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ZnO nanoparticles immobilized on the surface of stones to study the removal efficiency of 4-nitroaniline by the hybrid advanced oxidation process ($UV/ZnO/O_3$)

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ABSTRACT

4-Nitroaniline (4-NA) is one of the common pollutants in wastewater. Because of the toxicity, carcinogenicity and mutagenicity, it has been reported as priority pollutants. The purpose of this study was to synthesize ZnO nanoparticles and its immobilization on the surface of stones to study the removal efficiency of 4-NA by the hybrid advanced oxidation process ($UV/ZnO/O_3$). The SEM, TEM and XRD analyzes were used to investigate the physiochemical properties of nanoparticles. The effective parameters on the process including the initial pH of the solution, contact time, dose of immobilized nanoparticles, the initial concentration of 4-NA, were investigated. The kinetics of the degradation reactions were determined. Data analysis was performed using SPSS-16 software. By increasing the catalyst dose from 1 g/L to 3 g/L, the removal efficiency increased from 75% to 92%. The highest 4-NA removal efficiency of 96% was achieved by hybrid advanced oxidation process ($UV/ZnO/O_3$) in optimal conditions including pH: 5–7, the dose of immobilized ZnO: 3 g/L, the initial concentration of 4-NA: 10 mg/L and contact time: 60 min. Therefore, this process is recommended for the removal of resistant and toxic pollutants from aqueous solutions with a relatively high efficiency.

1. Introduction

Water pollution by chemical wastewater, especially in developing countries, is one of the most important environmental challenges in the world. Aromatic compounds such as 4-nitroaniline (4-NA) are one of the common pollutants in industrial wastewaters such as oil refinery, petrochemical industry, pesticides manufacturing and chemical paints [1–3]. Due to its toxicity, carcinogenicity and mutagenesis, this compound creates serious environmental problems [4]. This material has been reported by the US Environmental Protection Agency (U.S.EPA) as one of the important and priority pollutants in the water. The presence of 4-NA in water, even at very low concentrations, is hazardous to aquatic life and human health [5–7].

Various treatment processes including biodegradation, membrane processes, coagulation and adsorption have been developed for treatment of industrial wastewater, but some problems such as high costs, low efficiency, and failure to provide standards required for discharged effluents are limiting factors for the application of these methods [8–10]. In addition, some of these processes only condense and transfer persistent organic pollutants from the liquid phase (water) to the solid phase. Therefore, they require additional costs for the treatment of secondary pollutants and the recovery of adsorbents [8,11–14].

Because of these reasons, advanced oxidation processes (AOPs) have been proposed to remove persistent organic pollutants, especially those with low biodegradability [15,16]. AOPs have several advantages such as rapid degradation rate, mineralization

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of organic compounds, the ability to operate at ambient temperature and pressure, and reduction of the toxicity of organic compounds [17]. The photocatalyst process, as a kind of the advanced oxidation process, has a high degradation rate by producing hydroxyl radicals ($OH^•$). Due to its low cost and environmental compatibility, this method has been considered by many researchers [18–23].

In this process, semiconductors such as ZnO have attracted lots of attention due to high ultraviolet light sensitivity [24,25], non-chemical nature, high stability, high surface-to-volume ratio, high working life, wide energy gap and higher efficiency in electrons production [26]. The energy gap property attracts a large portion of the UV spectrum by this nanoparticle [27–29]. Nanoscience is an interdisciplinary field of science that has countless applications [30–33]. Also, there are special properties of ZnO nanoparticles including high chemical stability, low dielectric constant, high electromechanical coupling coefficient, high catalytic activity, Infrared and ultraviolet light absorption and its antibacterial properties [34,35].

When ZnO nanoparticles are exposed to UV or sunlight as energy source with photonic energy (hv), equals or greater than the energy of excitation energy (Eg), the electrons from the filled valence band (VB) are transmitted to empty conduction band (CB). This process produces electron-hole pairs (e-h^+). The pair of electrons migrates to the surface of ZnO and participate in oxidation and reduction reactions. These pairs of electrons react with water and hydroxide ions and produce reactive hydroxyl and superoxide radicals. Since these radicals have high degradation power, they attack 4-NA molecules adsorbed on the surface of ZnO, and consequently degrade 4-NA molecules and produce harmless CO_2 and H_2O molecules (Fig. 1) [27,36].

Two major problems including the hard recovery and UV light scattering that occurs when the nanoparticles are applied as a suspension in the photocatalytic process, are resolved by fixing them on the media [37,38]. Due to the rapid recombination of electrons and holes, production of hydroxyl radicals is decreased, and consequently leads to reduction in the rate of degradation [39,40]. Therefore, the use of stronger oxidizing agents, such as ozone, along with the photocatalyst process is suggested [41]. Ozone with high oxidation potential (2.07) along with other processes has high efficiency in oxidation of organic matter in a short time and reducing toxic and minor products [36,42]. Therefore, the purpose of this study is to synthesize ZnO nanoparticles and its immobilization on the surface of stones to determine the removal efficiency of 4-NA by hybrid advanced oxidation process (UV/ZnO/O_3).

2. Materials & methods

4-NA, $ZnSO_4$ 0.7 H_2O (99.5%; Merck, Germany), sodium carbonate, (Na_2CO_3, 99.9%; Sigma-Aldrich), deionized water, ethanol (CH_3CH_2OH, 99.5%; Merck, Germany), sodium hydroxide (NaOH; Merck, Germany), sulfuric acid (H_2SO_4; Merck, Germany) with high purity percentage were purchased from Merck, Germany. Flat and rough discarded stones in appropriate dimensions were used as a catalyst media. All applied materials were provided with pure quality.

2.1. Synthesis of zinc oxide nanoparticles

Preparation of ZnO nanoparticles was carried out based on conversion of Zn_4 (SO_4) $(OH)_6$ 0.5 H_2O according to the thermal method. At first, a zinc sulfate solution ($ZnSO_4.7H_2O$) with the concentration of 0.5 M was made in deionized water. Sodium carbonate at the concentration of 0.4 M was added dropwise at 70 °C for 45 min to a zinc sulfate solution with vigorous mixing to form Zn_4 (SO_4) (OH) $_6$ 0.5 H_2O.

The resulted sediment was collected by filtration. The sediment was washed several times with deionized water and ethanol and then it was placed at 70 °C in the oven to dry. The surface of the stones was shaved and roughed for better adhesion and immobilization of nanoparticles. Then, in order to activate the surface of stones for better immobilization, they were placed in concentrated sodium hydroxide for 24 h. After withdrawing the stones from the solution, they were washed several times with deionized water to reach the pH of washed water to7. After that, the sediment from previous stage was immobilized on the surface of three stones with dimensions of 3 × 20 cm and then they were placed at 850 °C in an electric furnace (BADi) for 1 h in order to calcinate [39].

2.2. Photoreactor

All experiments were carried out on a laboratory scale inside a reactor. The schematic of the reactor is shown in Fig. 2.

The reactor was made of a rectangular cube container made of plexiglas with a length of 25 cm, a width of 10 cm and a height of 5 cm. The applied volume of the reactor was 350 cc. The 3 ultraviolet lamps of 6 W with low pressure were placed at the top of the reactor. Also, ozone was injected into the reactor by a constant amount of 4 L/min by air diffuser. The distance between the catalyst bed surface and the UV radiation source for hydroxyl radical production was considered approximately 2 cm. The reactor was mixed with a peristaltic pump with a flow rate of 1 ml/s.

2. ZnO nanoparticles immobilized the surface of stones 3.

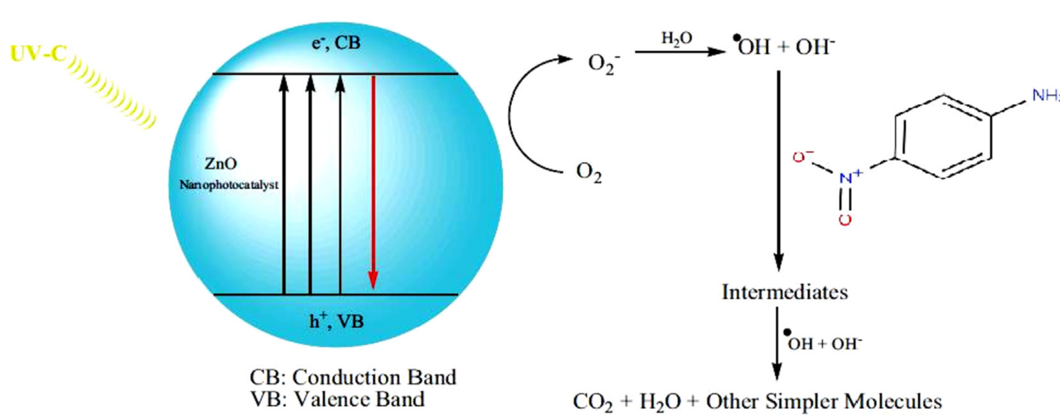

Fig. 1. Schematic diagram of mechanism of photocatalytic reaction taking place on the surface of ZnO nanoparticles immobilized on stones.