



Removal of Antibiotic Drug Wastes from Aqueous Solutions by Photocatalytic Ozonation Process

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Abstract

In this study, the effect of photocatalytic ozonation, ZnO/MMT dosage, SMX initial concentration, ozone flow rate, acidic pH (pH: 3) and effects of organic and inorganic cleaners were investigated for the separation of an antibiotic drug compound, sulfamethoxazole (SMX). The synthesized ZnO nanoparticles were immobilized between the layers of montmorillonite to prepare the ZnO/MMT catalyst as photocatalyst. The catalyst was characterized by X-ray diffraction (XRD), X-ray fluorescent (XRF), scanning electron microscope (SEM), high resolution electron microscope (HR-TEM) and N₂ adsorption / desorption. The adsorption for photocatalytic ozonation process achieved the highest SMX degradation efficiency compared to only ozonation, catalytic ozonation and photolysis. ZnO/MMT was a more effective photocatalyst than ZnO and demonstrated its usability as a promising photocatalyst for the removal of pharmaceutical contaminants in aqueous solutions.

Keywords: Photocatalytic ozonation, Hydroxyl radical, ZnO/MMT nanocomposite, Antibiotic

Introduction

The demand for new water treatment technologies has increased as a result of increasing environmental pollution with many different types. These processes have been preferred because advanced oxidation processes for water treatment and recovery are highly capable of decomposing persistent toxic organic compounds such as drugs, industrial waste and household chemicals [1]. Pharmaceutical compounds cannot be preserved by conventional unit operations in water treatment plants and are therefore released into natural water environments [2]. Therefore it is necessary to control the amount of antibiotics in the aqueous medium and set up treatment plants to remove such compounds. Sulfamethoxazole is an important antibiotic used on humans and animals to treat disease such as reducing



inflammation [3]. Due to the antibacterial properties of this compound, it resists biological water purification methods and is often found in domestic wastewater treatment plant wastewater [4]. Sulfonamides are known as important pollutants that are difficult to disintegrate in the aqueous environment, thus causing drug resistance for humans and other living things [5]. One of the approaches to reducing the pollution of pharmaceutical waste is heterogeneous photocatalytic ozonation. It is an emerging and promising application for water treatment and has been applied to the removal of different organic pollutants in water and wastewater [6]. Catalytic ozonation has emerged as a powerful technology for removing pharmaceuticals in water, even for durable and degradation resistant compounds [7]. ZnO as catalyst and montmorillonite as support material has attracted great attention in the last decade due to its interchangeable cations, thermal stability, nano-porous structure, swelling properties, appropriate surface morphology and large surface area beneficial to photocatalytic ozonation activity [8-9]. In the photocatalytic ozonation of sulfamethoxazole, the effect of operational parameters such as ozone flow rate, initial sulfamethoxazole concentration, ZnO/MMT catalyst concentration, acidic pH (pH=3) of solution, addition of inorganic and organic radical scavenger added to sulfamethoxazole removal was investigated.

Results and Discussion

UV-Vis spectral changes as a function time during the photocatalytic ozonation process of sulfamethoxazole, in the presence of 20 mg L⁻¹ SMX at pH 3 under the flow rate of 2 L h⁻¹ ozone gas and UV-A irradiation and the results are shown in Figure 1. The intensity of the maximum peak at the wavelength of 265 nm decreased depending on the reaction time and almost disappeared after the reaction time of 18 minutes. These results show that the photocatalytic ozonation method reveals SMX degradation on the ZnO/MMT surface. Complete degradation of the SMX was carried out after 30 minutes in optimized experimental conditions [10].

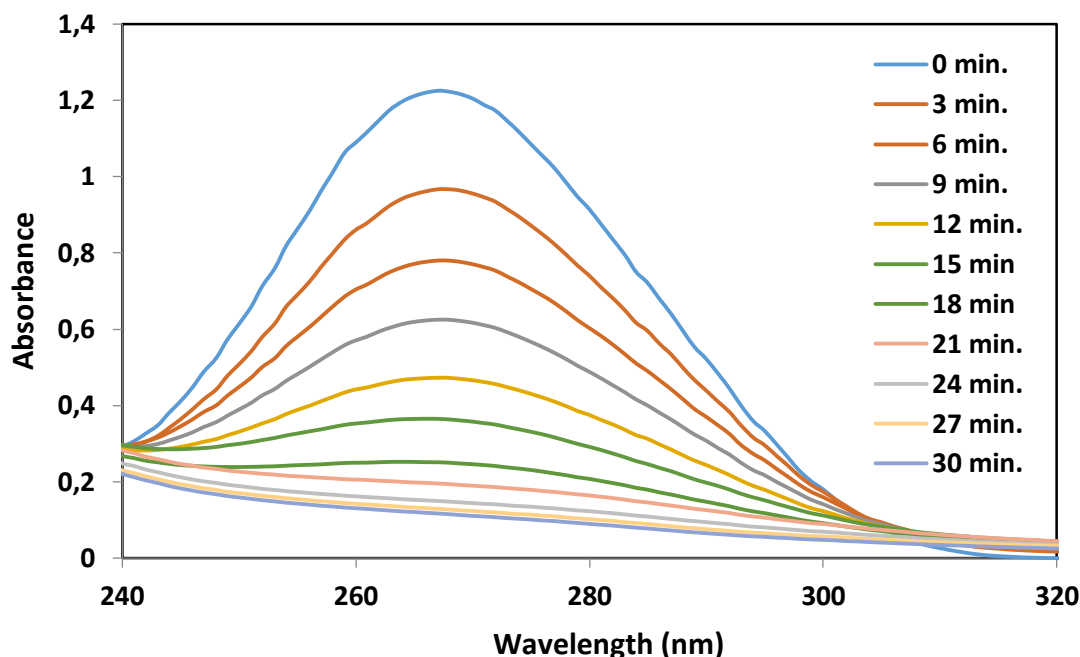


Figure (1). The changes in the absorption spectra of 20 mg L⁻¹ of sulfamethoxazole during different treatment time. Experimental conditions: [ZnO/MMT]: 0.1 g L⁻¹, [SMX]₀: 20 mg L⁻¹, ozone gas inlet flow rate: 2 L h⁻¹ and pH = 3.

When these results are compared with each other, it is evident that the presence of ZnO in the composite structure is significant, for example 48.01%. On the other hand, 66.90% SiO₂ and 13.80% Al₂O₃ amount in MMT was reduced to 36.30% and 10.30% in ZnO/MMT structure, respectively. This result clearly shows that ZnO is between the layers of MMT and between hybridization with MMT.

In order to evaluate the degradation efficiency of sulfamethoxazole by different processes, some preliminary experimental series were conducted in the investigated systems such as adsorption (ZnO/MMT), ozonation (O₃), photolysis (UVA), catalytic ozonation (ZnO/MMT-O₃), photocatalysis (ZnO/MMT-UVA), and photocatalytic ozonation (ZnO/MMT-UVA-O₃ and ZnO/UVA-O₃). The results are given in Figure.2. The values of initial sulfamethoxazole concentration, catalyst dosage, gas flow rate and pH were constant as 20 mg L⁻¹, 0.1 g L⁻¹, 2 L h⁻¹ and pH=3.0 respectively. As shown in Figure 2, SMX degradation was low (5.90%) by direct photolysis under UV-A irradiation (315-400 nm), exhibiting photolysis inefficiency in SMX degradation. This process can be explained as that the absorbed photons absorbed by the UV light source and / or the value of photon energy released by UV irradiation is insufficient

to break the bonds in the SMX [11-13]. SMX removal is only 10.33% in the adsorption process and indicates that the contribution of adsorption to the ZnO / MMT surface is not important in SMX degradation. Figure 2 shows that the efficiency of SMX degradation by photocatalysis is very slow and was performed at 23.17% in 30 minutes [14]. Accordingly, it was found that the complete degradation of the organic pollutant needed more reaction time due to the possibly recombination of the photo / h⁺ pairs produced in the presence of oxygen of the produced e⁻ / h⁺ pairs hydroxyl radicals [12]. The degradation efficiency of the SMX is 68.68 % after 30 min of reaction using single ozonation process, which is importantly higher than that of photocatalytic oxidation.

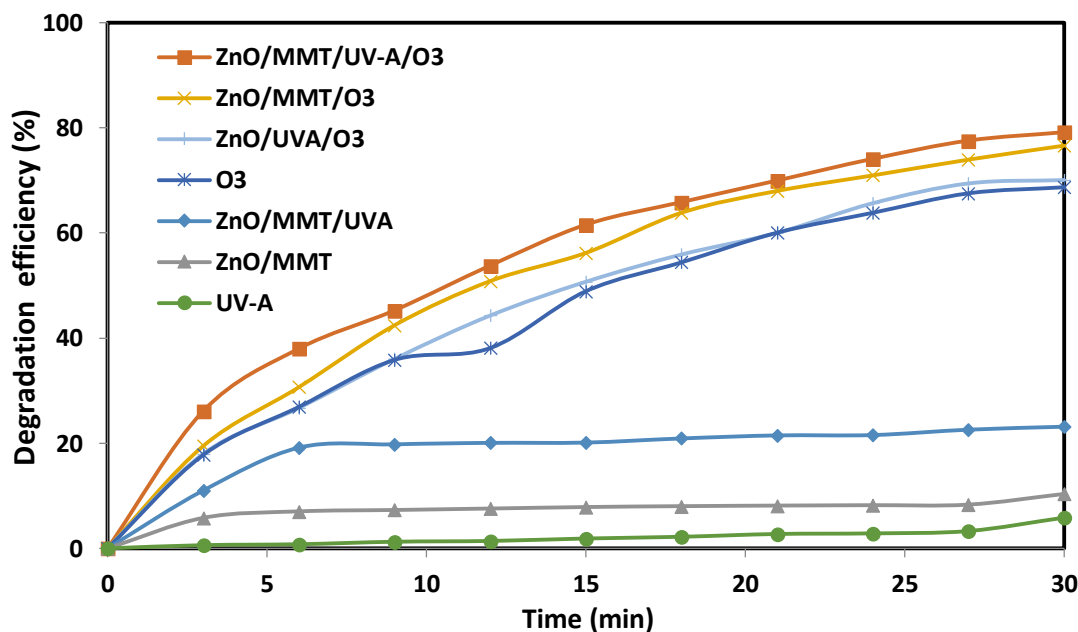


Figure (2) Comparison of different processes in the sulfamethoxazole degradation as a function of time. Experimental conditions: [ZnO/MMT]:0.1 g L⁻¹, [SMX]₀:20 mgL⁻¹ and pH = 3.

In the ozonation process of ZnO / MMT nanocomposite (76.63% at 30 min), the removal efficiency of ZnO was higher than the photocatalytic ozonation process (70.09% at 30 min). This is because the surface area of the MMT is large and the hydroxyl radicals break down SMX more easily [15]. Removal efficiency of ZnO / MMT nanocomposite (UVA-O3) in photocatalytic ozonation process (79.11% at 30 min) was higher than other processes.



This is due to the synergistic effect of UV-A and ozonation. In addition, due to the separate effects of ZnO and MMT, the photocatalytic ozonation removal efficiency of ZnO / MMT was highest [16].

Acknowledgments

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