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Application of TiO_2/perlite photocatalysis for degradation of ammonia in wastewater

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ABSTRACT

The purpose of this study was removal of ammonia by a new photocatalytic process from synthetic wastewater under UV irradiation. TiO_2 was used as the photocatalyst and immobilized on perlite granules as a supporter. The prepared catalysts were characterized by SEM and FTIR analysis showed that TiO_2/perlite catalyst has mesoporous structures and uniform coating of TiO_2 on support. Also, the optimum efficiency of photocatalytical degradation of ammonia was obtained at pH 11 for UV intensity irradiation with 125 W lamp. About 68% degradation of ammonia in wastewater was achieved after 180 min of irradiation by using the optimized reaction conditions.

1. Introduction

Ammonia is a useful chemical material in the manufactures and industrial plants. However, it is a common material in industrial effluents and when it's released into rivers in excess amounts, causes noticeable effects on fishes and human health [1]. It attacks the breathing system, skin, and eyes, and at a concentration higher than 300 ppm might lead to death [2,3].

Different technical methods were applied to remove ammonia from industrial wastewater, such as biological treatments [4], chemical precipitation [5], advanced oxidation processes [6], air stripping [7], ion exchange [8], adsorption [9], membrane [10], and photocatalytic processes [1,11–15]. The photocatalytic degradation of various toxic compounds has been proposed as a practical method in the decontamination of wastewater for renewable use [16–18]. Meanwhile, titanium dioxide (TiO_2) has been widely used as a photocatalyst due to its ability to oxidize toxic substances into nontoxic substances in polluted aqueous systems [19–21].

So far, the use of TiO_2 nanoparticle structures on the photocatalytic degradation of ammonia has been reported by several researchers [1,11–15]. The photodegradation of ammonia using TiO_2 catalyst reveals that this photochemical reaction treats the ammonia into harmless N_2 and H_2 gases [22]. The photocatalytic oxidation using titanium (IV) oxide is activated by ultraviolet (UV) light irradiation (Eq. (1)) [15].

$$TiO_2 + h_v \rightarrow h^+ + e^- \quad (1)$$

In photocatalytic reactions, the generated hole (h^+) and electron (e^-) play a main role. Also, the hydroxyl produced from the decomposition of water (Eq. (2)) facilitates ammonia oxidation to N_2 (Eqs. (3) and (4)) or to NO_3^- (Eq. (5)) [11]. It seems that the main difference, between the two mechanisms is in the final products.

$$h^+ + H_2O \rightarrow H^+ + {}^{\bullet}OH \quad (2)$$

$$NH_3 \xrightarrow{{}^{\bullet}OH} \underset{+\ H_2O}{NH_2} \xrightarrow{{}^{\bullet}OH} \underset{+\ H_2O}{NH} \xrightarrow{{}^{\bullet}OH} \underset{+\ H_2O}{N} \quad (3)$$

$$NH_x + NH_y \rightarrow N_2H_{x+y} \xrightarrow[(x,y=0,1,2)]{H^+} N_2 \quad (4)$$

$$NH_3 \xrightarrow{{}^{\bullet}OH} HONH_2 \xrightarrow{{}^{\bullet}OH} NO_2^- \rightarrow NO_3^- \quad (5)$$

The process of separation is inevitable by considering nano-sized TiO_2 particles in the photocatalytical reactor [11,13,21]. However, the application of techniques to eliminate the separation process that reduces costs and simplifies the wastewater treatment system has been considered by researchers. In this area many techniques have been applied for solving this problem with immobilizing TiO_2 catalysts onto a suitable solid inert

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support. Up to now, the different types of supports have been used, for example, glass [23], stainless steel [24], activated carbon [18], aluminosilicate [25], wool [26], rubber [27], zeolite [28] and clay [29]. In addition, some woven fabrics including cotton, polyester and flax fabrics were used as support and were treated to remove ammonia by TiO_2 photocatalysts [12]. In this regard, the use of mineral structures such as perlite is more interesting [17,30]. Perlite granules as support have porosity of more than 95% and density of 64–144 kg/m^3 that allows them to stay afloat on water surface [31]. Hosseini et al. [17] were investigated photocatalytic decomposition of phenol by immobilized TiO_2 on perlite. Their results showed that 90% of the phenol concentration decreased in 120 min of reaction time.

The aim of this study, for the first time was to investigate the photocatalytical activity improvement of TiO_2 (P-25) powder as a photocatalyst which immobilized on perlite granules to remove ammonia from synthetic wastewater. Perlite due to its unique characteristic from the processing point of view, which enables it to get wetted with the polluted solution and simultaneously be exposed to the radiation source when coated with the photocatalyst seems to be an ideal support for the immobilization of photocatalysts [17,30]. Also, the SEM and FTIR analyses were applied for the study of the structure of TiO_2/perlite photocatalysts.

2. Materials and methods

2.1. Materials

TiO_2 (P-25) photocatalyst was purchased from Degussa Co. Ltd., Germany (anatase 75%, rutile 25%, BET specific surface area 48 m^2/g, and mean particle size 25 nm). The perlite is a special type of glassy volcanic rock that can expand up when heated in a rotary kiln, at a high temperature (with grains size 1–5 mm) [31]. The main chemical components of perlite have been reported to be SiO_2 (~67 mol%), Al_2O_3 (~13 mol%), Na_2O (~6 mol%), K_2O (~5 mol%), CaO (>1 mol%), and others (<1 mol%) [32]. All used chemical materials such as ammonia, ethanol and nitric acid were purchased from Merck Co. Also, all experiments were carried out by double distilled water which produced in laboratory.

2.2. Preparation and characterization of catalysts

The titanium dioxide powder was added to ethanol as the medium base of the slurry in which the TiO_2 powder could be properly dispersed. Then, for convenient dispersion of titania powder in ethanol and having a cloud-shape manner producing a slurry, a quantitative dilute nitric acid with a pH 3.5 was added. The slurry was sonicated for 30 min, to separate the flocculated titania powder and obtain more uniform slurry. Perlite granules (which were previously washed in deionized water assisted by air bubbling for few minutes to remove dust and crushed perlite granules) were added to the slurry. In the final stage of process, those perlite granules which had adsorbed enough titania slurry were filtered from the slurry and dried at 120 °C for 12 h, then calcinated at 450 °C for 30 min. Morphology of prepared catalysts and perlite were determined by using a HITACHI-S4160 field emission scanning electron microscope (FESEM). Also, Fourier-transform infrared spectroscopy (FTIR) was recorded using MB160 FTIR spectrometer (ABB Bomem Inc., Canada) to characterize the TiO_2 and prepared TiO_2/perlite photocatalysts.

2.3. Photocatalytic reactor

Fig. 1 schematically illustrates the reactor system. The pyrex glass vessel reactor (inner volume: 1.5 L) was used for the photodegradation of ammonia from aqueous synthetic wastewater solution. The system was illuminated by a 125 W Hg lamp with a peak light intensity at 254 nm, standing 12 cm overhead the center of the pyrex glass reactor. The entire system was shielded by a metal case during the reaction to prevent interference from outside light. Catalyst granules (11.70 g) were floating on 1.0 L of ammonia wastewater solutions and exposed to UV source. An air diffuser at the bottom of the glass box was existed to provide oxygen required for the reactions, and to provide some agitations. The temperature of the suspension in the photoreactor was kept constant at 20 °C by the recycled water in an aluminum water jacket, and the irradiation time was 3 h. A needle-type probe was inserted in the reactor to extract samples. The liquid sample (<5.0 mL) was collected in a vial wrapped in aluminum foil to reduce interference from indoor fluorescent light before analysis. Also, the residual gas was collected in a syringe through a needle valve and was analyzed by using a commercial gas chromatograph (GC) GC-CGCA-1 apparatus equipped with a thermal conductivity detector (TCD). These analyses were done isothermally in a parallel setup of GC with two packed columns of Molecular Sieve 5 A and Porapak Q.

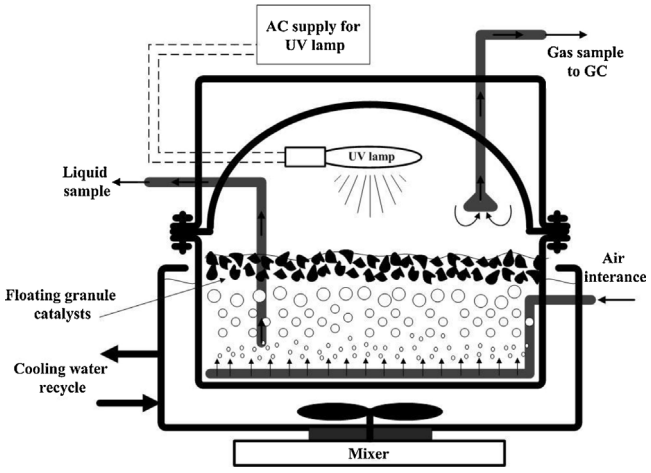

Fig. 1. Schematic of photocatalytic reactor.

3. Results and discussion

3.1. Photocatalyst characterization

The surface morphology of the TiO_2/perlite photocatalyst was investigated by FESEM, as shown in Fig. 2. The image of perlite granules which used as supporters was shown in Fig. 2(a). This image clarifies that perlite granules have high mesoporous structures, and the surface pores are 5–20 μm in diameter. Fig. 2(b) is showing the surface of perlite granules after TiO_2 nanoparticles were immobilized on them. The coating of TiO_2 nanoparticles is mostly distributed on the external surfaces of the perlites with dispersed aggregates of TiO_2. Similar results of the immobilized TiO_2 have been reported on different supports [18,25,28,33]. Yao et al. [18] was studied the immobilization of TiO_2 nanoparticles on activated carbon fiber (ACF) and its photodegradation performance for organic pollutants. They showed that, although TiO_2 coating has been deposited on fibers at such a large scale, the TiO_2/ACF system still retains the same spatial distribution of carbon fibers as in their unsupported state to allow UV light to penetrate into the photocatalyst to appreciable depth [18]. Also, Nikaido et al. [25] was investigated the photocatalytic behavior of TiO_2 nanoparticles supported on porous aluminosilicate. SEM photographs of their results, from papers mixed with TiO_2-supported aluminosilicate showed that coagu-