dosage > time > initial phenol concentration.

1. Introduction

Major source of phenol introduction into the aquatic environment is industrial wastewater. Phenol is harmful even at low concentrations. European Union (EU) has categorized several phenols as priority pollutants and the 80/778/EC directly announced a maximum concentration of 0.5 mg/l for total phenols in drinking water (Grabowska et al., 2012). More than 1000 compounds, which are emerged in various lists of hazardous materials, recognized by the US. Environmental Protection Agency (EPA), have been tested by photocatalytic technology. The heterogeneous photocatalysis is a tertiary water treatment process, belonging to the advanced oxidation processes (Moreira et al., 2012; Jafarzadeh et al., 2011). Titanium dioxide (TiO_2) is one of the most effective photocatalysts. It has been widely applied as a viable solution to environmental problems because of its excellent properties including high chemical stability, non-toxicity, and low cost. Considerable efforts have been made to improve the activity of TiO_2 (Pham and Lee, 2014; Lorret et al., 2009). Several studies reported high photocatalytic activity of Cu-doped TiO_2 (Choi and Kang, 2007; Sato and Taya, 2006; Carvalho et al., 2010; Sreethawong and Yoshikawa, 2005). Choi and Kang (2007), prepared TiO_2 photocatalyst loaded with Copper Oxide and used it to produce H_2 gas from methanol/water photodecomposition in a batch-type liquid photosystem. The amount of hydrogen production by the use of $CuO–TiO_2$ was reported higher compared with pure TiO_2. Sato and Taya (2006), reported that Cu aided TiO_2 films in photo-sterilizing microbial cells under irradiation by a white light fluorescent lamp and they declared that the enhancement of the activity of the catalyst originated from promoted hydroxyl radicals by the aid of copper component. Carvalho et al. (2010) investigated the photocatalytic degradation of methylene blue by TiO_2–Cu thin films. Cu-loaded TiO_2 exhibited an approximately twofold higher photocatalytic activity compared with Ni-loaded TiO_2

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under the optimum conditions (Sreethawong and Yoshikawa, 2005).

In conventional optimization experiments, one factor is variable while the others are kept constant. Such methodology usually disregards the interactions between variables. However, the use of response surface methodology (RSM) overcomes this problem. RSM is the combination of mathematical and statistical techniques for designing the experiments. It studies the effect of factors and their interactions involved in the optimization of the process (Hosseinpour et al., 2011). Soleymani et al. (2015) have applied titanium dioxide for photocatalytic degradation of azo dye C.I. direct red 16 (DR16). They considered the catalyst dosage, pH, and the dye initial concentration as the factors. The modeling and optimization was conducted based on central composite design (CCD) methodology. Fakhri (2015) studied mercury removal utilizing copper oxide nanoparticles as adsorbent. The selected process variables were pH, adsorbent dose, and temperature. The experiments were carried out based on Box–Behnken design (BBD) and were evaluated using RSM. Fakhri and Behrouz (2015) evaluated the adsorption properties of MgO nanoparticles and ZnO-MgO nanocomposites for linezolid antibiotic removal from aqueous solution using response surface methodology. Zuorro et al. (2013) studied the photodegradation of Reactive Green 19 (RG19) azo dye by the UV/H_2O_2 treatment. They presented the use of RSM approach combined with a model for analysis of dye degradation processes. Schenone et al. (2015) reported the application of photo-Fenton process for the degradation of the herbicide 2,4-dichlorophenoxyacetic (2,4-D). They investigated the influence of the temperature and peroxide to 2,4-D initial concentration ratio and the optimization was performed by the use of a three-level factorial experimental design combined with the Response Surface Methodology.

In the present research study, copper modified titanium dioxide nano-structured catalyst (Cu/TiO_2) was synthesized by the sol–gel method. The SEM method was used to characterize the morphology of the synthesized catalyst. Moreover, crystalline phases of pure and copper-doped TiO_2 were characterized by XRD. For the first time, the effects of these three process variables and their interactions on phenol photocatalytic degradation by this catalyst were experimentally studied. The investigated factors were initial phenol concentration, reaction time, and the Cu/TiO_2 dosage. The primary objective of this work is to determine the most significant parameter on the mentioned process and the secondary objectives are achieving the empirical model of phenol degradation in addition to attaining the optimum conditions of the process. This work is the first report on the application of combined RSM-BBD technique for optimizing the phenol degradation process by Cu/TiO_2 photocatalyst.

2. Materials and methods

2.1. Materials

To prepare the catalyst, titanium tetra isopropoxide or TTIP (98%), and Cu $(NO_3)_2{\cdot}3H_2O$ (99%) were used as the precursors of titanium and Copper, respectively. In addition, ethanol (96%) and nitric acid (65%) were used in the synthesis of the photocatalyst. H_2O_2 (30 wt.%) and phenol (99%) were used in the photocatalytic experiments. All the materials were purchased from Merck Company and used without any purifications. Double-distilled water was used in the preparation method of the catalyst and distilled water was used in the photocatalytic experiments.

2.2. Synthesis and characterization of Cu/TiO_2 photocatalyst

Based on the YOLDAS method, titanium precursor was added to double-distilled water. The molar ratio of TTIP to water was 1:100. Meanwhile, the mixture had been stirred and heated up to 85 °C. At that temperature, a specified amount of nitric acid was added so that the molar ratio of TTIP to nitric acid was 1:0.07. A solution of 2 wt.% of Cu was prepared by dissolving Cu $(NO_3)_2{\cdot}3H_2O$ in ethanol and 2 ml of this solution was added to the mixture. Afterwards, the mixture was under reflux at 85 °C for 24 h. The obtained gel was dried at 100 °C. Finally, the calcination process was carried out in a furnace at 600 °C for 2 h. The synthesized Cu/TiO_2 was crushed and sieved into 60–90 μm. The structure and morphology of the catalyst were investigated by scanning electron microscopy of the TSCAN Company at the acceleration voltage of 15.0 kV. TiO_2 and modified TiO_2 powders were characterized by X-ray diffraction (XRD) using X'PERT MPD DIFFRACTOMETER with Cu $K\alpha$ radiation at 40 kV and 40 mA. The XRD patterns were collected from 5 to 80° in 2θ at a scan rate of 0.2°/s.

2.3. Photocatalytic experiments

The Cu/TiO_2 catalyst was added to the phenol solution. Phenol was considered as the model synthetic wastewater, because it is a toxic hazardous material and it is a non-biodegradable contaminant. The catalyst loading and the phenol concentration are two of the process variables. Hydrogen peroxide (H_2O_2: 12.5 ml, 30 wt.%) was added to the solution as an oxidizing agent. The mixture was stirred at a constant rate and illuminated by the UV lamp (with light intensity of 757.38 mW/cm^2) which was installed 19.5 cm over the batch reactor. The UV light is required for the activation of the photocatalyst. As the Cu/TiO_2 surface is illuminated by the UV lamp, the excited electrons migrate to the conduction band of the photocatalyst; meanwhile, holes are created in the valence band. Either hydroxyl radical generation is implemented through the photolysis of H_2O_2 or it is the result of the oxidation of water molecules by the positive holes. Since the hydroxyl radicals decompose organics, increasing their number will improve the degradation efficiency.

2.4. Analytical methods

In order to prevent the interference from the outside light, the set-up was shielded by aluminum foil during the irradiation time. All the experiments were carried out at room temperature (27 °C). After the photocatalytic tests, supernatant solution was centrifuged and its absorbance was measured at 270 nm using a SPECORD 210 UV–vis spectrometer (Analytic Jena AG, Germany). The experiments were repeated for the blank. All the conditions of the blank were the same as the sample, but it had no catalyst. Photodegradation of phenol was calculated using the following equation, which is derived from Beer–Lambert law:

$$\text{Degradation\%} = 100 \times \left[\frac{(A_0 - A)}{A_0}\right] \quad (1)$$