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Preparation of nano N-TiO_2/graphene oxide/titan grid sheets for visible light assisted photocatalytic ozonation of cefixime

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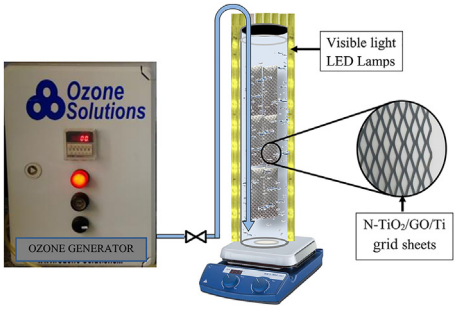
HIGHLIGHTS

- Electrochemically fabrication of N-TiO_2/graphene oxide/Titan grid sheets.
- Photocatalytic ozonation reactor was used for a cefixime degradation.
- The photocatalytic ozonation process efficiency was higher than other probable processes.
- GC-MS analysis approved the degradation of cefixime.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, nitrogen doped TiO_2 (N-TiO_2) and graphene oxide (GO) were prepared and immobilized on a titan grid sheet by electrophoretic deposition method. SEM, DRS, FT-IR, and N_2 adsorption-desorption were used for the characterization of the immobilized N-TiO_2/GO nanocomposite. Ability of prepared nanocomposite was studied for degradation of cefixime in water through visible light photocatalytic ozonation process. The effect of operational variables including dosage of catalyst and ozone concentration, pH, initial concentration of the cefixime, light intensity, contact time, inorganic and organic scavengers on the cefixime degradation were evaluated. The results showed that all of the variables have positive effect on the degradation efficiency except initial concentration of cefixime, organic and inorganic scavengers. The GC-MS analysis was employed to identify the intermediate products. The performance of immobilized N-TiO_2/GO nanocomposite in photocatalytic ozonation process leading to 80% removal of cefixime is much better than individual adsorption (17%), photocatalytic degradation (29%) and ozonation (51%) processes at the similar conditions. It is expected that N-TiO_2/GO can act as an efficient catalyst in the photocatalytic ozonation under the visible light.

1. Introduction

Presence of hazardous compounds in water streams is increased with rapid growth of the population and urbanization. Among the various wastewater pollutants, pharmaceutical contaminations especially antibiotics are considered as environmentally important issues [1]. These pollutants are released in the aquatic environment mostly from human excretion, veterinary clinics and runoff from agricultural applications [2]. A variety of antibiotics have been detected in many groundwater and surface water sources. This group of pharmaceutical contaminations have antibacterial nature. Accordingly, conventional biological treatment does not have enough oxidation potential to

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oxidize them. Furthermore, the presence of these compounds in water resources even at very low concentrations improves the bacterial resistance against them [3].

Among the various wastewater treatment methods, advanced oxidation processes (AOPs) are considered as the powerful methods. AOPs include various methods such as photocatalysis, ozonation, Fenton and sonolysis. These methods are based on the generation of very reactive species such as hydroxyl radicals (˙OH) to oxidize and degrade a broad range of organic pollutants [4]. In recent years, hybrid methods including two or more individual AOPs processes have been applied to improve pollutant degradation efficiency. Among hybrid systems, photocatalytic ozonation, i.e., the combination of photocatalytic oxidation and ozone processes, is thought to be one of the promising techniques for wastewater treatment. In this process, the photo-generated electrons produced on the surface of the photocatalyst can be trapped by ozone molecules as strong inorganic oxidative species. Subsequently, the rate of hydroxyl radical generation and organic compounds oxidation enhances [5]. In most of the photocatalytic ozonation studies, TiO_2 is the most used photocatalyst owing to its non-toxicity, good stability and excellent photocatalytic activity. However, there are some problems associated with TiO_2 in the photocatalytic ozonation process. The basic problem is the wide band gap of TiO_2 (3.2 eV) which restricts the utilization of visible light [6–8]. Doping of TiO_2 with non-metal atoms such as nitrogen has received much attention and the present authors also adapted such strategy to extend the absorption of TiO_2 to visible region. Some attempts have been made to doping of TiO_2 with nitrogen to enhance photocatalytic performance of this semiconductor by Khataee et al. [9], Kalantari et al. [10], and Vatanpour et al. [11]. Reported results show enhanced photocatalytic activity of N-doped TiO_2 nanoparticles in comparison with undoped ones.

Separation of TiO_2 nanoparticles from batch slurry photoreactor after photocatalytic ozonation process is the second problem. This problem can be tackled through the immobilization of TiO_2 on the surface of support material without the loss of activity.

Another interesting method to raise the photocatalytic efficiency of TiO_2 is its incorporation with graphene or graphene oxide (GO) [12]. Graphene is an attractive and significant material due to its two-dimensional nanostructure with unique properties specifically, excellent mobility of charge carriers, superior chemical stability and high specific surface area [13]. GO, a derivative of graphene, has a large number of oxygen functional groups on the surface and possess graphene's similar advantages [14]. Therefore, it is expected that GO can be an ideal electron carrier from TiO_2 and can help to enhance electron-hole separation efficiency.

The scope of this study was to immobilize N-TiO_2 and GO on the surface of titan grid sheet and evaluate performance of prepared catalyst in degradation of cefixime as a representative of pharmaceutical pollutants by ozone assisted photocatalysis process.

2. Experimental procedure

2.1. Materials

TiO_2 P25 nano-powder with an average crystallite size of 20 nm was obtained from Degussa (Germany). Industrial graphite was purchased from Qingdao Ruisheng Graphite Co., Ltd., China. 2-Propanol 99.97% was purchased from Dr. Mojallal co. (Iran). Cefixime was obtained from pars Pharmaceutical Co., Iran. The chemical structure of cefixime was shown in Fig. 1. All other chemical reagents were of analytical grade and supplied by Merck. Distilled water was used in all of the experiments.

2.2. Preparation of N-TiO_2

The N-TiO_2 nanoparticles were prepared by mixing TiO_2 nanoparticles with urea precursor as a source of nitrogen in a 1:6 wt ratio, followed by annealing at 400 °C in air atmosphere for about 5 h [11].

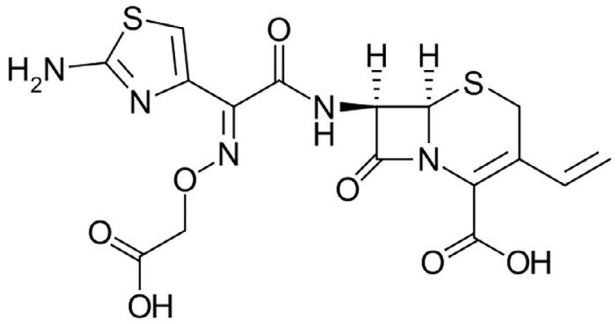

Fig. 1. Chemical structure of cefixime.

2.3. Preparation of GO

Modified Hummers and Offeman method was employed to prepare GO from the graphite powder [15]. Briefly, 5 g graphite powder was dispersed into a mixture of 100 mL concentrated H_2SO_4 and 30 mL HNO_3 in an ice bath and stirred for 30 min. Subsequently 15 g $KMnO_4$ was slowly added. Then, the mixture was stirred at 35 °C for 120 min. Afterwards, 250 mL distilled water was added and kept at 98 °C for 30 min. The reaction was terminated by adding 750 mL water and 20 mL 10% H_2O_2 solution. After cooling, the mixture was centrifuged and washed with distilled water until the neutral pH. Finally, the GO was obtained by vacuum drying [15].

2.4. Preparation of N-TiO_2/GO nanocomposite

The N-TiO_2/GO nanocomposite was prepared by coating N-TiO_2 nanoparticles and GO onto a titan grid sheet by the electrophoretic deposition (EPD) procedure. First, titan sheet was kept at 1:1 HCl/H_2SO_4 solution for 30 min in order to roughen the surface of titan, cleaned ultrasonically in acetone for 30 min and then rinsed successively with distilled water. The EPD suspension mixture included 0.25 g N-TiO_2, 0.25 g GO, 0.01 g magnesium nitrate and 150 mL 2-propanol. The mixture was sonicated for 40 min to disperse contents. After sonication step, the EPD process was conducted between the titan grid sheet ($4 \times 6\ cm^2$) and a stainless steel plate with the same size placed 0.5 cm apart in an electrochemical cell containing the suspension using a potential difference of 40 V through DC power supplier (Micro, Iran) for 7 min. Finally, the prepared nanocomposite was dried in air, and then calcined at 500 °C for 2 h [16].

2.5. Photocatalytic ozonation experimental set-up

The experimental apparatus which was used for photocatalytic ozonation processes is illustrated in Fig. 2. All experiments were carried out in a 1 L borosilicate cylindrical reactor placed on a magnetic stirrer. The reactor contains cefixime solution with desired concentration and pH. The N-TiO_2/GO/titan grid sheets were placed vertically inside the reactor and the reactor wall was covered by 432 (9 × 48) visible LED lamps (Mega, ZR-144-LED, china). The radiant flux was measured with a Coherent Labmaster power meter. The visible light intensity was 7.45 $W\,m^{-2}$. In the upper part of the reactor, three ports were provided for inlet and outlet of ozone as well as sampling at predetermined time intervals. Ozone was generated in an ozone generator (Ozone Solutions, USA). In the case of photocatalytic degradation experiments and ozonation process solely, the similar process to photocatalytic ozonation were used except ozone bubbling into the reactor for photocatalytic degradation process and visible light irradiation for ozonation process. The cefixime concentration was measured by a UV–Vis spectrophotometer (Spectronic 21D) at λ_{max} equal to 286 nm using the